### ADDITIVES

### http://fuelsandlubes.com/digital/fli/2015-Q3/HTML/#38

Guan Gregory: there are 3 major detergent's technologies: salicilate (Shell), phenate (Oronite) and sulphonate. Several blenders are using mixture of these, but salicilate isn't compatible with high base sulphonate (foaming) and some sulphonate have compatibility problems with PPD (pour point depressant). Also:

SIB (Sulphur isobutene) = EP anti-wear performance-robbing

\_\_\_\_\_

Russell Bolden Business Development at Green Goanna

### Crystalline particles of BHT forming in gas engine oil

Crystalline particles are forming on the venturi and clogging up the filters on 2 x V16 MWM gas engines operating side by side in the plant. On analysis these particles have been found to be crystals of BHT (Butylated Hydroxytolune). The oil manufacture states that BHT is the antioxidant component of the additive pack for the Group 1 base oil they use. Does anyone have any ideas as to why the BHT is crystallising during the operation of these engines? What conditions would lead to BHT crystallising? The oil manufacturer states they have never had another customer report such a thing after many years of supply into hundreds of gas engines (this denial cannot be validated). It does not seem to be a batch issue as a number of batches have been supplied over the last year with no improvement.

V.S.S. Sarma Use of Bright Stock 150 while formulating an SAE 40 NGEO must be avoided. NGEOs can not tolerate Viscosity Modifiers and Bright Stock. The heavier Bright Stock can have residual moisture that can form crystals with chemicals present in the additive package. I never had this problem because I never used a BS 150 or a VM while making a NGEO.

<u>Jean-Michel Demaret</u> Hello Russel. Sometimes additives sublimate, they change from a gas state to a solid state in presence of a cold flow . The sublimation turns the the additives vapour into crystals. I have seen this phenomena with Phenol (similar to BHT). You need a rapid cooling of the vapor. It does not need to be a minus temperature, just a cold flow. You use a venturi to suck the vapours out of the sump, condensate them and then reinjecting them. The venturi will create the cold flow. You may need to fit a blower instead of the venturi. Not all additives sublimate, It would be worth to talk with the manufacturers and ask them if they may have seen some deposit when they were testing the oil through performance test involving vapours, for example the Noack test.

\_\_\_\_\_

<u>David Wedlock</u> Most PIBs have an olefinic end-group and are oxidatively unstable. They make poor substitutes for VM.

Denisa Ivana PIB could increase your viscosity, yes, but I would point more the dispersant effect attached to it. Unfortunately is not so shear stable, neither resistant towards oxidation. To get the best as you wish, no matter costly, I would use some VI with a good SSI, depending about the oil you want to formulate. If it is a 5w30 I would choose some SSI 5-10 VI.( alkylated polystyrene ).To have also an improved volatility and anti-wear/EP properties there are many polyesters of different viscosity. There are also very stable towards thermal oxidation.

\_\_\_\_\_

**Infineum**, one of the world's leaders in the formulation, manufacture and marketing of petroleum additives for lubricants and fuels, has announced a **new viscosity modifier** which offers the benefits of fuel economy combined with soot and viscosity control.

"The increasing fragmentation, complexity and tightness of performance requirements is making formulating more and more challenging for the industry," said Marco Di Gennaro, portfolio manager at Infineum. "With Infineum SV600 we have developed a high performing viscosity modifier that, in combination with the Infineum additive package, can deliver outstanding performance in engine durability, soot handling and fuel economy."

Oils formulated with Infineum additives and with Infineum SV600 recently met a major European OEM specification, which required passing a series of highly challenging engine tests. This specification defines oils with extraordinary properties of durability and cleanliness, and the latest version combines this with the stringent fuel economy requirement.

According to Infineum, the Infineum SV600 technology can help deliver significant benefits in the latest generation of engine tests that focuses on fuel economy and soot handling. Oils formulated within Infineum SV600, in conjunction with Infineum additives, have demonstrated fuel economy advantages in test procedures representing different driving modes, including the NEDC (New European Driving Cycle), as well as the Japanese JC-08, the company said.

This fuel economy advantage is delivered directly by the unique design of the Infineum SV600 molecule structure, which contracts, reducing viscosity contribution at the critical operating temperature. At the same time, Infineum SV600's uniform molecular weight and distribution gives superior shear stability so oils are highly resistant to mechanical stress. Combined with outstanding soot handling and viscosity control, this means less engine wear and overall increased engine protection. **0116** 

\_\_\_\_\_

VM are additives made of long, flexible molecules called polymers. They come in various types, with different molecular architectures. Some of the main types of VMs include:

\*Olefin copolymers (OCP), which have a long, polymer backbone and can be semicrystalline or amorphous; amorphous OCPs have regular branching that prevents crystallisation at low temperatures. (The crystallinity here refers to the solid state of the polymer before it is added to the engine oil formulation.)

\***Polymethacrylates (PMA)**, which are amorphous and very versatile, because many different functional groups can be incorporated.

\*Additional polymers with a star shape, with several polymer chains connected at a central point. These include Hydrogenated Styrene-Diene (HSD) stars or Hydrogenated Styrene-Isoprene (HSI) stars.

BEYOND SAE J300 SAE J300 is a document that defines the rheological limits for classifying engine oils—that is, it defines engine oils in terms of viscosity. While VMs are, by definition, meant to impact the engine oil's viscosity, viscosity cannot be the only consideration when choosing VMs, experts said. They all emphasised that formulators should look beyond J300, as each VM has different molecular weight and architecture, impacting its performance in different areas, such as shear stability, compatibility with other components in the formulation, low-temperature performance, retention of performance through ageing and soot handling.

J300 defines viscosity grades in terms of kinematic viscosity at 100 degrees Celsius (C) or KV100 and high-temperature, high-shear viscosity at 150 degrees C (HTHS150). Kinematic viscosity is the ratio of the oil's dynamic (or absolute) viscosity to density. It is measured in centistokes (cSt or mm2/s).

HTHS viscosity is measured to see how engine oils will hold up in the engine environment. ASTM D4683, "Standard Test Method for Measuring Viscosity of New and Used Engine Oils at High Shear Rate and High Temperature by Tapered Bearing Simulator Viscometer at 150 C," was developed because the viscosities of engine oils under these conditions are related to fuel efficiency. It is measured in centipoise (cP) or millipascals times seconds (mPa•s).

THE RIGHT TEST MAKES A DIFFERENCE As with any product, the right test makes all the difference when determining how a VM will behave in the real world. Daniella Baxter, who works in the Technology Deployment group of Infineum, discussed the company's field trial for heavy-duty oils that has been operating in the U.S. for several years. It tests SAE 15W-40 and SAE 10W-30 engine oils with VMs of different chemistries: two HSD stars with different shear stability indices, an amorphous OCP and a semi-crystalline OCP. In measuring viscosity performance, all four VMs kept the engine oils in grade when KV100 and HTHS 150 were measured. Infineum also measured low-temperature pumpability, using a mini-rotary viscometer (MRV), MRV TP-1, for both fresh oil and 35,000-mile (56,327 kilometres) aged oils. The semi-crystalline OCP at 35,000 miles failed the MRV test by a large margin. The conclusion was that the fresh oil MRV test is not a suitable indicator of low-temperature performance in the field, Baxter said. Following some real-world field failures due to poor used oil pumpability, the Coordinating European Council (CEC) developed an ageing test, CEC SG-L-105, that puts the oil through mild oxidation in the presence of biodiesel and measures MRV performance. This test correlates much better to field data, Baxter said. The semi-crystalline OCP in aged oil failed this test as well, but by a smaller margin. Using the correct ageing test is necessary to better predict field performance, she concluded.

FORMULATING FOR LOW-TEMPERATURE PERFORMANCE Chevron Oronite's Alex Boffa, viscosity index improver technical team leader, and co-author of John Fang, senior research scientist, said that the key in formulating for low-temperature performance is to properly match the base oil, VM, and other additives with a pour point depressant (PPD). Improperly formulated oil will give poor results in lowtemperature bench tests or field tests, whether the VII is amorphous or crystalline in solid form, he said. He added that higher crystallinity can make the solid VII less tacky and easier to handle in manufacturing. In oils, VM polymers are solubilised to dilute concentration, and characteristics in dilute solution are different than in solid, he explained. Whether amorphous or crystalline in solid form, an important concern is to avoid unwanted interactions in the fluid, which happen at low temperatures when waxes can start to form in the base oil or VM. For instance, the optimised OCP has a low crystallinity in solid form, said Fang. However, when dissolved in oil, highly sensitive rheology testing showed negligible yield stress, indicating no interacting networks between polymer chains. Fang provided additional insights on the development and evaluation of an optimised OCP, which involved a series of structure property studies to demonstrate robust low-temperature properties and advantages in the thickening efficiency, deposits and extended shear durability. Robust low-temperature performance is a primary focus, as demonstrated in tests such as MRV, pour point. Scanning Brookfield, and used-oil, low temperature tests, such as CEC L105, with a range of PPD and base oil types. Another benefit of optimised OCP is low deposit formation in the high-temperature regions of the engine, due to more thickening, leading to lower polymer treats.

EXTENDED DRAIN PERFORMANCE Regarding extended shear stability, Fang compared an optimised OCP and an HSI star polymer. Both were put through extended shear cycles, and targeted to meet the same KV100 after 90-cycle shear in ASTM D7109, the Kurt Orbahn test. While both passed, the test was extended to 720 cycles, eight times the 90cycle limit, at which point the linear optimised OCP had only sheared an additional 5%, as opposed to significant deterioration in the HSI structure after continuing the test beyond the current limits. Fang pointed out that "different chemistry really has an impact on shear stability." The optimised OCP demonstrated robust extended shear stability, retaining most of its architecture instead of breaking down. This can aid in supporting extended drain performance, he said. The shear stability index is a measurement of a viscosity modifier's ability to resist permanent viscosity loss due to shear. As Baxter explained, "the counterbalance to shear stability is thickening efficiency." Thickening efficiency is the measure of added viscosity at 100 degrees C per unit mass of polymer. Both are dictated by molecular weight. High molecular weight molecules are less shear stable, but more thickening-efficient, meaning that a formulator has to add less polymer to achieve the desired viscosity grade.

FUEL ECONOMY GAINS Optimised polymers can translate to significant gains in fuel economy, as Torsten Stoehr, global product manager for driveline and industrial gear fluids, Evonik Oil Additives, showed. He spoke on dispersant and nondispersant comb polymers and their advantage over conventional PAMA (poly alkyl methacrylate). Using correctly formulated comb polymers can offer a 3 to 4% gain in fuel economy, if improvements in the engine oil, automatic transmission fluid (ATF) and axle oil are combined, he said. A comb polymer has a main backbone with several linear side chains; these optimised combs have enhanced ability to collapse and expand. In a chassis dynamometer test of fuel economy in automatic transmission fluids (ATF), Evonik demonstrated that comb polymers have a significant advantage over conventional PAMA in terms of fuel consumption. In each section of the New European Driving Cycle (NEDC) and the Japanese driving cycle JC08, a 6.0 cSt ATF formulated with a comb polymer consumed less fuel than a 6.0 cSt ATF formulated with a conventional PAMA, with up to a 1.2% overall advantage in the NEDC. A 4.5 cSt ATF with comb polymer was also tested, and while it offered lower fuel consumption in most of the NEDC, it consumed more than the 6.0 cSt ATF with comb polymer during the extra-urban portion. Overall, in the "warmer" and thus more challenging JC08, the 4.5 cSt ATF with comb polymer actually consumed 0.1% more fuel than the conventional PAMA, whereas the 6.0 cSt formulation with the comb again offered a 0.5% fuel economy advantage. "We cannot at all recommend going to a 4.5 cSt viscosity level," Stoehr said, because during the extra-urban driving portion of the NEDC and most of the JC08, it was pushed into mixed lubrication, which meant increased fuel consumption and increased friction.

LONG-TERM PERFORMANCE Regardless of the application of a viscosity modifier, its purpose is to keep the engine oil's viscosity in the right range, no matter how stressed inside the engine. Phil Hutchinson, Asia-Pacific technical manager at Evonik Oil Additives, said "different viscosity index improvers have different formulation viscosities, despite being formulated in the same SAE grades." SAE J300 specifies both KV100 and HTHS150. However, "Formulating to two viscosity targets, such as HTHS and KV100, can actually force you into getting a low-VI oil and poor fuel economy," Hutchinson said. In addition, KV100 is not a good indicator of viscosity for modern engine oils, he said. For engine protection. HTHS150 has taken over this role. When formulating for fuel economy. a formulator needs to select the Phil Hutchinson viscosity measurement and temperature that best represents fuel economy in the particular engine and testing cycle being targeted, he said. Different VMs can display dramatically different viscosity values relevant to fuel economy, depending on which viscosity value is measured. For instance, Evonik found that four types of VMs (comb polymers, PAMA, low ethylene-OCP and HSI stars) have very similar viscosities when measured at 150 degree C (HTHS), but widely different viscosities at KV40. The comb VMs gave the lowest KV40 values, thickening the least at the lower temperature, and incidentally contributing 1.9% toward the 3-4% fuel economy gain. Hutchinson's point added another aspect to the usual message about low viscosity oils: if an engine is suitable to be lubricated with them, then yes, a gain in fuel economy can result from low viscosity. "But which viscosity?" Deciding which viscosity measurement best represents their goals should be part of the equation for all formulators, he said. Finally, looking past the requirements in SAE J300 and extending tests for longer periods

will provide more insight into a viscosity modifier's long-term performance.

### 22 May 2015 | Made from microalgae, Soleum is a dry powder

Solazyme has introduced a solid lubricant, trademarked Soleum, during the Annual Meeting of the Society of Tribologists and Lubrication Engineers (STLE) in Dallas, Texas, U.S.A., this week.

Made from microalgae, Soleum is a dry powder, each granule containing triglyceride oil. Soleum, which is currently in the product development phase, is meant to offer similar lubricity and friction-reduction as other dry lubricants, such as graphite and molybdenum disulfide.

