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Oil Soluble Polyalkylene Glycols

Abstract

The lubricant industry has a history of innovation spanning more than a century. Recently a new range of API Group V base oils, called oil soluble polyalkylene glycols (OSP), has been introduced. Unlike conventional polyalkylene glycols (PAG), the new OSPs can enhance the properties of existing hydrocarbon oils by providing a range of functionalities. This article will briefly describe OSPs, highlight some of these functionalities and also illustrate their practical benefits for use in synthetic gear oils as a selected application to illustrate their multi-functionality. Research in this area is still new but formulators and equipment builders now have another tool for solving some of their tribology and lubrication challenges.

Introduction

Most lubricants in use today are derived from API Group I-III base oils as the dominant formulation component. However for some applications and equipment, semi-synthetic or indeed full synthetic lubricants are needed to provide a desired functional performance. These lubricants often comprise an API Group IV (polyalphaolefin) or a Group V base oil in which they are used as primary or co-base oils in formulations. Group V base oils include several classes of products such as synthetic esters, alkylated naphthalenes and phosphate esters. These are often polar materials with lower aniline points than classical mineral base oils and offer a plurality of functionalities some of which can include good film forming behaviour, high solvency power and cleanliness features, anti-wear and extreme pressure properties and so on. Many of these materials are used as co-base oils in hydrocarbon oils to enhance their performance or as performance enhancing additives.

Polyalkylene glycols are another class of Group V base oil. They were first invented in the 1940s and are used in many niche applications such as worm gear lubricants, rotary screw air compressors, reciprocating gas compressors, anhydrous hydraulic fluids [1, 2] and more recently gas turbine oils [3]. In these applications they demonstrate excellent deposit control, good thermo-oxidative stability and fluid longevity, and offer excellent friction control for improving energy efficiency of equipment. PAGs are also used as additives in water based lubricants and functional fluids such as metal cutting fluids, fire resistant water glycol hydraulic fluids and quenchants. However unlike other Group V base oils, their use as additives to boost the performance of hydrocarbon oils has not been possible in the past simply because they have a low hydrocarbon oil solubility. The majority of polyalkylene glycols used today in lubricants are derived from downstream derivatives of ethylene oxide and/or propylene oxide. Recent research has shown that butylene oxide and its combination with other oxides can lead to oil soluble polyalkylene glycols (OSP) and if carefully designed, these polymers can offer many of the excellent functional properties of traditional PAGs and provide formulators with a new building block for solving problems that may not be possible with existing technologies.

Research into the functional performance of OSPs is still in its infancy but in the past three years some unique features and benefits have been discovered. This article will explain more about OSPs and some of their key functionalities. It will have a special focus on gear oils and particularly their unique air release properties. In recent feature articles in "Lube" magazine [4, 5] the importance of fast air release for lubricants in some types of equipment has been discussed and this article builds on that theme.

Aspects of Oil Soluble PAGs

The oil soluble polyalkylene glycols in use today span a wide range of molecular weights and viscosities. Table 1 provides an overview of some of their key properties. Since there is a high degree of flexibility in designing OSPs, it is possible to extend this range and build polymers with even lower or higher molecular weights and functionalities. The polymers range from the classical ISO-32 through to ISO-680 viscosity grades. The lowest viscosity polymer, OSP-18, has a kinematic viscosity of 4mm2/sec at 100°C which is similar to a classical PAO-4 base oil. Their viscosity indices range from 123 to 196.

	Method	OSP-18	OSP-32	OSP-46	OSP-68	OSP-150	OSP-220	OSP-320	OSP-460	OSP-680
Kin. viscosity at 40°C, mm²/sec	ASTM D445	18	32	46	68	150	220	320	460	680
Kin. viscosity at 100°C, mm²/sec	ASTM D445	4.0	6.4	8.5	11.5	23.5	33	36	52	77
Viscosity Index	ASTM D2270	123	146	164	166	188	196	163	177	196
Pour point, °C	ASTM D97	-41	-57	-57	-53	-37	-34	-37	-35	-30
Fire point, °C	ASTM D92	220	242	240	258	258	258	260	265	270
Density at 25°C, g/ml	ASTM D7042	0.92	0.94	0.97	0.97	0.97	0.97	0.97	0.97	0.97
Aniline point, °C	ASTM D611	<-30	<-30	<-30	<-30	<-30	-26	n/d	n/d	n/d

Table 1. Typical physical properties of Oil Soluble Polyalkylene Glycols (OSP).