Kathryn Lee, director of product marketing for industrials, explained that Solazyme sees metalworking as the main application for this product at first, but that it hopes to branch out to other applications later.

The main goal is to develop a sustainable, high-performance lubricant ingredient that reduces the amount of additives that a formulator would need to use in a formulation.

"This is brand new," said Lee. "The next step is to work with folks in the value chain to find the right finished formulation."

The formulation is currently water-based, but Lee said that Solazyme is also working on oil-based formulations as well.

"From this, we also have some derivatives," she said, including an ester and an acid, in case customers want to start from a different building block.

Solazyme is headquartered in South San Francisco, Calif., U.S.A. Its main production facility is located in Moema, Brazil, which has a capacity of 100,000 metric tonnes per year.

# 22 May 2015 | Lubrizol<sup>®</sup> PV1116 additive

The Lubrizol Corp., based in Wickliffe, Ohio, U.S.A., announced its new Lubrizol<sup>®</sup> PV1116 additive solution for oil marketers seeking to establish leadership with higher-performance, fuel-efficient lubricants. The proposed ILSAC GF-6 specification will include SAE 0W-16 viscosity, as part of the GF-6B category.

"Through its continued market engagement and dedicated product development, Lubrizol is able to identify market needs and offer oil marketers the chance to lead in the ULV space," says Jon Vilardo, engine oils product manager.

"We are the first in the industry with this sort of technology, and it's an important step toward the advanced, higher-performance lubricants that modern fuel efficient engines require."

Lubrizol's advanced chemistry delivers fuel economy benefits beyond ultra-low viscosity (ULV), the company said. Lubrizol PV1116 delivers:

- Enhanced friction control
- Uncompromising engine durability and catalyst protection through HyperZDP(TM) technology
- Superior cleanliness and greater turbocharger protection
- Compatibility with ethanol-blended fuels

# 20 May 2015 | Fujifilm additive

Expanding upon its industry-leading liquid crystal coating technology, FUJIFILM Manufacturing

U.S.A., Inc., based in Greenwood, S.C., introduced a new, novel lubricant additive at the Society of Tribologists and Lubrication Engineers' (STLE) Annual Meeting & Exhibition being held in Dallas, Texas, U.S.A., from May 17-21.

The Fujifilm material, called FFJ-1, is a derivative of Fujifilm's industry-leading Liquid Crystal coating technology for flat panel displays, including televisions and tablets. Fujifilm researchers modified the original technology to produce a novel lubricant additive that achieves low friction and high-wear resistance. FFJ-1 has the advantage of not containing heavy metals, sulphur and phosphorous.

Data from comparison tests with conventional materials have shown that FFJ-1 can improve performance, providing lower friction under high temperature and high shear with a smaller wear scar, the company said.

This product has a wide range of applications, including as a friction modifier or as an anti-wear additive for motor oils, industrial oils and automatic transmission fluids.

### **PIB** as additive

### <u>John Neale</u>

PIB is used in many different types of lubricant, it has a high viscosity index, cleanly anneals, cleanly burns.

### <u>Ashok Pati</u>

Polyisobutene used as additives in engine fuel for minimizing sludge and oxidation products deposit precursors.

### **George Abernathy**

Everyone has a usage that is important. I would formulate drawing/stamping oils with it( various Mwts.) for cleaner dies and parts, and easier clean-off to go to the end-user. There was some final chromate, plating, and painting in some of these final products.

I did the same as Mr. Neale for temper rolling and cold mill rolling oils. Good burn-off in the temper furnaces( less carbon build-up-black).

### (Leroy) Martin Graves (Jr.)

Polyisobutene is commonly used in 2-stroke cycle engine oil as a low smoke agent (also antiblocking, good lubricity, clean burning for JASO). Typically grades Indopol H-7 through Indopol H-300 (Mn = 440 - 1300) are used to replace some of the base oil. Unaware of it being used otherwise in motorcycle engine oils (i.e. 4-stroke cycle).

As noted, the higher molecular weight grades are commonly used as thickeners (very good thickening efficiency), especially in gear oils (where it also exhibits good shear stability). Lower molecular weight grades can find use in metalworking fluids, like rolling applications (especially aluminum, where they are non-staining and burn off cleanly). The various grades are also used in food grade lubes, hydraulic lubes, greases, wire rope lubes and so on. Polyisobutene is also further chemically processed to create certain types of lubricant additives.

### V.S.S. Sarma

(Leroy) Martin Graves (Jr.) is right.

In the far east & India, 2-stroke API-TC / JASO-FC level engine oils are manufactured. They are used in the petroil systems of air-cooled engines at concentrations of about 2% (rest is gasoline). These engines follow all-loss situation and the burnt 2T oil goes away into the atmosphere as emissions. Environment damage with 2T oils is enormous. Hence country after country stipulated that these oils should meet JASO-FC level which has a smoke control test. In order to meet this

requirement, blenders use 1,000 molecular weight PIB to the extent of 25%. If you use a nonaromatic solvent in the 2T oil, you can reduce the dosage to say 12%. I feel that you should discuss your need with Lubrizol who will be happy to furnish you the required formulation using base oils of your area.

Mazher - I make JASO-MA oil regularly without using PIB. This component is not necessary at all. Handling PIB is not easy and use it only if there is no alternative like API-TC / JASO-FC oils.

### alkylated diphenyl amine

"As the automotive industry sets more stringent regulations and requirements for fuel economy, there will be an unmet demand for **antioxidants** in the marketplace by 2017," said Kerim Wewer, head of asset management in Europe, the Middle East and Africa for **Chemtura** Europe's Industrial Performance Products division.

ADPAs are one of various chemistries that the lubricant industry uses to help slow the process of oxidation, one of the main factors limiting lubricant performance life. According to Chemtura, nearly 75 percent of global lubricant antioxidant output goes to automotive applications.

### VM

### Larry Ludwig, CLS, OMA, CMFS

### **Difference Between Viscosity Improver & Viscosity Index Improver**

Basically the terms are the same. They are also known as Petr pointed out a Viscosity Modifiers.. These are generally polymers that consist of

ethylene-propylene-diene copolymers,

ethylene-propylene copolymers,

styrene-butadiene copolymers,

polymethacrylates and

hydrogenated polyisoprenes. They are primarily used in the formulation of multi-grade oils.

-----

For decades, lubricant blenders have used polymers to change VI. Chosen correctly, the right polymers will make the oil less viscous when it's cold, and more viscous when the thermometer rises.

Additive manufacturers and oil marketers call these polymeric materials V.I. improvers or, less frequently "viscosity modifiers." The terms are interchangeable, but by any name it's a big business. According to a study published last year by Kline & Co., V.I. improvers account for about 23 percent of global lubricant additive sales, by volume.

Additive companies have an assortment of V.I. improver molecules to work with. Historically, the first were polyisobutenes, introduced in the 1940s. The classic of the genre is Paratone N, originally supplied by Exxon Chemical's Paramins division but sold to Chevron Oronite in 1998 when Paramins came together with Shell Chemical's additives business to form Infineum.

In the 1950s, Rohm and Haas introduced the Acryloid brand of polymers to the North American market. Now sold under the Dynavis name by Evonik Oil Additives, these are based on polymethacrylates (PMA), and are widely used for both engine oil and powertrain applications. PMA also can be tailored to provide additional properties such as dispersancy.

Olefin copolymers (OCP) of ethylene and propylene also made their appearance in the late 1950s and early 1960s. OCPs were originally supplied by Paramins and also by Texaco Chemical, which was acquired in the 1990s by Ethyl Corp.; now Afton Chemical, it sells them under the HiTec brand.

OCPs are the most widely used V.I. improvers, and other suppliers include Lubrizol, Infineum, Oronite, Mitsui Chemicals and Lion Copolymer. They offer good performance at reasonable cost, which makes them attractive. In the mid-1980s the processes used to manufacture these workhorse polymers were improved to allow for the formation of so-called "block" copolymers, which optimize thickening efficiency while allowing for improved low-temperature performance.

Styrene-isoprene polymers were introduced by Shell Chemical in the 1970s. Sold under the Shellvis brand, they brought some advantages in shear stability and low-temperature performance. These polymers also continue to be widely used, especially in engine oil applications.

U.K.-based consultant David Wedlock has described how polymeric V.I. improvers work. Many believe it's due to the polymers' temperature-dependent solubility. At lower temperatures, the theory goes, the polymers are less soluble (or the molecule is more coiled up), while they become more soluble at higher temperatures (the molecule relaxes).

This is a popular misconception, but in fact, Wedlock says, solubility is largely irrelevant. Writing recently in *Lubes'n'Greases Europe-Middle East-Africa*, he explains that V.I. is affected by the carbon number (a means of expressing molecular size) of a molecule. The higher the carbon number, the higher the V.I. Simply stated, V.I. improvers are bigger molecules and will raise the V.I. of any base oil having a much lower carbon number.

The net effect, as Wedlock explains, is that viscosity is low enough to enable an oil to flow freely at lower temperatures, and at higher temperatures the viscosity is high enough to provide protection against metal-to-metal wear.

One of the benefits is that automakers can write their lubricant specifications around lowerviscosity base oils, which have lower overall internal friction and less viscous drag. That adds up to better energy efficiency. This property is especially useful for engine oils and powertrain fluids and is accomplished through a phenomenon called "temporary shear loss."

When an oil containing a V.I.-improving polymer is subjected to high pressure and/or high shear rates, the polymer molecules tend to become more organized and line up with the direction of flow; this results in a lower apparent viscosity. When the pressure or shear is removed, the polymer once again becomes randomly dispersed in the oil, raising the bulk viscosity.

The downside of V.I. improvers is that repeated shearing tends to break down the polymer into shorter chain lengths which are not as effective at thickening. This is referred to as "permanent shear loss." Depending on the polymer structure and size, permanent shear loss can be minimal or quite substantial. The larger the polymer, the larger the shear loss; smaller polymers don't shear as much, but they also are less efficient at thickening. The trick is to balance performance against molecular size.

Today's V.I. improver market is seeing a great deal of activity. In discussions with the major V.I. improver marketers, several common themes developed. While the approach varies from supplier to supplier (who tend to be closemouthed about their proprietary research), all are giving a great deal of thought to this component and how it can be even more useful in the future.

Chevron Oronite's Bill Paschal, global V.I. improver product manager in Bellaire, Texas, says his company is actively evaluating alternative chemistry. "Oronite remains committed to our core technology but is also looking outside of our immediate toolbox to expand our portfolio," he says, adding, "There are new molecules we are looking into, but aren't able to share any information at this stage. Broadly speaking they are unique polymer structures, such as block copolymers, tailored to specific application requirements."

Olefin copolymers will continue to represent the bulk of the market, says Bill Dimitrakis, VM commercial manager at Lubrizol in Wickliffe, Ohio. However, in 2008 Lubrizol introduced a bristling new PMA structure. This star-like polymer, called "Asteric," offers a very high V.I. which results in fuel economy gains, according to Dan Visger, Lubrizol's VM technology manager. He says Asteric polymers are favored in markets like Japan, where OEMs recommend very low viscosity grades. Visger notes that Asteric is also well suited for automatic transmission fluids and rear-axle lubes where lower-viscosity products can provide added fuel economy.

Darmstadt, Germany-based Evonik also has a new patented PMA technology, which Thomas Schimmel, product manager, hydraulic fluids, describes as having a "comb" structure. He says it too provides excellent fuel economy performance in lower viscosity fluids such as Japanese engine oils and ATF.

Of great interest these days is how future engine oil specifications will impact V.I. improver design. Carlo Rovea, Infineum International's segment manager for VM and pour point depressants, points out that the coming upgrades of gasoline-fueled engine oil (GF-6) and heavy-duty diesel oil (PC-11) both are heavily emphasizing fuel economy.

The lubricant itself provides for some level of fuel economy, but just as important, it must protect the engine against wear, reminds Rovea, who is based in Savona, Italy. "Viscosity modifiers play a key role by allowing formulators to meet viscometrics in order to maximize fuel economy and deliver engine protection in all climates. Different viscosity modifiers can deliver best-in-class shear stability and low-temperature pumpability and wear protection." The ideal viscosity modifier would also allow for significant formulating flexibility, in order to optimize base stock selection.

However, Lubrizol's Dan Visger cautions that the new oils' need for both better shear stability and lower viscosity may provide less blending cushion, resulting in a narrower formulating window. As well, tougher stay-in-grade requirements for heavy-duty engine oils are being investigated for PC-11, he says. "This could lead to use of more shear-stable VMs in those oils compared to today's market."

Infineum's Rovea agrees that the formulating window is getting tighter, especially compared to today's most common SAE viscosity grades. "Viscosity modifiers may be very critical in meeting some very tight formulation windows, and in order to deliver maximum fuel economy while still protecting the engine."

Alex Boffa, Oronite's technical team leader for V.I. improvers, doesn't antici pate that drastic changes will be needed for the bulk of the market. "We think any new V.I. improver designs will not impact the core GF-6 or PC-11 products but rather be targeted to specialty products," like the fuel-conserving version of PC-11.

"In addition," Boffa continues, "we believe the pressure on fuel economy will drive the need for more polymer options, especially for PC-11. Formulators will want more choices – another reason we believe Paratone to be positioned well. The need for cost-effective solutions may impact V.I. improver designs, so we also believe that economics may play a part in driving improved performance."

Evonik's Thomas Schimmel points to other applications, beyond the automotive crankcase, where V.I. improvers are being challenged. "While the objective of fuel economy is shared by driveline, engine oil and hydraulic fluid applications, the concepts and technology addressing fuel economy are fundamentally different among them. It is low viscosity and high V.I. for driveline and engine oils; it is high viscosity and high V.I. for hydraulic fluids."

Transmission hardware is also becoming more diverse, leading Lubrizol to observe that ATFs may become more specific to transmission type. Result: Even more splintering of the transmission fluid market than seen today.

Drivers for automatic transmissions include longer drain intervals, higher power density, smaller

sumps, better efficiency, and greater durability. All of these have an impact on the V.I. improvers, especially durability and power density.

Lubrizol cites gear lubricants as another application where more shear-stable V.I. improvers could result in better fuel efficiency. They might also allow for the use of API Group III base stocks, as opposed to polyalphaolefins, for such grades as SAE 75W-90 or possibly SAE 75W-85.

Both Lubrizol and Evonik say they are delving into the possibility of using lower molecular weight, highly branched V.I. improvers at higher dosages for areas such as gear lubricants for stationary engines and industrial applications. These products promise much improved shear stability as well as greater efficiency and reduced operating temperatures in critical equipment such as wind turbines.

Maryam Sepehr, Lead Polymer Scientist at **Chevron** Oronite Company LLC, will be presenting the topic – Viscosity Index Improvers with Optimized Structure and Performance in Lubricating Oils – at the upcoming Moscow International Lubricant Week 2014.

"Modern lubricants must satisfy progressively stringent performance criteria such as low temperature, engine deposit, and long drain performance, and viscosity index improvers (VII) are an important additive component that helps meet those performance demands," said Sepehr. "In this presentation I will report on the development of a **HE-OCP VII** with an optimized structure that provides robust low-temperature properties and advantages in thickening efficiency, deposits, and extended shear durability.

\_\_\_\_\_

### **TBN Additives**

Asad Perwaiz Lubrication Analyst at ExxonMobil

Magnesium base tbn r weak bases and they only neutralize strong acid and left weak acids. On the other side calcium base tbn r strong base and they neutralize both strong and week acids and deplete earliar than that of magnesium base. By experiments it has been proved that calcium base tbn performs better.

Ranju Pilani Owner, Octane Incorporated FZC

On the contrary all the Multinational Additives manufacturers are recommending Magnesium as a superior metal to impart the base to the lubricants. Ex. Infenium and Afton.

V.S.S. Sarma Technical Manager

Magnesium Sulphonate is an excellent detergent is a known fact. But what is not very well remembered is that it is also an excellent rust & corrosion inhibitor. For a diesel engine oil, this fact is considered while using Magnesium Sulphonate.

Jean-Michel Demaret Technical Expert, Concentrating Mill Maintenance at PT Freeport

Magnesium sulphonate more expensive than Calcium Sulphonate. Some engine manufacturer with rotating exhaust valves mentioned seeing more wear with high calcium oil versus high magnesium oil. They believe that magnesium deposit on the valve seat and valve face create less wear because the deposit is softer. Never been able to measure or obtain test results.

### V.S.S. Sarma Technical Manager

Calcium is hygroscopic and has a tendency to form deposits with moisture in air. Companies like Afton which went the Magnesium way appear to have come back to Calcium because of the non-

availability of quality Magnesium Sulphonate. Manufacturing Magnesium Sulphonate is more difficult than manufacturing Calcium Sulphonate. Hence the cost is high.

### Karim Ibrahim GM & Consultant

Mg better on several fronts such as more extended life, softer deposits and less hygroscopic which helps giving them better rust protection properties. However, to the best of my knowledge, cost and availability are the main reason the industry prefers the Calcium based products esp that this is a high consumption product.

-----

### Steve King Independent Consultant - Lubricants

Is it true that the conventional materials/chemicals currently used in TBN additives, are inherently harmful to the lubricant? I heard that they reduce the lubricity and so increase friction and wear. Is this true, and has it always been like this in the industry? What about if synthetic base oils are used - does the problem still exist, or it is overcome? I'm looking for some comments on this from some lubricant techies, please!

### <u>Alexey Muralev</u> Lubricants Field Engineer at ExxonMobil

Hi. Can you elaborate on your question, what do you mean by conventional TBN additives? If you mean overbased Calcium Sulphonates or other various detergents, then no. I haven't seen anywhere that those affect lubricity. Their chemical properties are such, that they can hold onto metal surface with hydrophobic part outside and that will only reduce surface tension and ease the flow of oil along this surface.

Sometimes you can add lubricity agents that interfere with overbased detergents, but usually that is not the case.

### <u>Ali Durrani</u>

Steve I am not sure what you mean and how you concluded that TBN is harmful but in any formulation of engine oil there is competition of different additives for the same surface and not to forget the chemicals can react with one another in given circumstances so they can effect one another's performance and that is why you have people who specialize in making the additives formulation. They have and outstanding understanding of Chemistry and balance the act of creating a product that meets the OEM, API, ILSAC etc requirement. This is a creative and very stressful job. Satisfying them all is not very easy. In short one additive individually might not have the properties but with combination of the right chemicals you can produce a package that suites the OEM and others. The package has to been seen as a whole and not individually unless you are facing a problem.

### Steve King Independent Consultant - Lubricants

I have been in the industry for many years, but I am not a chemist, although I do fully understand the concept of a balanced formulation to achieve optimum performance with often competing materials. What are overbased calcium sulphonates?

Maybe I didn't explain it very clearly. Someone told me recently that the material used to provide TBN in an oil (is it sodium hydroxide, I'm really not sure?), has both positive and negative effects. The positive is the ability to combat acids in the oil, but the negative is a reduced lubricity and even a premature ageing of the oil, from the time it is added, thereby reducing the life of the oil. So I am just trying to check this out - is it actually true, or is this nonsense? Is it a known fact in the industry when formulating oils with TBN that this is how it is, and is this problem overcome by use of other additives perhaps? Or is this issue not even a problem?

### <u>Ali Durrani</u>

Steve I am not a chemist either therefore cannot discuss chemistry like a chemical or synthesis

engineer. I have worked with chemical companies and learned all the chemical stuff on the job.To my knowledge there is no detrimental effect of detergents or dispersants on wear because if you go back in time API CD performance additive package the two components where almost 60% of the formulation if not more. Today as well major part of the engine oil additive package is detergents and dispersants.

<u>Fernando Oscar Bilotti</u> Senior Field Engineer Support - Argentina Area - Minería y Marine & Aviation Lubricants en Axion Energy S.R.L.

Some times, in marine X-head engines like MAN or Wartsila operating with Low Sulphur fuels, if you add more TBN additves, you can reduce the film protection and produce scuffing in the liners (cylinder wall) like a mirror. Is like a wash out the lubircantt in the cylinder wall. I have information about the chemical reaction, and the OEM's have a table with the right TBN levels according to the load operation and the sulphur content in the residual fuel. In the marine trunk piston engine operating with low sulphur fuels or marine diesel (medium speed engine) i had the possibility to conduce sevale boroscope or visual inspection when the engines runs with higher TBN and I saw white-yellow deposit in the top of the piston crown and in the valve seat. Some times this accumulation of salts (TBN additive in excess) produce cylinder wear, like the soot. The ides is to use the right TBN amount according to the Sulphur level in the fuels. Other important issue is the kind of TNB additive, because the TBN retention in some lubricants (Gas Engine Oil, Marine Diesel Oil or Stationary Diesel engines ) deplet faster than other and the combination of the chemestry and base stocks are very important. Of course, the synthetic areb better, bur some of then like PAO requires special additive package and mabe an other synthetic base stock like esters or AB in order to improve the solubilization of the additives.

Please teake in consideration the applications according to my experience. I agree with Ali, the total TBN takes in consideration detergents and dispersants.

### <u>Ali Durrani</u>

Fernando you bring in a good experience on Marine engines. Higher the TBN higher the Sulphated ash (SA). SA does contributes to engine deposits which intern is the cause of wear that is why based on engine fuel types there are restrictions on SA by the OEMs.

Having made the link between TBN and wear, what I thought Steve point was does TBN weakens the oil in wear properties by adding Detergents and dispersants (TBN contributors).

Michael Merritt Group Lubricants Technical Advisor at THE SOL GROUP

No. Sodium Hydroxide is not used to provide BN protection. Your friend may have been confusing the chemical with potassium hydroxide (KOH), which is although not used as an additive is used as a reporting measure. i.e. BN (correct term) is reported as if you asked the question what quantity of KOH would be necessary to get the same neutralization effect as the oil being tested and the results reported in units of KOH.

Secondly, modern engine oils are tested for performance in a combination of laboratory and engine tests. As Ali suggested the individual chemicals are less important than the performance of the total package inclusive of base oil and additives.

Fernando mentioned his experience with TBN levels in low sulphur fuel applications. While ash (generated from the burning of the metallic additives can contribute to wear, one likely phenomena occurs during the breaking in period. Most manufacturers actually want some acid attack and etching on the cylinder walls during break in to allow for better lubricant retention. However if the fuel sulphur is low and the BN is too high, the etching does not take place leading to less oil film retention, then when engines are brought up to full load accelerated wear occurs.

Zainudin Yahya Managing Director at CbM Solutions Sdn. Bhd.

TBN is added in lube oil primarily to counter acid build-up. The concentration is lowest for Natural Gas Engine Oil and highest for Cylinder Oil for Crosshead Engine (Slow speed Marine engine.)

The TBN concentration is intended for the application, like anything there will always be an optimum level either technically or economically. In NGEO too high will cause troble with ashing, which can develop as layer on valves, worsening the thermal efficiency of the internal engine surface (particularly valve) and in severe cases cause material damage. In Gasoline Engine, too much ash blocks catalytic converters pores. In Slow speed marine engine the unused TBN additives (Calcium Sulphonate), formed deposits (Calcium Carbonate) which is abrasive to cylinder liners, causing problem.

I do agree with getting the right chemical balance but are not aware of any study to suggest direct impact to lubrication protective surface. The main issue with overbased (too much TBN) for me is related to the ash/deposit by-product.

OEMs, upon field experiences and trials often work with formulators to set practicable maintenance schedules and practises to manage all these impacts. However, situation on the ground is far from perfect with many variables that can push the oil to it's limit, hence monitoring is a strategy needed to protect equipment. There are technologies available to detect wear debris with every 30 minutes of running and TBN within minutes of sampling.

Mark O'Brien Lubrication Excellence Champion

It is not about the engines, it is about the sulphur level in the fuel.

- Engines that burn heavy fuel do so for economic reasons, not mechanical. And, the higher the treat rate of reserve alkalinity chemicals, the lower you must make the anti-wear treat rates. This has much to do with why some engines see more wear, the highest TBN users have the most wear

- With the new laws for sea-going vessels this will soon be old news anyway.

If the additives are harmful, I will bet they are not nearly as harmful as the acids they eliminate.

### V.S.S. Sarma

TBN boosters are added to engine oils for decades. No, they are not harmful to lubricants. They enhance lubrication, do not reduce it. But don't over-treat which will be a problem. High TBN promotes catastrophic wear. There was a ChEvron paper on this in the past.

\_\_\_\_\_

Jean-Michel Demaret Technical Expert, Concentrating Mill Maintenance at PT Freeport

John, what will be the advantage of Graphite over MoSO2 or PTFE?

John Neale Director at John Neale Ltd

Graphite is highest temperature stable, PTFE is usually used where white /cleaner lubricants are desired.

MoS2	Graphite	PTFE
Very wide temperature range -180 °C up to 450 °C Under vacuum up to 1100 °C	High thermal stability up to 600 °C Poor efficiency at vacuum	Max service temperature of 260 °C Good lubrication at vacuum
Very high load carrying capacity Up to 3000 N/mm <sup>2</sup> Good against fretting Needs running-in (high loads)		Limited load carrying capacity Low µ at low loads

Very good adhesion on metal surfaces	Poor adhesion on metal surfaces	Non-coatable
Very low conductivity	High conductivity	Low conductivity
Humidity sensitive (µ increase)	Good lubrication in presence of humidity	
Good resistant against radiation and chemicals	Good chemical stability	
Black	Black	Translucent / white / whitish
Good lubrication in the presence of oxygen	Works synergistically with MoS2	

## Climax to launch spherical iteration of molybdenum disulfide

### 10 March 2015 | Additives

Yakov Epshteyn, chief engineer of lubrication at Climax Molybdenum, said the company has developed molybdenum disulfide (MoS2) that can be sprayed into a spherical form called spherical molybdenum disulfide (SMD). Epshteyn was speaking at the pre-conference workshop of F+L Week 2015 at the Pan Pacific Singapore on Tuesday.

SMD can substitute for regular MoS2 as an additive for greases, coatings, lubricating oils and other applications. Epshteyn said the new product works well under extreme pressure conditions and while It has not been shown to greatly reduce friction, it did greatly decrease wear. MoS2 is a powder and usually presents in a crystal form, with a hexagonal or rhombohedral shape. Development of the spherical version took four to five years, he said.

SMD is formulated by spray drying the slurry of superfine MoS2. Initial trials have been conducted proving that it is possible to make a homogeneous blend of MoS2, wherein the blend, as well as the particles themselves, are homogeneous, meaning the sulphur is evenly dispersed. Formulating and granulating conditions can be arranged to modify the particle size, shape and hardness, so that the ideal size and shape of the particles can be obtained.

SMD is not yet commercially available. He said that the product will be launched during the European Lubricating Grease Institute (ELGI) annual meeting in April.

### **BASE OILS**

\_\_\_\_\_

\_\_\_\_\_

### V.S.S. Sarma Sept'15

Take 99.2% by weight of **base oil** (Group 1 or Group 2) at a landed cost of USD **750/MT**.

Add to this the **hydraulic additive package at 0.6% by weight** at a cost of about USD **5,500/MT**.

Add **PPD at 0.2% by weight**, it costs about **USD 3,000/MT**.

So, the **product cost** can be about **USD 783/MT**.

Add to this the **blending and filling cost** of about **USD 45/MT** (4 cents a litre).

Take density at 0.88. Final cost will be about USD 0.73 per litre.

Some people may use cheaper base oils and can bring down the cost to about 0.70 USD/litre.

\_\_\_\_\_

A low-viscosity base oil, Chevron Neutral Oil 60R, produced by Chevron U.S.A. Inc., in Europe, produced by an all-hydroprocessing technology, has very low sulfur and contains almost no impurities, used instead of Group I base oils, oil life can be extended by as much as 300%.