The polymers have excellent low temperature properties with pour points for the lower viscosity grades less than -50°C. The lower viscosity grades have high levels of biodegradability and the higher viscosity grades are more bio-resistant.

An interesting property of OSPs is their low aniline points which are typically less than -20°C. The aniline point measurement is considered to be a measure of the degree of solvency power or polarity of a base oil. Thus base oils that are rich in ester, ether or aromatic functionalities tend to have lower aniline points than those simply derived from paraffinic or iso-paraffinic feed stocks. Figure 1 illustrates the typical aniline points for a wide range of API Group I-V base oils. API Group I base oils have typical values of about 100°C. This increases for modern Group II and III oils since these base oils have much lower levels of aromaticity and polar compounds in their compositions. Polyalphaolefins (PAO) usually have the highest values which are typically about 130°C for commodity lower viscosity PAOs or significantly higher for the heavier viscosity grades. Formulators of modern hydrocarbon lubricants based on Group II-IV oils sometimes find conventional additives are less soluble in base oils with high aniline points and to improve their solubility they often include a more polar base oil such as an ester or an alkylated naphthalene at low treat levels. Esters have typical values in the range 5-40°C and alkylated naphthalenes have values which are slightly higher. Since OSPs have very low aniline points they provide formulators another option. Unlike esters which are sometimes hydrolytically unstable in environments where water or moisture ingress occurs in a lubricant, OSPs are more hydrolytically stable and may provide greater fluid longevity and peace of mind.

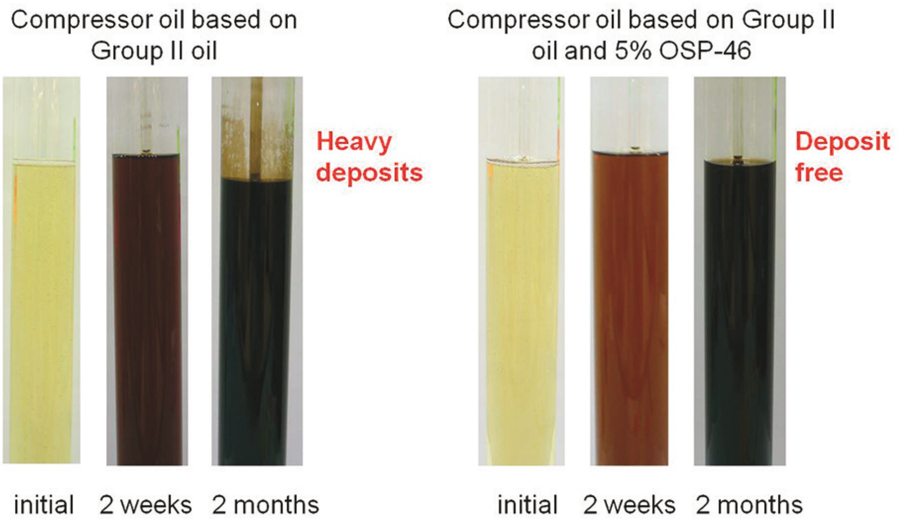

Figure 2. Visual assessment of the deposit control characteristics of two compressor oils that have been aged in a modified ASTM D2893B test.

Research and application testing has shown that OSPs offer a number of key features [6, 7]. For example field experience has shown that they have the ability to help control deposits when used as co-base oils or additives in hydrocarbon oils such as hydraulic fluids and compressor oils. They are also surface active polymers and at low treat levels can reduce friction under mixed elasto-hydrodynamic and boundary conditions. Furthermore OSPs have unique air release properties. These performance attributes will be explained in more detail.