4/15

\_\_\_\_\_

As a buyer, what **features of the base oil** (SN 500) are your top priorities?

VI, PP, FP or Color ?

### V.S.S. Sarma

Lubricant base oils should be as pure as possible. They must have very low pour point (indicating that all wax material has been removed), very low neutralization number (indicating that all acidic and basic materials have been neutralized), high viscosity index (indicating that all low VI causing elements such as aromatics have been removed), low colour number (indicating the degree of refinement and the extent of hydrogen treatment), high flash point (indicating that fuel components have been successfully removed), low cloud point (indicating that the wax has been removed from the base oil and that the low pour point is not achieved by adding a PPD), very low Sulphur content (indicating the extent of the operation of hydro-desulfurization), high Aniline point (indicating the degree of refinement), high content of saturates (unstable unsaturates are removed) etc. May be as a QC measure, you can use refractive index too.

Now the most important aspects are: Saturates, VI and Sulphur content. Not that the other aspects are not very important.

### Mukesh srivastava

color, flash point, Viscosity index

\_\_\_\_\_

### NYCO's synthetic ester base stock, NYCOBASE 43608 FG, earns NSF HX-1 registration

NYCO is pleased to announce it has recently gained NSF HX-1 registration for NYCOBASE 43608 FG, an ISO VG 320 complex ester, responding to the growing demand for Food Grade products from its customers and the market.

NYCOBASE FG series include 7 ester base stocks suitable for the formulation of H1 lubricants for incidental food contact. These oils are used in multiple applications including hydraulic fluids, gear oils, compressor oils, greases, chains lubricants.

Products from NYCOBASE FG series are also Halal and Kosher certified, show high biodegradability and renewability levels, and possess superior thermal stability as well as good low temperature properties. 0815

\_\_\_\_\_

### 1 July 2015 | Lubricants

Elevance Aria<sup>™</sup> WTP 40, a high-performance synthetic base stock, has been certified as HX-1 food-grade by <u>InS Services (UK) Ltd</u>. Elevance Renewable Sciences, Inc., based in Woodridge, Ill., U.S.A., said this certification expands its current potential applications — industrial gear, transportation gear, compressor and grease markets — to include applications in the food processing and cosmetic industries.

Elevance Aria<sup>TM</sup> WTP 40 is "acceptable as an ingredient for use in an H1 lubricant, anti-rust film or release agent with incidental food contact up to 10 parts per million (ppm), for use in and around food processing areas where there is a potential exposure of the lubricant to food," according to the certificate issued by InS. InS Services was created in the UK by Sid Stone and Eric Gard to fill the market need for an alternative H1 registration body, the company website said.

HX-1-certified base stock, as a component of H1 lubricants, is important in lubricant applications for materials manufactured according to Good Manufacturing Practice (GMP) that are common in the pharmaceutical and cosmetic industries.

"The HX-1 certification provides Elevance Aria<sup>™</sup> WTP 40 customers globally with the ability to meet growing demand for a food-grade solution that **performs better than traditional PAO**-based formulations and can be used across a wide range of applications," said Robin Weitkamp, senior vice president, lubricants and additives. "In addition, we continue to work with new customers

every day to uncover expanded uses for this innovative base stock."

Elevance Aria<sup>™</sup> WTP 40 is a **high-viscosity base stock co-polymer** that has GRAS (generally recognized as safe) status from the <u>U.S. Food and Drug Administration (FDA)</u>. It **combines the composition and properties of esters and poly alpha olefins (PAO) into a single, high-performance product**.

\_\_\_\_\_

Li contended that **base stocks in metalworking fluids** today have a significantly greater impact on industrial lube performance than they did in years past.

The Lubrication Research Institute is one of China's main centers for the study of industrial oils. It also has a commercial arm, Jetsun Lubrication Technology Co., which is one of China's largest suppliers of metalworking fluids. Li said the lubrication institute conducted a preliminary study recently of base stock performance in metalworking fluids and other industrial lubes. They concluded that base stocks should be selected based on characteristics such as viscosity, viscosity index, performance at different temperatures, oxidative stability and interaction with equipment and workpiece materials. But requirements can differ widely for different applications. LRI researchers looked specifically at requirements for fluids used in metal forming.

"A low-viscosity oil with low surface tension will provide optimal permeability and cooling performance, so it is a relatively good choice as base oil, especially in processing soft metals like copper and aluminum," Li said. "Base oils with too high viscosity have poor cooling performance and strong adhesion. They remove chips easily, but they are hard to clean. Thus, they should not be used as a cutting oil base stock."

Li said there are additional considerations when selecting a base stock for microemulsion metalworking fluids, because the oil is interacting not only with tools and workpieces but also with the water portion of the formulation. Naphthenic base oils perform well because they have low pour-points and help the microemulsion to maintain a low freezing point.

Low-viscosity paraffinic base stocks are also good choices, he said, because they are stable and allow good clean-up. Non-standard oils would seem a good choice, he said, but they make cloudy mircroemulsions – an undesirable characteristic in the eyes of end users. Tower oils meet most performance requirements at typical operating temperatures but tend to agglomerate during winter and therefore should not be used, Li said.

\_\_\_\_\_

With more stringent emissions and fuel economy regulations driving OEM requirements and industry specifications, the lubricant industry is searching for innovative solutions to rise to this challenge.

The next opporunities for growth in the synthetic lubricants segment will come from Group V base oils, functionalized esters and alkylated napthalenes, predicts Brad Rinderknecht, synthetics global marketing manager for the Houston Texas-based ExxonMobil Chemical Company. 11/14

\_\_\_\_\_

### **RE-REFINING**

Too short:

http://www.machinerylubrication.com/Read/29239/understanding-re-refining-process

#### \_\_\_\_\_

Daniel M. Cheng, Managing Director, Dunwell Enviro-Tech (Holdings) Ltd talks about Industrial & Hazardous Waste Management.

### MEWS: What are your main projects internationally?

DMC: We have been proactively seeking partners around the world to establish a low temperature (85 deg C), low pressure (50 psi) used lubricant recycling operation using our proprietary advanced vibrating membrane technology - VMAT.

We have already setup this oil recycling venture in Hong Kong, China (Beijing and Shenzhen), Mongolia, Indonesia (Jakarta). More will be installed in Australia, Romania, South Africa, China (Shanghai) in the next 9 to 12 months.

VMAT recycles used lubricants such as engine oil, hydraulic oil, gear oil, etc. into green lubricants again. Unlike other processes that recycle used lubricants into fuel oil, or creates a lot of secondary pollution (acid sludge), VMAT has become a popular option being enquired from international recyclers and even governments.

MEWS: What are the best technologies for waste oil recycling? What processes are currently being implemented in the Middle East and are they adequate?

DMC: We have to define "the BEST". There are many different options of technologies ranging from the mega scale investment hydro-finishing, to the cheapest but very polluting acid clay treatment process used in the industry. Before selecting any of the process, we have to understand the local government environmental standards, availability of local technical expertise, the market expectation on recycled oil products, market sizes, number of recyclers, etc. The best technology really implies if one could adopt an internationally proven, economic feasible, energy efficient technology for the Middle East Market.

In Middle East, there has been acid clay process being adopted for years. Due to the highly polluted nature of the process, most of the governments around the world have restricted this application after they have found the acid sludge have polluted the underground water and soil severely. This is going to be an outgoing technology.

Some recyclers are using simple dewatering and centrifuge techniques to produce fuel oil, which is of low value to the Middle East market that has abundant supply of fuel products.

Some recyclers may be using high temperature distillation process, but this process is too energy consuming and requires extensive engineering support.

The Middle East market is steering towards the directions of adopting a clean (non polluting) technology that can recycle used oil into finish lube products, with a low energy level and reasonable level of engineering requirement. Our VMAT fits into this context with a fast payback (less than 2 years) scenario.

MEWS: When does Dunwell Enviro-Tech work with the oil and gas industry? DMC: Dunwell has been involved in the oil recycling business since 1993, when we acquired and turned around a bankrupted Australian oil re-refinery operation (with a loss of US\$ 10 million) in Hong Kong. For the last 16 years, we have been building our engineering capability and investing in R&D for coming up a better process for the used oil recycling industry.

The low temperature (85C) process does not crack the hydro-carbon structure of used oil and would not cause air pollution problems. The absence of chemical (acids) used would not cause further damage to the water and soil.

VMAT is a modular expandable process to allow users to start with a smaller volume (5000 m3/year) and expand to 20,000 m3/year when they are familiar with the new business models and technology. Users can even setup the VMAT systems in various locations across the country, to minimize the transportation and enhance flexible operation.

For further information on VMAT, please visit www.dunwellgroup.com/vmat/en or email to vmat@dunwellgroup.com

### By H Adeni

Depending on how much you wanna pay, there are two popular methods:reclamation and **re-refining**. The cost of Refining is much higher than reclamation.

During reclamation the mechanical contaminations are removed and the treated used oils are applied as an energetic feed (heating and fuel oil, or fuel oil blending component).

There are several different ways in doing the recycle, depending on how much you wanna spend, reclamation and re-refining are two popular methods.

During reclamation the mechanical contaminations are removed and the treated used oils are applied as an energetic feed (heating and fuel oil, or fuel oil blending component).

During re-refining the mechanical, physical and chemical contaminations are removed with the following processes:

- distillation, 3 stage vacuum distillation process
- acidic refining,
- solvent refining,
- clay treatment,
- hydrogenation,
- combinations of the formers.

There is a famous process from Germany named VAXON PROCESS.

### By Jing Lin

### REFINING

### Lubricant base stocks are in the range of 26 to 40 carbon atoms.

**Crude oil** consists of Carbon (83 to 87%); Hydrogen (10 to 14%); Nitrogen (0.1 to 2%); Oxygen (0.05 to 1.5%); Sulfur (0.05 to 6.0%); Metals (< 0.1%). Crude oil contains Paraffinic Hydrocarbons (15 to 60%); Naphthenes (30 to 60%); Aromatics (3 to 30%) and Asphaltenes (remainder).

Petroleum Products Yielded from One Barrel of Crude Oil in California:Finished Motor Gasoline51.4%Distillate Fuel Oil15.3%

Still Gas 5.4%
5tin Gas 5.470
Marketable Coke 5.0%
Residual Fuel Oil 3.3%
Liquefied Refinery Gas 2.8%
Asphalt and Road Oil 1.7%
Other Refined Products 1.5%
Lubricants 0.9% (Adds up to 99.6%)

Source; <u>http://energyalmanac.ca.gov/gasoline/whats\_in\_barrel\_oil.html</u>

One barrel contains 42 gallons of crude oil. The total volume of products made from crude oil based origins is 48.43 gallons on average - 6.43 gallons greater than the original 42 gallons of crude oil. This represents a "processing gain" due to the additional other petroleum products such as alkylates that are added to the refining process to create the final products.

Additionally, California gasoline contains approximately 5.7 percent by volume of ethanol, a non-petroleum-based additive that brings the total processing gain to 7.59 gallons (or 49.59 total gallons).

\_\_\_\_\_

JAMSHED BAKHT • Generally feed is charged to atmospheric and vacuum towers at 390-400 Deg C depending on charachterization factor of crude. Cracking is temperature and time dependent and kinetics depend on size and type of molecules. Temperature drops in flash-zone of the tower and residue is section is designed to allow minimum residence time to control the cracking. Slight cracking uccurs in both atmospheric and vacuum towers wich is unavoidable.

# FORMULATIONS

John Neale Director at John Neale Ltd

Chlorinated paraffin (long chain to avoid hazard labeling) gives EP performance to water-mix metal working fluids.

It is a low cost additive to give this EP effect.

You can design chlorine-free products using a variety of esters and phosphate esters and chlorine-free oils can do almost all applications. However chlorine-free is a more expensive approach.

Satinder Bhatia Regional Manager at DA Stuart India Pvt Ltd (a Houghton Company)

Agree with John

But to add on that only long chain Chlorinated Paraffin are allowed to use, not medium and short chain as they are carcinogenic .

Other than esters , now Polymers are also popular to make Chlorine Free oils yet have performance like chlorinated ones.

Patrick Duffy Independent Industrial Marketing Consultant

Chlorinated parafin's were introduced as an EP additive for Soluble cutting fluids in the 1950's and 1960's .In those days the Health and safety and the environment were not huge issues and not much consideration was given to disposal cost and the effects of the environment. There is now a pull from end users to eliminate chlorinated paraffin from their sites. In 1997, Ford Motor company banned the use of chlorinated paraffins on their sites. Chlorinated paraffins were a cost effective way of .providing good EP performance to soluble cutting fluids by extending tool life and improving surface finish outcomes. Many countries legislatory authorities are forcing manufacturers of soluble cutting fluids to have severe hazardous warning printed on the containers and some countries have even banned the use of CP's.

\_\_\_\_\_

Larry Ludwig, CLS, OMA, CMFS Chief Chemist/Technical Director at Schaeffer Mfg

The terms ZDDP and **ZDTP** are basically the same. ZDDP is zinc dialkykldithio phosphate while ZDTP is the term used for zinc dithiophosphate..

ZDDP or ZDTP in its different forms has been used for over last 60 years as an anti-wear and antioxidant in different lubricant formulations. By far it is the most prevalent anti-wear chemistry deployed in engine oil and hydraulic fluid formulations.

ZDDP is a class of oil soluble organometallic chemicals that are that are intended to sacrificially decompose at areas of metal-to-metal contact and in doing so, depose a protective layer thus reducing wear. ZDDP consists primarily of the elements of zinc, carbon, phosphorus and oxygen. ZDDP is synthesized by the reaction of either primary short chain or long chain, or secondary short chain or medium chain alcohols with phosphorus pentasulfide and zinc oxide. The reaction of these constituents result in formation of what is known as zinc dialkyldithiophosphates, Another type of zinc dithiophosphates called aryl zinc dithiophosphate are formed by the reaction aryl alcohols (alcohols that contain aromatic hydrocarbon rings) with the pentasulfide and zinc oxide. ZDDP's properties, including the way they decompose, control wear, prevent oxidation and volatilize and thermal stability depend upon the starting alcohol used and the nature of the alkyl chains that make up the ZDDP. In other words all ZDDPs are not the same and the type of ZDDP used must be carefully selected to address any given performance requirement for a given application. In different applications it is not unusual to find a mixture of different types of ZDDP used in gasoline engine oil formulations and diesel engine oil formulations as compared to the type of ZDDP that is used in hydraulic fluid formulations.

In engine oil formulations mixtures of primary and secondary ZDDP are used in order to provide the proper balance of anti-wear and anti-oxidant protection that is needed. The levels of ZDDP used in gasoline engine oil formulations that are typically used due to phosphorus restrictions that have been set by the ILSAC GF-4 and GF-5 specifications (0.08% by weight or 800 ppm maximum) typically range from 0.5 to 1.5% by weight (5000 to 15,000 ppm) depending upon the alkyl chain length used. In diesel engine oil formulations depending upon the API Service classification the engine oil is formulated to meet the levels of ZDDP used can range from 0.5 to 2% by weight (5,000 to 20,000 ppm). It should be noted that the percent weight or ppm mentioned here is much higher than one would expect. This is because when the ppm levels or percent weight levels that are often used to identify the amount of ZDDP used in an engine oil formulation it is actually the actual zinc content that makes up only a small part of this chemical is usually quoted or used as the measure of the engine oil's ZDDP content although phosphorus is really the critical element that needs to be looked at. Generally phosphorus levels are typically 75 to 95% of the zinc concentration. Typically for ILSAC GF-4/API SM and ILSAC GF-4/API SN passenger car engine oils zinc levels are 0.065 to 0.09% by weight (650 to 900 ppm) and phosphorus levels are 0.05 to 0.075% by weight (500 to 750 ppm). For API SM and SN only type oils there is no limit other than a minimum limit of 0.06% (600 ppm minimum) for phosphorus. For API CJ-4 heavy duty diesel engine oils the zinc levels are typically 0.11 to 0.13% by weight (1100 to 1300 ppm) and phosphorus levels are 0.1 to 0.12% by weight (1000 to 1200 ppm).

In hydraulic fluid applications the type of ZDDP used as an anti-wear and anti-oxidant are the primary short and long chain types of ZDDP. These types are used due to their better thermal and hydrolytic stability. Typically, the ZDDP levels run between 0.2 to 0.7% by weight (2,000 – 7,000 ppm). In gear lubricant and greases ZDDP can also be used. In these applications either secondary type ZDDPs or mixtures of primary and secondary ZDDPs are used. The use of secondary ZDDPs is preferred due to the thermal instability of these types of ZDDPs. This thermal instability results in quicker film formation under high load conditions. Typically if used in grease or a gear lubricant the levels of ZDDP used are typically 1.5 to 4% by weight (15,000 – 40,000 ppm).

When exposed to the conditions found in an engine ZDDP undergoes thermal decomposition through a complex cascade of reactions. These reactions involve the formation of a combination of phosphates, thiophosphates, polyphosphates, dialkyl sulfides, meracaptans, olefins, etc. The nature and composition of this thermal decomposition mixture is dependent upon the type of ZDDP used and the specific starting alcohol used to produce the ZDDP. There are three mechanisms through which ZDDP protects the surface of an engine from wear. These mechanisms are as follows:

1) During mixed film lubrication conditions the ZDDP reacts with the metal surfaces by absorbing onto metal surfaces. As contact temperature rise catalytic decomposition of the ZDDP occurs to the phosphorus containing components. These thermal degradation products not only absorb on to the metal surface but also react with the metal surfaces to form a protective glass like structure which is 10 to 20 nanometers (0.01 to 0.02 microns) in thickness. As this film wears off it is reformed again. 2) The stripping away of corrosive peroxides and hyperperoxides that are generated by fuel combustion and oil oxidation by direct attack of these peroxides and hyperperoxides on the metal surface as they are formed. This reaction also forms an iron sulfide film that is absorbed onto the metal surfaces to form an additional anti-wear film.

3) Absorption of abrasive iron oxide particles that may be formed.

Though these films protect the moving parts of the engine the phosphorus component of these films has been found to reduce the effectiveness of three-way catalysts and other catalyst systems used by OEMs to reduce exhaust gas emission. This phenomenon is referred to as catalyst poisoning or deactivation. When ZDDP decomposes volatile phosphorus species can be formed. These volatile species can enter the exhaust system either by oil consumption past the rings and down the exhaust

valve guides or due to volatilization. Once in the exhaust system the phosphorus along with any sulfur compounds from the ZDDP and the engine oil's detergent and base oils can form a glassy coating that coats the three-way catalysts used in gasoline engines or the catalysts used in the DPF/DOC systems used in 2007 and 2010 on-highway diesel engines. Once this coating is formed these catalysts which are primarily platinum or palladium are prevented from contacting the exhaust gas thus rendering them ineffective.

In the 2007 and beyond on-highway diesel engines and in off-highway diesel engines that employ the use of DPF and DOC to meet Tier IV Interim and final regulations for emissions the main concern regarding heavy duty diesel engine oils is their SAPs levels.

The term sulphated ash relates to the amount of metallic elements in the engine oil, which are mostly present in the engine oil's detergent and anti-wear additive chemistry. Modern engine oil additive packages contain multiple components based on metals such as calcium, magnesium, zinc, etc. Since a 100% seal between the piston rings can never be achieved a certain amount of engine oil will enter the combustion and be burned.

When the engine oil containing these elements enters the combustion chamber and is burned the residue that is left behind is an ash like material. This ash like material can contribute to deposits in the crown land above the piston ring as well as to deposits in the ring grooves. These deposits can lead to rubbing wear on the cylinder liner and piston rings that do not operate freely. Ultimately, as the cylinder liner-to-ring interface is compromised high oil consumption can occur. In addition to these deposits inorganic compounds from the additives of lubricating oil can become oxidized in the combustion and generate metal oxide particles. These particles can be carried downstream with the exhaust and collect on the diesel particulate filter. These metallic oxide ash particles are not removed by filter regeneration because they are not combustible. As the ash particles accumulate, they reduce the porosity of the filter resulting in filter blockage. This filter blockage increases back pressure to the engine, increases fuel consumption and decreases power. Furthermore, reactions with the ash in the filter and high temperatures, along with the increased pressure drop across the filter can lead to permanent filter substrate cracking. Ash particle build up also results in the particulate filters having to be cleaned more often by mechanical means such as with compressed air or water.

The engine oil's sulphated ash content is determined by the use of the ASTM D-874 Test Method. In this test up to an 80 gram sample of oil is weighed into an either a porcelain or fused silica dish. The dish is placed into an electric muffle furnace and heated until it is ignited and burned. After cooling, the residue is treated with sulphuric acid and distilled water and heated to 775° C (1427° F) until oxidation of the residue is complete. The ash is then cooled, retreated with three drops of water and ten drops of sulphuric acid and heated at 775° C (1427° F) for 30 minutes. At the end of 30 minutes the sample is cooled and weighed. The sulphated ash content is expressed as a percentage by mass and is determined by the use of the following equation:

### % wt ash content = (wt. of residue left/wt. of sample) X 100

The engine oil's sulphated ash content also directly relates to the engine oil's acid neutralization capabilities (TBN), since most of an engine oil's TBN comes from the metal-containing detergent additives. Generally, the higher an engine oil's TBN, the higher its ash content and the greater its ability to prevent acidic corrosion in the engine.

Heavy duty-diesel engine oils are comprised of approximately 75 to 85% base oil with the remainder made up of additive systems. The sulphur concentration in the base oil can range from essentially zero (synthetic base fluids such as PAO's) to as high as 0.5% by weight (Group I base stocks). Sulphur content in base oil can be reduced by the use of hydrotreating and hydrocracking methods to levels ranging from less than 0.1 to less than 0.3% by weight. The additive systems used

are also major sources of sulphur. The sulphur containing additives used in the formulation of heavy-duty diesel engine oils include the detergents, anti-wear agents primarily from Zinc Dithiophosphate, corrosion inhibitors, friction modifiers and anti-oxidants. The sulphur in these additives is in the form of sulphonates, phenol sulphide salts and thiophosphonates.

The sulphur content of API CH-4, CI-4 and CI-4 Plus engine oils can range from 2500 ppm to as high 8500 ppm of sulphur by weight. It has been estimated by the EPA that anywhere from one ppm to seven ppm of sulphur can be contributed to the diesel engine's exhaust, when the engine oil enters the combustion chamber and is burned. The worst case estimate of seven ppm is based upon nominal heavy-duty diesel vehicle fuel and oil consumption rates of six miles/gallon and one quart per 2000 miles respectively. During normal operation, only a small percentage of the engine oil consumed by open crankcase ventilation heavy duty diesel engines travels past the rings and burns in the combustion chamber. The remainder of the consumed oil is lost through evaporation by being emitted through the crankcase ventilation tube and is not combusted. If an engine oil that contains a sulphur level of greater than the 0.4% maximum limit for API CJ-4 were used in a 2007 and 2010-compliant engine, the closed crankcase ventilation system would recover the evaporated oil and carry it through the exhaust stream.

Once in the exhaust stream sulphur can inhibit the effectiveness of the particulate filters by poisoning the catalysts. This poisoning can increase the conversion of sulphur oxides to sulphates, which increases particulate emissions and accumulation of particulate material. Accumulation of particulate material can lead to reduced engine performance, due to increased backpressure and ultimately failure of the trap.

The primary source of phosphorus in heavy-duty diesel engine oils comes from the anti-wear agent zinc dithiophosphate. Phosphorus can also come from corrosion inhibitors, friction modifiers, corrosion inhibitors, and anti-oxidants. The phosphorus in theses additives is in the form of dialkyldithiophosphates, thiophosphonates, phosphoric acid esters, and amine phosphates. Typically, heavy-duty diesel engine oils contain 0.11% to 0.15% by weight of phosphorus. Once in the exhaust stream, phosphorus can reduce the efficiency and deactivate the noble metal catalysts by coating and building up on the active catalyst sites, causing irreversible damage that accumulates over time. As a result, increased levels of harmful emissions such as NOx, carbon monoxide and hydrocarbons pass through the catalytic converter unchanged resulting in an increased level of NOx, CO and hydrocarbon emissions.

Regarding deposit build up the concentration of ZDDP used in an engine oil formulation does not contribute to, cause or lead to increased deposit formation. There are many causes and source for the buildup of deposits in an engine. If 1400 ppm ZDDP ( using the zinc concentration to define the ZDDP concentration) was the limit than many engine oils that are designed for use in older vehicles or in racing applications would be fouled with deposits.

You will also find one additive company has a patented novel ZDDP that is used in their engine oil formulations for their passenger car engine oil additive systems that they offer. This novel ZDDP is not a separate component that is added it is part of the complete additive system package used to formulate the passenger car engine oils. In diesel engine oil formulations the mixture and types of ZDDP used are totally different than what is used in passenger car engine oils. Further the use of the novel ZDDP will not necessarily allow for any increase in ZDDP levels. There are still limits for phosphorus that have to be adhered for engine oils that meet API SM and ILSAC GF-4, API SN and ILSAC GF-5 and API CJ-4 that come into play. The only time ZDDP levels can be increased is in engine oil formulations that are not API licensed or in engine oils that are API licensed as meet API Service Classification SM or SN only. In our racing oils for the past year the levels of ZDDP have been raised leading to a concentration of 1750 to 2000 ppm of zinc.

Finally, regarding ZDDP, ZDDP is considered to be not only an anti-wear additive it can also be classified as a mild E.P additive.

An anti-wear additive is used to reduce friction and wear under mixed film and boundary lubrication conditions. It can also prevent galling; scoring and seizure of critical moving parts such as valves and spools Anti-wear additives prevent metal-to-metal contact by adding film forming compounds that protect the surface either by a physical absorption or a chemical reaction with the metal surface in order to form a low shear film at the point of contact. These film forming characteristics are activated by either heat and /or pressure. Extreme pressure additives are additives that prevents metal-to-metal adhesion or welding when a high degree of surface contact occurs due to high-speed, high load, low speed high shock loading or high temperature conditions. They react chemically with the metal surface to form a protective film. The film formation for extreme pressure additives is a two-step process It consists of a physical/chemical adsorption on the metal surface to form a soap like film and a thermal decomposition to form an iron – EP film. This film fills the asperities to

- Reduces friction
- Prevent metal to metal contact
- Prevent welding and surface wear

The Hyper ZDP that is being touted by some companies is form of the novel ZDDP. In passenger car engine oils there are now specific tests for phosphorus retention in the engine and this is just a marketing term used to identify less volatile ZDDP chemistries.

\_\_\_\_\_

# **BASE OILS**

In 2014, Shell announced that all of its premium motor oil brand Shell helix Ultra with PurePlus Technology is made using **Shell PurePlus Technology base oils from Pearl**. These base oils, which typically make up 75-85% of motor oil, are cleaner, more effective, offer better performance than typical group III and are cost comparable with other fully synthetic lubricants.

"The Shell PurePlus Technology is based on their proprietary **Shell Middle Distillate Synthesis** (SMDS) process," said Frost & Sullivan Programme Manager, Avril Harvey. "Through this process, natural gas (methane) is piped from the ground and mixed with pure oxygen to create synthesis gas, which is catalytically converted to liquid form known as 'syncrude'. The syncrude is then cracked into the product ranges and distilled to create Shell PurePlus Technology base oils, which are completely clear and colourless base oils."

**The Shell PurePlus Technology base oil contains significantly more iso-paraffins than Group II and other Group III base oils derived from crude and contains fewer impurities.** The synthetic oil is then enhanced with Shell's Active Cleansing Technology that protects against the build-up of performance-robbing deposits to deliver enhanced cleaning power that exceeds industry standards by as much as 65 percent. Pureplus Technology is also differentiated in that it can be used to formulate motor oils such as SAE 0W-16 viscosity.