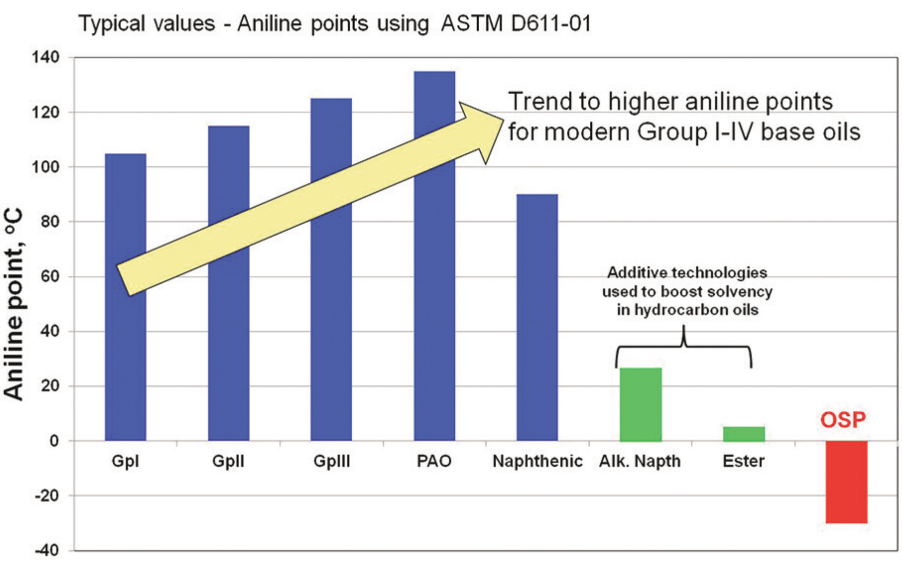

Figure 1. Typical aniline points of common API Group I-V base oils.

OSPs and Deposit Control

It is well known that the thermal and thermo-oxidative degradation of hydrocarbon lubricants and ester based products can lead to deposits, gums and varnish formation in equipment. The presence of these degradation products can cause serious equipment damage or poor equipment reliability. This is especially true in turbine, hydraulic and compressor equipment. Equipment builders continue to add new specification requirements or tighten existing ones to improve deposit control of lubricants. For example specifications for passenger car engine oils continue to evolve such that better piston cleanliness and engine sludge control are attained. Oil soluble PAGs can play a role in helping our industry solve some of these problems. To illustrate this, two formulations were assessed in a modified ASTM D2893B test in which the fluids were aged for two months at 121°C in which air was blown through the fluid at a fixed rate. Both compressor fluids contained an API Group II base oil and one contained 5% of an OSP. Figure 2 shows the visual effect of including an OSP as a co-base oil. After two months of ageing visual evidence of deposits were observed in the compressor fluid that did not contain the OSP. However the inclusion of the OSP showed a fluid with significantly improved cleanliness. As hydrocarbon oils age, they usually form more polar oxidation by-products that are sometimes not soluble in the parent base oil. When this occurs, deposition onto surfaces can occur that can ultimately lead to varnish formation. Since OSPs are inherently polar materials, they help solubilize the degradation products of hydrocarbon oils and therefore minimize the effect of deposit formation.

Improved deposit control and system cleanliness has been observed in many types of equipment that have operated in the field using API Group I-IV hydrocarbon oils including hydraulic, gear, compressor and metalworking fluids. But in addition this effect has also been observed when OSPs have been included into natural esters (vegetable oils). When vegetable oils oxidize they can form highly viscous gums as the olefinic moieties of the acid fractions of the triglycerides oxidize and then cross-link. The inclusion of an OSP to vegetable oils at typical treat levels of 10% by weight can help solubilize the degradation products and keep equipment cleaner for longer periods. Furthermore, hydrolytic stability tests show that OSPs can help improve the stability of vegetable oils to hydrolysis by acting as polymeric sponges to water ingress into a lubricant.

OSPs and Friction Control

Oil soluble polyalkylene glycols also act as friction control additives. Since every third atom along the alkoxide backbone is an oxygen atom, the materials offer a high degree of polarity and surface activity. It is well known that conventional PAGs, that are polymers derived from ethylene oxide and propylene oxide derivatives, offer excellent film forming properties. In some applications for example in worm gears, significantly better energy efficiency can be achieved versus using hydrocarbon oils. However since conventional PAGs are not soluble in hydrocarbon oils, this inherent feature has not been exploited. OSPs are now offering this functionality.

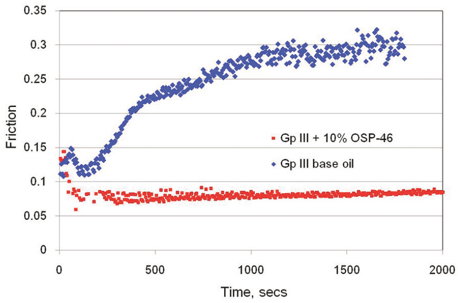

Figure 3. Friction profile of a Group III base oil (blue) and a Group III base oil with 10% OSP-46 (red). Measurements made using a Mini-Traction Machine, (steel ball on steel disc) at 80oC, a contact pressure of 0.75GPa, speed 15 mm/sec and 10% slide-roll-ratio.