Due to its **purity, improved viscosity, and volatility**, the product ultimately requires consumers to top-up less often, even on the longest OEM oil drain intervals. This reduces the consumer's overall maintenance costs and helps extend the longevity of the vehicle and vehicle parts.

"Shell credits its success in continuous innovation to its matrix structure. Although it has large technology, marketing and supply chain teams, they operate as a single team," noted Avril Harvey. "Furthermore, the large volume of production from the Pearl GTL plant allows the GTL base oil to be distributed globally from Pearl to distribution hubs, and is then re-distributed from there. As a result, the formulation is consistent globally."

Shell is the only manufacturer to have produced base oils from natural gas on a commercial scale.

Over the lifetime of the project, Pearl GTL can process nearly 3 billion barrels of oil equivalent of gas. It produces GTL liquids, including base oils, at a rate of 140,000 barrels of liquid per day, while other plants can process less than 20,000 barrels per day. It is the sheer scale of Pearl, and the unique manufacture of base oils from the GTL process, that will continue to differentiate Shell into the future.

\_\_\_\_\_

The highest widely available viscosity in Group II is SN 600 (with a KV@40 °C of ca. 100 cSt), and for Group III the highest available viscosity corresponds to a SN 300 (with a KV@40 °C of 50 cSt; slightly lower than SN 300 SUS).

Crude oils and base oils are categorized as either naphthenic or paraffinic; however, there is no sharp distinction, rather a sliding scale from the "very naphthenic" to the "very paraffinic". Oils with a paraffinic carbon content ( $C_p$ ) of 42-50% (measured by infrared, IR) are considered to be naphthenic base oils; the rest of the carbon content being naphthenic ( $C_N$ ) 35-50%, and aromatic  $C_A$  5-15%.

Naturally occurring paraffinic crudes have a paraffinic content up to 67% ( $C_p$ ), but more importantly, both API Group II and III have ( $C_p$ ) content well beyond that, with saturates ( $C_p$ ) + ( $C_N$ ) (i.e. *non*-Aromatic) content often above 99%. The naphthenic content in Group II base oils is in the range of ( $C_N$ ) 30-40%, with a negligible amount of aromatic  $C_A$ . Thus, the *solvency gap* is readily explained and understood from the principal analysis chemical composition differences.

The solution to the Group I deficiency in most cases, i.e. where retention of both viscosity and solvency properties are required, is thus not to be found by switching to Group II or Group III base oils, as the differences simply are too large.

However, an oil very similar to Group I may readily be re-created by carefully blending naphthenic and paraffinic base oils- remember the sliding scale between naphthenic and paraffinic base oils!

Essentially, by adding paraffinic content to a naphthenic blend, a base oil range closely matching a broad selection of Group I base oils, from SN 70 to SN 600, can be created.

Naphthenic base oils are in ample supply in Europe and worldwide.

http://www.nynas.com/Media/News/Reliable-Group-I-Replacement-Supply-from-Nynas-Naphthenics/

\_\_\_\_\_

# How can we improve hydrolytic stability of phosphate ester-Tri xylenyl phosphte for its use in lubricants as base fluid?

Victor Bakunin Dr.Sci. Petrochemistry

TXP is usually pretty stable against hydrolysis, if compared to TCP. Hydrolysis is catalyzed by STRONG acid impuririties, which can be detected not by TAN, but by pH of aqueous extract. The simplest way to avoid hydrolysis is addition of base-type compounds, e.g. trilakylamines. Activated alumina is also possible. The possibility of PAGs use depends on the application: phosphates are HFDR type fluids, PAGs are related as HFDU fluids.

\_\_\_\_\_

Jean-Michel Demaret Qualified Engineer / Senior Account Manager

TCP is an antiwear, Some ZDDP are used as antiwear some are used as peroxide scavenger depending on the position of the alkyl chain, The main anti oxidant are amine (high temperature action against varnish) and phenol (low temperature action against sludge). Mobil publishes an excellent book called "lubrication fundamentals" written by Mr Denis Pirro (I think) in which the different type of additives and their limits are described.

TCP contains Phosphate. Phosphate level is limited in API CJ-4 oils.at 0.12%

John Neale

Director at John Neale Ltd

There are 2 main types of oxidation inhibitor - phenolic and aminic. I suggest you talk to a supplier of these to ascertain the best options for your application. Afton, BASF, Rhein Chemie etc are worth talking to.

David Stevenson EHS/HR Manager at Dane Color UK Ltd.

It depends on what your aim is, Hussam. Some inhibitors are free radical scavengers, others are designed to neutralise or buffer oxidation products, while other are designed to suspend oxidation products, e.g. sludge dispersants. John's suggested companies and also Lubrizol Corp. are certainly worth taking to for advice and guidance.

andy cao Lab technologist at Chemtura

Phosphate is usually the anti wear and extreme pressure additive in lubricant and phosphite can play the role of anti-oxidation by decomposing peroxide.

Some **OCP polymers** into my country imported go gelly after two weeks.

### Arupanjan Mukherji Regional Sales Manager

this is known as geletaion and this happens because of the quality of the polymer - at what temperature this happens? You need to look at the CCS and MRV values. Pl contact me if you require further information .

### <u>andre de rycke</u>

This phenomenon is known as "sudden death". The OCP further polymerise due to temperature increase .Could points to the quality of the OCP. Finally the liquid will become solid.

Rico Lee Technical Sales Manager at BASF South East Asia Pte Ltd

Possible reason is the high-ethylene content in the OCP. Coupled with low temperature environment which magnified the gel formation.

V.S.S. Sarma Technical Manager

Happened to me twice in my 35+ years of career. In one case, it was excess dispersancy. In another case, it was incompatibility of DI package with the VI Improver. Please use the right formulation. Jesse Dambacher Manager - Global Components Development at Valvoline

High ethylene content is the problem, US VM manufacturers went through that issue in the early '90s.

We checked its ethylene content. It has 65% ethylene content. I think 60% of ethylen is maximum percent.

### Jorge Villafuerte HEAD LABORATORY

Ethylene is very high. It do loss solubility in base oil.

\_\_\_\_\_

# Super Canola 5 times more Oxidative stability than AW46

khan azar Quality Assurance and Control Manager at OIL Top Contributor

This is my ongoing research to successfully change the internal structure of Canola and make it more stable than mineral oil. Price 2.35\$/L as a base oil.

High temperature oxidation stability and D-1500.

The test performed at 212 C.On the other hand AW 46 OXIDIZED at 180C.

Jai Bansal Global Technology Advisor /Chief Scientist at Infineum (Retired Feb 2014)

Could you be a bit more specific than "high temperature oxidation stability"? There are many many tests that purport to measure oxidation stability of oils but are irrelevant to their performance under the in-service conditions. ASTM D-1500 is just an appearance test...it only measures the color of the material on a relative scale, not its oxidation performance.

I would suggest a combination of several bench tests to get a preliminary assessment of this material such as pDSC (pressurized differential scanning calorimetry in presence of oxygen), RBOT (rotating bomb oxidation test), and ABOT(aluminum beaker oxidation test).

A: FED-STD-791, METHOD 5308

Mile Stojilkovic Director of development lubricants at NIS Gazprom Neft

My research RBOT oxidation stability according to the method ASTM 2272 are as follows:

- Rapeseed oil 13 min
- Rapeseed oil + additive antioxidant 109 min
- Rapeseed oil + additive antioxidant + 10% mineral oil, 120 min
- Rapeseed oil + additive antioxidant + 20% mineral oil, 149 min

- Mineral oil, 214 min

I think that an antioxidant cannot get 5x higher oxidation stability of rapeseed oil. It iss probably the that high-tech production of vegetable oil. Congratulations.

### V.S.S. Sarma

Bad quality of VI Improver used.

### steve swedberg

Since an **SAE 50 engine oil** would not likely have VII in it, I doubt that would be the cause. An SAE 50 has a relatively high viscosity at 100C so I would bet that bright stock was used in the blend. If the base oil is not dewaxed, and assuming that it sat for one year unagitated, it is quite possible that wax in the base oil could separate in the blend.

As a check, heat the oil with stirring and see if the particulates in the oil go back into solution. While motor oil doesn't get old (oxidize) it can separate.

### **Boris Zhmud**

Steve, you would have been absolutely right if we talked about a SAE 50 motor oil 20-30 years ago. Nowadays, **due to the shortage of bright stock supply, OCP is often used** as its replacement. The use of OCP lowers the solubility of the blend, eventually causing wax precipitation after a while.

### glossary

PAMA: polyalkyl methacrylate, enable better oil flow at low temperatures. In addition, they promote adequate lubrication at high temperatures

BS: Bright Stock, Bright stock are lubricating oils of high viscosity, obtained from residues of petroleum distillation used for blending with neutral oils in preparing engine lubricating oils. Typical characteristics: VI: 95, Kinematic viscosity: 471 cSt@ 40C

HTHS: High Temperature / High Shear Test:ASTM D5481 - 10 Standard Test Method for Measuring Apparent Viscosity at High-Temperature and High-Shear Rate by Multicell Capillary Viscometer

OCP type VII: Olefin Copolimer Viscosity Index Improver

SAE J300: SAE Engine Oil Viscosity Classification

850 SPN (or 850 SN): Paraffinic Mineral Oil Solvent Neutral 850, viscosity, 850 SSU @ 100~F

### VM: Viscosity Modifier

-----

# Are you aware of any issues with GP II base oils in hydraulic oils and compatibility with rubber (Viton) seals?

The short answer is "no" with the caveat that Group II base oils tend to be slightly more aggressive than Group I base oils. The testing we have evaluated tends to suggest the Group II base oils may cause a bit more hardening of the seal than Group I base oils. In either case, Viton® significantly outperforms commonly used nitrile rubber (NBR).

\_\_\_\_\_

To add a bit of polar material **to enhance additive solubility**, any of several **esters** will work. Diesters are the least expensive (DIDP, DiPE) and widely used. We use about 15% in our products. Be careful, though, that you don't knock yourself out of the viscosity range that you need.

David Sundin

Josef Barreto-Pohlen

DITA and DTDA are different abbreviations for the same ester - Di-iso-Tridecyl-adipate No problem to use, but as David said, pay attention to the viscosity. DITA has ca. 25 mm<sup>2</sup>/s @ 40°C

\_\_\_\_\_

Surely if we consider the polarity I suggest Ester like adipate DIDA or better DTDA or polyadipate ISO 320.

Ester like DOA, DINP, DIDP can work but they are used in large way as plasticizer, for this reason used less.

In General DITA and DTDA are the same ester but BASF made a product with different alcohol and called it DITA. Actually we prefer to make DTDA with Exxon alcohol because we can garantee a viscosity around 28 or 29 cSt at 40 C but with viscosity index higher, around 135. If you need a viscosty around 15 cSt at 40 C you use DIDA or if you need a higher viscosity we can do an ester like DTDA structure with a viscosity around 400 cSt. Vincenzo Arula

\_\_\_\_\_

Defoamants are typically polydimethyl siloxanes of various molecular weights and are only required at a few parts-per-million concentration to control lubricant foaming. It should be noted that the siloxanes are dispersed in the lubricant in the form of small particles or globules with specialized equipment. These small particles can be seen through the use of a phase contrast microscope similar to that used in clinical laboratories.

### Why use conventional PAO over mPAOs?

Ray Bergstra

Owner, MTN Consulting Associates

There are some small differences in the properties of the two types of PAO, but this is a supply side technology change, i.e., not driven by performance as lubricating oils. There is a cost advantage and improved molecular weight control using metallocene catalysts for olefin polymerization. <u>Ariel Hernandez</u>

Machinery Lubricant Analyst II

I see the mPAOs as an improvement over PAOs.

Certainly, it will not be a quantum leap in performance, as Mr. Bergstra has pointed out, but I think that using mPAOs in new formulations, will improve performance of finished lubricants. Since I am not a formulator, what I can say is that I expect to use lubricants that are made using the optimal balance in components for a great performance, if given some operation conditions PAO based lubes are better than mPAO, i would stick to PAO, if that is not the case, I would prefer mPAOs. Overall performance would be my bet. <u>V.S.S. Sarma</u>

mPAOs perform a lot better than PAOs, my friend.

1) Use of mPAOs reduces the need for use of High Viscosty PAOs. For example: to blend a VG 68 Synthetic oil, one uses 80.32% of PAO 8 + 19.68% of PAO 40. The same product can be achieved by blending 86.01% by weight of PAO 8 + 13.99% Wt of mPAO 100 thus reducing the use HVPAO by 28.9%. Furthermore, VI improves from 138 to 145; Pour point improves from (-) 58 Deg C to (-) 61 Deg.C.

2) Cold temperature properties are better with mPAOs, in CCS test.

VI and low temperature properties are better with mPAOs. Sometimes, it may work out cheaper to use mPAO instead of the conventional PAOs. <u>Allen A Aradi</u>

Technical Liaison Manager - Albemarle Catalysts Global Business Unit

Metallocenes facilitate a more accurate targeting of desired molecular weight / molecular weight distribution for performance, and type / degree of hydrocarbon backbone substitution for consistent properties over a wide temperature range of operation.

Aminic and phenolic antioxidants. Which is the peculiarity in their activity?

### Mikko Oksanen

They have different activity temperature. Phenolic are active from 0C degrees and aminic only over 85C degrees.

DILIP SHAH, Osvaldo Paterno and 1 other like this

### <u>Ross Kovanda</u>

Antioxidants function by reducing the energy of free radicals. Organic peroxides that are formed when oxygen interacts with hydrocarbons are acted upon by the aminic antioxidants.

The aminic oxides are converted back into aminic antioxidants by phenolic antioxidants.

The phenolic antioxidants are gradually depleted in the system. It is a cycle that stops chain reactions of the highly reactive organic peroxides.

Osvaldo Paterno, Alexey Muralev and 3 others like this

### **Guillaume Kalfon**

General Manager Middle-East & Africa at Fluitec

The phenol regenerates the amine in the lower temperature parts of the system. It's able to take back from the amines free radicals that had reacted with it. Then the phenol is spent. Nothing regenerates the phenol. In most cases, the phenol depletes (becomes reacted - deactivated) faster than the amine. Nothing regenerates the phenol. Amines are high temperature AOs and phenols lower temperature.

### V.S.S. Sarma

Phenols are no more used in turbine oil formulations as excellent multi-purpose anti-oxidants like Irganox are now being marketed. Phenols are old technology, not considered environmentally safe, considered carcinogenic and can not work at high temperatures. If you are a formulator, identify what specifications the end product should meet and then contact Lubrizol / Afton / Rhein-Chemie / IPAC / BASF to suggest suitable additive package that can work in your base oils.

congxiang zha

This is totally misleading. As matter of fact, most Irganox antioxidants are phenolics. The fact is that more and more phenoliucs are used because aminics are inherently sluge former. Ross is right, more and more people use phenolic/aminic combination, so they can take advantage of the higher activity of aminics, and the better deposit control property of phenolics. Ethanox 4702, for example is an excellent phenolic antioxidant with good sctivity and excellent deposit control properties.

### V.S.S. Sarma

Congxiang Zha: I have been handling lubricant formulations for over 25 years and have never used phenols as anti-oxidants in turbine oils. I have always used amines because of what was informed to me. I am not a chemist and I go by the research done by great companies like BASF in this regard. Irganox L-57 with Reomet 39 used to be a great combination of additives to blend turbine oils but then technology is rapidly changing because of changing equipments and also the changed specifications of OEMs like Siemens.

**Amine anti-oxidants** in lubricant possess exellent oxidation resistance even at high temperature, such as these two BASF products, L57 and L06.

However they make the colour of lubricant changed under light. The colour will become reddish brown, blood red and rufous.

-----

Colour is a selling point. Colourless products may be perceived to be very clean. Castrol used to sell red-coloured oil which was again perceived as quality product. Depends on buyer-psychology.

Vibhushit Dave: For every 100 Kg of oil, take 2 Kg of activated **bleaching** clay. Heat oil to 45-50 Deg C. Mix the clay. Stir it well. Filter out the clay. Send the oil through micronic filters to remove particles. Test the oil before & after treatment for key characteristics. Once you are satisfied that the characteristics are intact, release to customer.

Ediek Schutten • You can't do much about the colour. Actually the colour change is a sign that the anti-oxidant is doing its job. Most aminic anti-oxidants are alkylated diphenylamines. These type of anti-oxidants act as oxygen scavengers. In this process the alkylated diphenylamine is transferred into a nitroxide. The absorption spectrum of the nitroxides lies in the visible part of the spectrum and has a high molar absorption coefficient. As a consequence the colour change is already noticeable at very low concentrations.

A solution to prevent discolouration is to use opaque packaging. The other solution proposed by some writers viz. masking the colour change by using titanium dioxide can be dangerous. Uncoated titanium dioxide especially the anastase type promotes breakdown of organic molecules under influence of near UV-light (wavelength less then 400 nm). Colouring the oil with an oil soluble dye is probably a better option for masking. Treating the oil with activated clay is just a way to remove most of the additives and therefore not a good idea as already explained by other writers.

### Dr. Colin Gatward

Head of Rhein Chemie Business at Lanxess Ltd

Use ADDITIN RC7110 in veg esters to improve oxidation resistance but be aware veg esters are unsaturated and therefore very prone to oxidation.

For polyol esters use ADDITIN RC 9321 additive package for oxidation and corrosion improvements.

### Why naphthenic base oils are suitable for cutting fluid not paraffinic?

### <u>Lane LeBert</u>

Lubrication Specialist Division Manager ,Senior Blending& Technical Supervisor, at Network Lubricants

Nap base oils do to there high airamatic property's are good cleaners. This is desired in metal cutting fluids . They are also added to products that come in contact with water in there formulations . To help with solvency .

### Gangadharan Shaji

### Head Lab Chemist at PIKA INTERNATIONAL INC. KUWAIT

Naphthenic base oil offers perfect emulsion with water. Paraffinic base oil consumes much amount of emulsion additives and even after mixing with water, there is a tendency of slight oil layer separation on keeping .

### V.S.S. Sarma

Paraffinic oils have very high Aniline points, high viscosity indices (HVI) and low levels of aromatics. Cutting oil additives are mainly sulphonates (the emulsifiers) which dissolve better in aromatic oils than in paraffinic oils. This is the reason why cutting oils are not made in paraffinic oils but are always made in low viscosity index (LVI) base oils. Many manufacturers of cutting oil additives tried to make products which can be used in paraffinic oils but are not always successful. Instead of stable emulsions, what we end up are mata-stable emulsions. Emulsion Stability Index (ESI) is more controllable with LVI oils.

### <u>david philip</u>

The napthenic base oils have a carbon chain structure that binds the anionic molecuels of sulfonates etc in case of anionic emulfiers and other additives better in comparison with paraffinic oils which have a linear structure , However a different additive package will serve equally well for paraffinic oil.

### OIL SOLUBLE POLALKYLENE GLYCOLS - Ucon OSP vs POLYALPHAOLEFIN - PAO

<u>Jairo Ortiz</u> • In soluble oils applications as metal working, the OSP can less tendency to give off fumes and also a low oxidation ratio.

Ariel . According to Matlock, there are 5 "classes" used as lubricants:

1. Homopolymers of propylene oxide (polypropylene glycols), which are the waterinsoluble type. These show limited solubility in oil.

2. Copolymers of ethylene oxide and propylene oxide, which are the water-soluble type.

3. Polymers of butylene oxide. These show greater oil solubility than the homopolymers of propylene oxide.

4. Polymers of propylene oxide and higher epoxides designed to give greater oil solubility.

5. Polymers of propylene oxide that are dimethyl ethers.

http://www.linkedin.com/redirect?url=http%3A%2F%2Fwww%2Egearsolutions%2Ecom

<u>%2Fmedia%2F%2Fuploads%2Fassets%2FPDF%2FArticles%2F2004-03-</u> 01\_Polyglycols\_for\_Lubricating\_Large\_Gear\_Drives %2Epdf&urlhash=ET4I&\_t=tracking\_disc

### Dolf van Asbeck

Technical Support Engineer at Shell Global Marine Products Ltd

Birger, PAO is cheaper than PAG. PAO is more popular than PAG and greases with PAO base oils are therefore more common. There are greases available using PAG base oils.

PAO gives excellent and cost-effective service in most worm gear applications over a wider load and temperature range than mineral oils of the same viscosity. However, PAG offers better shear resistance than PAO for the same application, and has a legitimate place in the most highly loaded applications.

A grease is popular in simple gearboxes because the sealing is simpler (cheaper) and they work fine as long as cooling is not a problem. Some OEM provide filled-for-life (say 10,000hrs) gearboxes using PAG products either as an ISO VG 460 oil or a >320 base oil in a semifluid grease.

### Ross Kovanda

Owner/Vice President at American Chemical Technologies, Inc.

Old technology PAG's might have had conventional seal issues, but today's product lines are **completely compatible with buna and viton seals which are the predominate seals we see** in the industries we serve. We have conducted many seal studies from all types of our PAG formulations used throughout the Metals Industry, Mobile Equipment OEM's, Power Generation and Marine Industries and these fluids have surpassed all others. PAG's have been given a bad name from years past and when it comes to performance and long term benefits, no other can compete!

### J<u>igar Shah</u>

Partner at Chemo India

PAO is a dry lubricant as it is not polar. PAG has excellent lubricity and they are polar. The new Oil Soluble PAG are excellent for grease. Because of chemistry structure it has -30 aniline point, excellent solvency characteristics , -40 to -50 pour points, inherent corrosion protection, better seal compatibility, oxidation stability, high VI.

\_\_\_\_\_

### V.S.S. Sarma

OEMs want their finger in the pie, to brand lubes and earn royalties. Otherwise, imagine how much of lube oil is used compared to the fuel, about 0.4-0.5% ? And what all controls they have on lube oil ? How genuine are 'genuine oils' ? I asked Mercedes guys to give me the data sheet of their brands and they have flatly refused the same. What rights do the end users have in the matter ? None.

\_\_\_\_\_

What kind of solubility improver should be ideal for PAO without affecting VI, Noack Volatility and other important parameters? *Lubricant Specialists* 

Although PAO is unbeatable in terms of pour point and volatility, at the same time having lowest lubricity and solubility ranking. While we increase solubility by dropping aniline point of PAO, we sacrifice important parameters like Viscosity Index, Pour Point, stability, Noack Volatility etc. Feel to increase the solubility (which we cannot eliminate either) we sacrifice so many important parameters... Any idea which can minimize / eliminate the loss of important parameters...

V.S.S. Sarma • Exxon Mobil has an ester which is used upto 2% by weight to improve solubility of additive in PAOs. I remember that a UK company is also marketing one such additive.

I used Exxon Mobil's Esterex product at 2% dosage in a 5W50 PAO-based formulation of API SN. By V.S.S. Sarma

### OIL SOLUBLE POLALKYLENE GLYCOLS -OSP vs POLYALPHAOLEFIN -PAO

<u>Jairo Ortiz</u> • In soluble oils applications as metal working, the OSP can less tendency to give off fumes and also a low oxidation ratio.

<u>Carlos Nazario</u> • Hello Jigar; it is difficult to determine or answer this. OSP as have been nominated is new technology developed and offered by Dow chemicals, but it is not available in all ranges of viscosities, while more heavy is the viscosity less soluble are. It is necessary to determine the application; PAO lubricants are more safe for when you need to change from a mineral or PAG to a PAO lubricant.

<u>Jigar Shah</u> • Please consider OIL SOLUBLE POLYALKYLENE GLYCOL [ UCON OSP mfg by Dow Chemical USA ] base fluids. The aniline point is approx in -30 range thereby highly effective in solubility parameters. Also the pour points are in range of -40 to -50. You want to consider a blend of 10%-15% these oil soluble PAGs in PAO based formulations. There are some solubility issues of these polymers in high VI PAOs. The commerically available grades of these polymers are from ISO VG 18 to 680 cst @ 40 deg.

UCON OSP has the following advantages:

- Excellent oxidation & thermal stability
- Very high VI
- Very good hydrolytic stability. Can increase hydrolytic stability of esters.
- Excellent cleanliness characteristics (very low varnish and sludge formation tendency)
- · Highly pure, and does not have any ash content
- Very high film strength
- Very good lubricity
- Very low co-efficient of friction
- · Very good rust & corrosion protection characteristics
- High pressure viscosity coefficient (inherent high load bearing characteristic)
- Inherent dispersancy quality and
- Fully compatible with both Mineral oil (Gr.I,II & III), Esters and PAO.
- Anilines points are in negative i.e.-30 range
- Pour point is also in negative i.e. -40 to -50 range.
- Excellent solvency characteristics.

OSP PAG are polar and the degraded products are also polar with lower particle size. Due to negative aniline points the solvency is higher so it doesn't form sludge or varnish. Most of the additives like PPD , anitwear, detergents, antioxidants are also polar. So this is a very important characteristics of OSP.

Yes I am a big fan of PAG. Yes I am dealing in it. I have been promoting traditional PAGs and now this new Oil soluble pags.

Since it is a new technology at many places it is under evaluation and also commercialised at some places.

There has been commercial success in air compressor oil, greases, chain oil, gear oil, engine oil, hydraulic oil, heat transfer oil, quenching oil etc.

Lot of trials are going on the fleet and car racing area.

Pricing is similar to High VI PAO and esters. I would recommend to use fully OSP based formulations OR combination with PAO & ESTER.

Water absorbing characteristics lower for OSPs than traditional PAGs. OSP act as polymeric sponges binding water within the structures (water is not free at levels of several thousand ppm). By Jigar Shah

Oil soluble PAGs are made of from oxide of propylene, Excellent high temp stability and high VI make suitable for high tep application like on refractory kiln bearing 2000 deg F. PAGs performance depends on the monomer used, M.wt and nature of terminal groups.

On the other hand water soluble PAGs are made of ethylene oxides and used as water base fire resistant hydrolic fluids, used as valve actuators of large gas transmission line located outdoors in sub zero climates insolubility in natural gas makes them use full in gas compressor. By Shah Faisal

<u>Samer Akram</u> • I would agree with Jigar's sentiments regarding the Oil Soluble PAGs from Dow Chemicals, marketed as the UCON range - we are supplying this product into the South African market and are seeing very good results and interest.

It is priced fairly similarly to the PAOs but offers different attributes - we also are supplying ExxonMobil's PAO range exclusively in Africa and the Middle East, and their Elite range of Hi-Vis metallocene PAOs have excellent characteristics and better treat rates than the previous SpectraSyn 40 and 100.

If anyone is interested on further data and supply of either of the OSP PAGs or metallocene Hi-Vis PAOs, please email me at samer@unichem.co.za

We are able to supply the Low-Vis PAO grades (2,4,6,8,10) in bulk, Flo-bins and drums. I have both products and different grades in stock at my warehouse in Durban, South Africa, and customers are already purchasing them.

UCON OSPs can be used as a component additive or co-base oil in Grp II and III mineral oils for turbine oil applications.

It has been shown to improve deposit control, reduce risk of varnish formation and hence reduce risk of equipment failure.

OSP 32 and 46 are recommended for base oil uses, and can also be used as an additive as a friction modifier and deposit control additive.

<u>Jigar Shah</u> • OSP PAG are polar and the degraded products are also polar with lower particle size. Due to negative aniline points the solvency is higher so it doesn't form sludge or varnish. Most of the additives like PPD , anitwear, detergents, antioxidants are also polar. So this is a very important characteristics of OSP.