Figure 3 illustrates the film forming behaviour of OSP-46 in a Group III base oil (ISOVG-46). The test was conducted using a Mini-Traction Machine in which a steel ball rotates on a steel disc such that the slide-to-roll ratio is 10%, speed is 15 mm/sec, contact pressure is 0.75GPa and a fluid temperature is 80°C. The rubbing cycle was about 30 minutes. In the absence of OSP, friction gradually increases over time and the data points show increased scatter suggesting the surfaces are becoming rougher. However with the inclusion of an OSP, the friction coefficient stabilizes after less than 5 minutes. Simplistically this provides some evidence of friction reducing behaviour. This effect has also been observed in other types of Group I-III base oils and polyalphaolefins. Figure 4 shows a further example in which friction profiles have been recorded for a Group III base oil (ISOVG46) with 1% of an OSP and compared to the base oil alone. Boundary friction is reduced when the OSP is included and again supports the good film forming properties of these polymers.

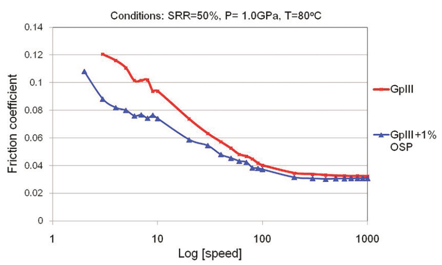

Figure 4. Friction performance of a Group III base oil with and without OSP-46 using a ball on disc Mini-Traction Machine operating at 80°C, contact pressure 1GPa and slide roll ratio of 50%.

OSPs as components of Gear Oils

Today OSPs are being adopted in a broad range of applications and as more research is conducted into their functionality and performance their practical use into solving tribology problems is expected to grow. One area where OSPs could provide multi-functionality is in industrial gear oils where they can be used as primary base oils in fully synthetic gear oils or as performance additives in for example, PAO gear oils. Some of the reasons why an OSP solution should be considered will be explained.

Research has shown that OSPs have unique and very fast air release properties. The air release properties of gear oils and other lubricants are often measured using ASTM D3427. The entrainment of air into lubricants in operation is a common occurrence and up to 10% of air by volume can be entrained. The rapid release of the air in hydraulic, turbine and gear equipment is a critical requirement for modern equipment. Fluids with poor air release properties can cause erosion, cavitation, spongy controls, noise and faster ageing of the fluid through oxidation. The air release properties of most classes of fluid generally become worse (i.e. higher values) as its viscosity increases. For example an ISO-320 fluid will usually have a much higher air release value than an ISO-46 fluid. Some of the trends in gear box design are shown in Figure 5.

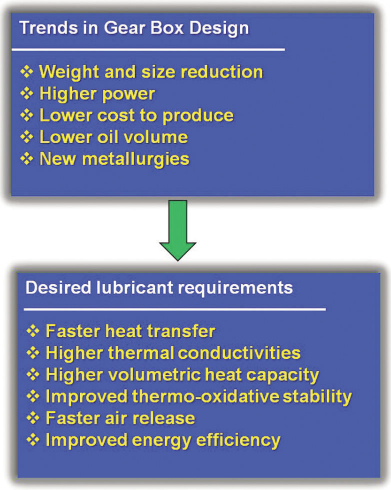

Figure 5. Trends in gear equipment design and fluid development.

Modern gear boxes are being designed to have lower weights and size, higher power and sometimes use newer metallurgies. There is also a trend to design equipment with smaller reservoirs. These trends will have an impact on future lubricant requirements and it is expected they will need to have improved thermo-physical properties such as higher thermal conductivities and faster heat transfer, improved thermo-oxidative stability, and preferentially higher volumetric heat capacity. But in addition faster air release times may be needed. The requirements for air release times of lubricants have been trending down in equipment builder specifications.