My understanding is PAG has zero varnish therefore very good in turbine oil application or for that matter any high temp application. Have there been successful gas turbine usage or not yet? what happens to the oxides?? By Ali Durrani

#### \_\_\_\_\_

<u>Richard Widman</u> • what the reasons are, other than cost, that <u>Borate additives</u> aren't used more in industrial gear lubes rather than sulfur/phosphorous. I bring this up because I've such good results with it, usually saving 9 to 10% in temperature and energy on small gear boxes, and lasting 10,000 hours in heavy gears and bearings where 2500 overheated with Sulfur/Phos. with less wear particles.

Richard Widman • It has not been removed. Our additive comes from Oronite, and the

borate gear oils are our best sellers, although limited to those who have the will to try something 20% more expensive.

<u>Michael Hession</u> • Going back many years the main objection initially to borate in gear and final drive lubes was water sensitivity, pushed by competitors,. I think that the Jap authorities decided autocratically to ban B on environmental grounds and so B did not take off as well as it should have.

<u>Ali Durrani</u> • It was sensitive to water/moisture contamination (product became corrosive). But it was gentler on bronze and copper material, also you did not get surface polish which you get with S/P additives. The process was different s/p reacts with metal surface whereas Borate was coating, it gave very good EP protection. You generally used lower visc oil with matching FZG results. Chevron is the only one using the technology.

<u>thierry chaponnay</u> • For your information Boric acid and Disodium tetraborate, anhydrous are part of ECHA list : Candidate List of Substances of Very High Concern for Authorisation in Europe. See below...</u>

<u>Philippe Boileau</u> • Boron is an essential mineral for health. I don't see the problem with it. I do not think you need boric acid in nanoparticles size as it is a relatively soft product (around 2 on the scale if I remember well) contrary to BHx. I like to try these things in my car. It gives a smoothness to the operation of the car. My favorite remains WS2.

thierry chaponnay • The Echa european list is severely controlled by Toxicologist, I'm not talking about Boron, but about Boric acid an disodium tetraborate which are reprotoxic. You have to diferentiate chemical composition, the best example is ethylene glycol (toxic) and propylene glycol (suitable for food industry). only one carbon difference!!!

Some VM and VIIs - a well-known example is PAMA - do actually improve lubricity of the finished product, and so does BS. By Sarma

PAMA is used in quite a few commercial engine oils, both as VII and PPD additive. OCP is more common just because of it's cheaper. However, PAMA, as well as esters, have lower stability at high temperatures (as compared to BS and heavy PAOs, for example). It's also true that competitive adsorption issues do exist between some EP/AW additives and esters (or, to be more precise, between their decomposition products, such as monoglycerides and fatty acids). Finally, once additive solubility is concerned, BS sits right in between heavy PAOs (e.g. PAO100, very poor solubility) and heavy naphthenics (e.g. Nynas T4000, great solubility). To answer Siddiqur's question: the advantages of BS: exceptional shear stability, high FP, adequate solubility and compatibility. The disadvantages: availability and inferior oxidation stability, sometimes causing sludge issues.

Boris Zhmud

David Benjamin • Huge concern with group I plants at very tight capacity. I agree with most of the comments. The use of an ester, possibly malienated with excellent hydrolytic stability which is very desirable in the heavy duty applications, could be a very good option. Mono grades for pcmo and low vis requirements for fuel economy no bright stock usage should be applied as a correction fluid or vis enhancement. Regarding formulation going to an ester, be cautions of additive response. If too polar the ester, increase in wear will occur due to low response from the anti-wear additives. However, one will find that values will remain very clean and also low deposits. BS will also cause additive solubility issues, thus one can be challenged to balance the formulation to ensure a engine will pass each sequence test.

\_\_\_\_\_

# ODD

### Ionic liquids as lubricants

http://digital.ipcprintservices.com/display\_article.php?id=1265962

\_\_\_\_\_

## Nano-materials as lubricant additives

### ezry akkerman

Nano particles will be very effective if you could keep a stable emulsion in oil.

If you cannot assure that, due to difference in density, all the particles will sediment at the bottom without any advantage.

Surface modification of the nano particles should be applied.

BTW Our company has the knowledge to do it :)

### Kirk Schlup

Managing Director at KS Resources LLC

Franz,

Not sure exactly what they are referring to when they say nano particles. Almost all motor oils contain calcium sulfonates that have sub 100 nanometer particles and therefore qualify as nano particles - if this is what they are referring to, its nothing novel or mysterious.

### OLDER;

### Alexey Muralev

Head of Technical Service Department at Kulan Oil

It is relatively new and unproven field in my opinion. There are a lot of companies that sell and promote nano-addtives. Mostly those are metal oxides - nanoceramics.

I came from colloid chemistry background so I find word "nano" mostly irritating.

Basically there are some physico-chemical mechanisms that can allow those around micron size particles to provide self-repairing of microfractures, formation of thin protective layer and in the end - better lubricity and longer life of components.

BUT, this field is not studied in full yet.

The main problem is wide spectre of efficiency - from 0 to 30% of energy efficiency (fuel consumption), different decrease in friction coefficient etc etc

So, every such company is shouting about huge benefits, but they are not consistent.

And if they offer such huge benefits (for around 10 years this tech exists) why no one adds those particles to finished lubes? That is because they cost a lot for unproven efficiency. But, some big companies use those for marketing purpouses (no proven substantial advantage yet) - one with "liquid molybdenium" and other with "60-fullerens".

That is just my opinion. Would be glad to hold a discussion or read some trustworthy papers on the matter.

### vijay deshmukh

General Manager R&D at Standard Greases & Specialties Pvt. Ltd.

Off late people have started using Nano additives. I myself have tried fullerene type nano additives in greases and have found to be effective. It can give the same load carrying property as moly with a lesser percentage. The coefficient of friction is also reduced to a great extent.

### Jacob Neubauer

Technical Director, Champion Brands, LLC

It seems like the business is growing and perhaps that is a good thing. I think that there may be some performance advantages for some products over organic chemistries. There have been great advances in organic chemistries, though, and there is a cost and aesthetic disadvantage to the nano stuff. Not many of my customers would want to put a milky, opaque colloid in their equipment. They would probably be afraid the oil was contaminated with water!!

<u>Alexander Roberts</u> • If you look at the spec sheet of ARCHOIL's AR9200 Nano **WS2** Friction Modifier you'll get a better picture:

AR9200 is a nano tungsten disulfide (WS2). WS2 is one of the most lubricious substances in the world. It offers far superior performance to molybdenum, graphite, Teflon® or any anti-wear additive in racing and gear oils. AR9200 penetrates and bonds to metal, wood, rubber, plastic and most surfaces. The lubricating, micro thin film features an ultra-low coefficient of friction (0.03 dynamic; 0.07 static) that prevents sticking and wear. It is ideal for sliding mechanisms and heavy load lubrication environments.

AR9200 can also be used in high temperature and high pressure applications. It offers temperature resistance from -450° F (-270° C) to 1200° F (650° C) in normal atmosphere and from -350° F (-188° C) to 2400° F (1316° C) in vacuum. Load bearing ability of coated film is extremely high at over 300,000 psi.

### FEATURES/BENEFITS

WS2 is chemically inert High temperature lubrication Very high load properties Practically creates a frictionless surface (COF 0.03) Excellent penetrating abilities Prevents galling, seizing or cold-wielding Long lasting Preassembly applications Fills in surface asperities creating a very smooth and hard surface Dramatically reduces wear Ultra-thin coating (0.05 microns) Suitable for high precision components Non-toxic

<u>Alexander Roberts</u> • This is part of a document available thru the EPA and Argonne done with what's now Archoil's AR9100 (boric acid), the same nano technology used to create the before mentioned tungsten product. You should try it out, it's a "liquid wonder"

Nano-boric acid makes motor oil more slippery Argonne researcher Ali Erdemir performs a friction test on a metal disc coated with a solution of motor oil with nanoboric acid particles.

Scientists at the U.S. Department of Energy's Argonne National Laboratory have begun to combine infinitesimal particles of boric acid – known primarily as a mild antiseptic and eye cleanser – with traditional motor oils in order to improve their lubricity and by doing so increase energy efficiency. Ali Erdemir, senior scientist in Argonne's Energy Systems Division, has spent nearly 20 years investigating the lubricious properties of boric acid. In 1991, he received an R&D 100 award – widely considered the "Oscar of technology" – for showing that microscopic particles of boric acid could dramatically reduce friction between automobile engine parts.

Metals covered with a boric acid film exhibited coefficients of friction lower than that of Teflon, making Erdemir's films the slickest solids in existence at that time.

"Ali was looking at large, micron-sized, particles," said

George Fenske, who works alongside Erdemir at Argonne. "He was just sprinkling boric acid onto surfaces." But driven by a conviction that he could fashion boric acid into an even better lubricant, Erdemir continued to chase the ultimate frontier: a perfectly frictionless material. Glimpsing the potential of nanotechnology, Erdemir went smaller – 10 times smaller – and was astonished by the behavior of much thinner boric acid films. "If you can produce or manufacture boric acid at the nanoscale, its properties become even more fantastic," he said.

Reducing the size of the particles to as tiny as 50 nanometers in diameter – less than one-thousandth the width of a human hair – solved a number of old problems and opened up a number of new possibilities, Erdemir said. In previous tests, his team had combined the larger boric acid particles with pure poly-alphaolefin, the principal ingredient in many synthetic motor oils. While these larger particles dramatically improved the lubricity of the pure oil, within a few weeks gravity had started to separate the mixture. By using smaller particles, Erdemir created a stable suspension of boric acid in the motor oil.

In laboratory tests, these new boric acid suspensions have reduced by as much as two-thirds the energy lost Argonne National Laboratory is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC August 2007

For more information, please contact: Eleanor Taylor, Phone: 630-252-5565, E-mail: etaylor@anl.gov

This diagram illustrates the crystalline structure of boric acid. Boron atoms are shown as blue spheres, oxygen pink, and hydrogen brown. Molecular forces that bind the layers in the lattice enable them to slide over one another with very low friction. through friction as heat. The implications for fuel economy are not hard to imagine, Erdemir said.

"You're easily talking about a four or five percent reduction in fuel consumption," he said. "In a given day, we consume so many millions of barrels of oil, and if you can reduce that number by even one percent, that will have a huge economic impact."

Argonne is currently in talks with materials and lubricant manufacturers to bring boric acid technology to market, Erdemir said.

PM me if you need more formal (pdf format), scientific research data backing up such claims or visit <u>http://archoil.eu/Summary%20Kotug%20AR9100%20SD%20Jacoba%20ENG.pdf</u> of a field test done on Rolls Royce trusters.

fahri syafiawan chamim achmadi Maintenance Engineer at Antara Steel Mills S.B

single sheet gasket is almost impossible (not easily available) to be used with **big split housing gearbox**, paste type gasket maker is more favorable. Please suggest heavy duty, safe for oil, & oil resistance gasket maker for this kind of application.

### <u>Wayne Kyffin</u>

Rotating Equipment Maintenance Manager

Hylomar sealant.

### OLIVIER PETRILLI

responsable SAV chez CMD engrenages et reducteurs

Up to date sealing paste use for split housing gearboxes are defitive anaerobic pastes such as Loctite 573 or equivalent from other brands.

#### \_\_\_\_\_

### Fraunhofer Institute Develops New Type of Lubricant

Together with a consortium, the Fraunhofer Institute for Mechanics of Materials IWM in Freiburg, Germany has developed an entirely new class of lubricating material: **liquid crystalline** lubricant. Its chemical makeup sets it apart; although it is a liquid, the molecules display directional properties like crystals do. When two surfaces move in opposite directions, the liquid crystal molecules between the two surfaces align themselves so that the frictional resistance is extremely low. This enables nearly frictionless sliding.

Liquid crystals are known for its use in liquid crystal displays (LCDs) in TV screens, mobile phones or touchscreens. The unusual idea to use them as a lubricant was proposed by Nematel GmbH, which then turned to Fraunhofer IWM to see if it would work. There, Dr. Tobias Amann applied the lubricant made from liquid crystal between two metal workpieces. "Even in the first test, we measured extremely low friction coefficients," remembers Amann.

The researchers at Fraunhofer IWM discovered that liquid crystal is well suited for lubricants because its molecules are long and thin. "When used as a lubricant between two surfaces that slide past each other, the molecules become aligned in parallel to each other in ordered boundary layers," explains Dr. Andreas Kailer, acting director for the Tribology business unit at Fraunhofer IWM. These layers are very stable but slide easily over each other, keeping friction and wear to a minimum.

Still, much was missing before a liquid crystal lubricant suitable for practical applications could be developed. Fraunhofer IWM launched a project along with Nematel GmbH and the lubricant experts at Dr. Tillwich GmbH in 2010, sponsored by the German Federal Ministry of Education and Research (BMBF).. Susanne Beyer-Faiß, a chemist at Tillwich, improved the liquid crystal's stability with help from additives. At the same time, her colleague, Werner Stehr, built a special test unit that uses laser technology to enable contact-free measurement of the extremely low friction coefficients. At Fraunhofer IWM, Tobias Amann tested different liquid crystals manufactured by Dr. Holger Kretzschmann at Nematel; among other things, Amann conducted friction experiments with various materials, including iron, copper and ceramic. He also examined the chemical mechanisms displayed during friction and the effects of mixing different liquid crystal molecules. Tobias Amann deciphered the mechanisms that are responsible for these ultra-low frictional coefficients and discovered how to further optimize the new lubricants in specific ways. He also examined the chemical mechanisms displayed during friction and the effects of mixing different liquid crystal molecules. When the project came to an end, the partners had produced a liquid crystalline lubricant prototype that performed best in sliding bearings made of iron. For this pioneering work, Dr. Tobias Amann, Dr. Andreas Kailer, Susanne Beyer-Faiß, Werner Stehr and Dr. Holger Kretzschmann received the Stifterverband Science Prize, which is awarded every two years for scientific excellence in applied research projects.

Currently, the award winners are developing innovative sliding bearings lubricated with liquid crystal for small electric motors for use in the automobile industry, for instance in alternators or windshield wiper motors.

\_\_\_\_\_