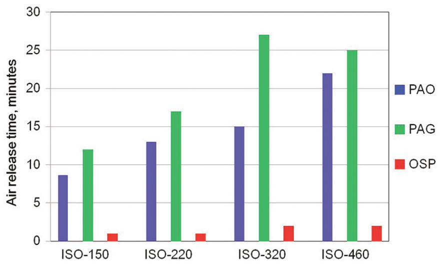

Figure 6. *Air release values measured at 75°C using ASTM D3427 of commercially available PAO and PAG synthetic gear oils (ISO VG150-460) and new OSPs.*

Figure 6 shows the air release times of two types of commercially available synthetic gear oils that are based on PAOs and conventional PAGs for ISO-150 to 460 viscosity grades. These times are compared to a range of formulated OSP gear lubricants in which the OSP represents more than 95% of their compositions. For example one can compare the data for the ISO-320 products which is a common class of viscosity grade for industrial gear and wind turbine lubricants. Conventional PAG and PAO products give typical air release times which are 15 minutes or higher. However the OSP product shows a significantly lower value of about 2 minutes. This differentiation is observed across all viscosity grades. Furthermore, very low air release times of less than 1 minute have been recorded for other types of fully synthetic OSP products such as hydraulic oils in the viscosity range ISO-32-68. For equipment builders that are seeking to redesign their systems to include much smaller oil reservoirs and perhaps reduce capital costs, the new OSP technology may provide a logical solution.

OSPs provide some interesting benefits as performance additives in synthetic gear oils and especially those based on PAOs. Formulations of PAO gear oils often contain a synthetic ester as a co-base oil. The ester provides a range of functionalities. One of these is to provide a seal swelling effect on certain elastomers to negate the seal shrinkage effect of higher viscosity PAOs. In addition the ester provides a degree of friction control and helps to maintain good fluid cleanliness during its service life. One known disadvantage of esters is that they are prone to hydrolysis especially under mildly acidic conditions. Therefore as a fluid ages to form acidic by-products, hydrolytic degradation can accelerate. Formulators of future gear oils may wish to consider using OSPs as an alternative to esters. For example it is known that the ISO-VG32 grade of OSP has similar seal swelling effects to an adipate diester that is commonly recommended as a co-base oil in formulating PAO gear oils.

	KV40, mm²/sec	KV100, mm²/sec	Viscosity Index	Pour point, °C
Adipate ester	28.0	5.2	135	-54
OSP-32	32.0	6.5	146	-57

Table 2. *Physical properties of adipate ester and OSP-32 co-base oils.*

Table 2 compares their simple viscometric properties and suggests a direct replacement is possible on these properties alone.

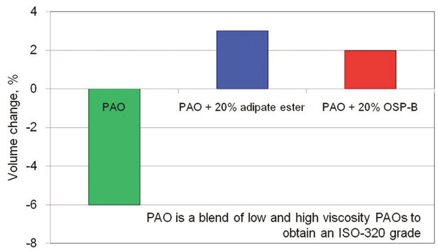

Figure 7. *NBR elastomer volume swell of formulated PAO blends for 168 hours at 100°C.*

Figure 7 compares the effect of the two co-base oils as seal swell additives on nitrile butadiene rubber (NBR) under a short duration elastomer test. In the absence of an ester or OSP co-base oil, the PAO shrinks NBR. However when the co-base oils are included, it is possible to negate the shrinkage to achieve a mild seal swelling effect.

Figure 8 compares the friction performance of both compositions in a Mini-traction Machine test in which a

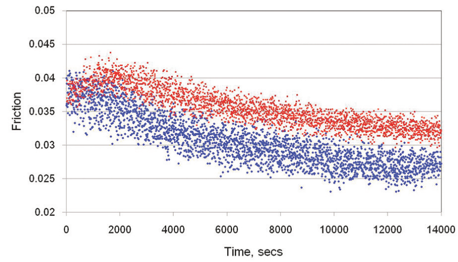

Figure 8. *Friction performance of a PAO gear oil containing 20% diester (red) and a PAO gear oil containing 20% OSP-32 (blue).*

steel ball rotates on a steel disc at a contact pressure of 0.75GPa, the fluid temperature is 80°C, speed 15 mm/sec and a 10% slide roll ratio. Esters are known to be surface active and act as friction modifiers or friction reducing agents. There is a greater degree of friction reduction for the OSP containing product versus the ester under these test conditions. This provides supporting evidence that OSPs may help improve friction control and improve energy efficiency of gear oils when they are used as co-base oils or additives in formulations. Therefore in synthetic PAO gear oils the inclusion an OSP can provide multi-functionality and improve deposit control as fluids age, improve friction control, act as seal swell additives and also provide enhanced additive solubility. OSPs may be a preferred choice over esters especially if there are concerns about hydrolysis when using an ester and if longer fluid life is desired.

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