

Oil Soluble Synthetic Polyalkylene Glycols

A New Type of Group V Base Oil

Abstract

Since their commercialisation over 50 years ago, polyalkylene glycol (PAG) lubricants have continued to solve problems that mineral oils cannot. Conventional polyalkylene glycols that are derived from the polymerisation of ethylene oxide and/or propylene oxide provide many performance benefits such as excellent friction control, good low temperature properties, high viscosity indices and excellent deposit control. One limitation is their poor miscibility in hydrocarbon oils. A new range of oil soluble PAGs (OSP) has recently been developed and derived from downstream derivatives of butylene oxide. These new API Group V base oils offer many of the traditional advantages of PAGs. Moreover, they offer formulators an additional tool for upgrading hydrocarbon oils by using them as a co-base oil or performance enhancing additive to improve deposit control, friction control and extend fluid life.

Introduction

Conventional polyalkylene glycols (PAG) are generally regarded as niche synthetic lubricants and are used across the lubricant industry to solve problems that petroleum oils can't solve. Most PAGs in use are manufactured from downstream derivatives of ethylene oxide (EO) and propylene oxide (PO). They offer many technical benefits over mineral oils such as excellent lubricity, good load bearing characteristics, good low temperature properties, high viscosity indices and high flash points making them suitable for a variety of applications [1]. Furthermore, synthetic processes used for manufacturing PAGs are very versatile which allows polymers to be designed to have many different functional properties [2]. In the

lubricant industry today there are over 100 different polymer chemistries that are used and there are many hundreds more for applications beyond lubricants.

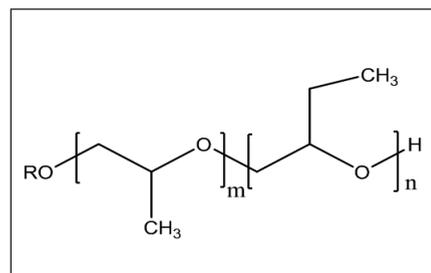
This versatility can be exemplified in the design of water soluble PAGs from copolymers of ethylene oxide with propylene oxide. These polymers can be synthesised to have a broad range of molecular weights and viscosities (e.g. up to 50,000cSt at 40°C) with different EO/PO ratios and polymer architectures such as random or block structures. These are the only major water soluble lubricant base oil available today. This unique feature provides functional advantages for fire resistant hydraulic fluids, metalworking fluids, quenchant, textile lubricants and many more.

One known disadvantage of conventional PAGs is their poor oil miscibility. This has two key implications. Firstly when end users wish to convert their equipment from a hydrocarbon oil to a conventional PAG, extensive flushing procedures are often required. Secondly, formulators can't use conventional PAGs as co-base fluids or additives in their hydrocarbon oils to enhance performance. This is in contrast to other synthetic lubricant chemistries such as polyalphaolefins (PAO), polyisobutylenes (PIB) and esters which are used to form semi-synthetic lubricants that can meet higher performance specifications. Therefore it is envisioned that the design of oil soluble PAGs that offer many of the inherent benefits of conventional PAGs can provide opportunities to formulators to upgrade hydrocarbon oils and solve many of today's lubrication challenges by leveraging the inherent functional benefits of PAGs.

Synthesis & Physical Properties of Oil Soluble PAGs

The design of oil soluble PAGs can be accomplished by synthesising downstream derivatives of butylene oxide (BO) to form polybutoxylate homo-polymers or by synthesising copolymers of PO and BO. Butylene oxide is available on an industrial scale and is used to produce polymers for other applications such as fuel additives but has been largely unexplored as a building block for lubricant base oils. Figure 1 illustrates a typical polymer architecture of an OSP base oil.

Figure 1 – Structure of oil soluble PAG



Note: for OSP copolymers, PO and BO are randomly distributed; for BO homo-polymers then $m = 0$.

The molecular weight and thereby the viscosity of PAGs can be influenced during the preparation and can be adjusted within narrow limits. This way, a very broad product design space is available and polymers can be tailored and engineered according to the specific application needs. Table 1 shows the physical properties of the new oil soluble PAG base oils. The polymers have been labelled OSP-32 to 680 with the numeric digits referring to the ISO viscosity grade classification. The PO/BO copolymers are OSP-32 to 220 and the BO homo-polymers are OSP-320 to 680.

Table 1 – Physical properties of OSP Polymers

	Method	OSP-32	OSP-46	OSP-68	OSP-150	OSP-220	OSP-320	OSP-460	OSP-680
Kin. viscosity at 40°C, cSt	ASTM D445	32.0	46.0	68.0	150	220	320	460	680
Kin. viscosity at 100°C, cSt	ASTM D445	6.4	8.5	11.5	23.5	33	36	52	77
Viscosity Index	ASTM D445	146	164	171	188	196	163	177	196
CCS viscosity at -20°C, mPa.s	ASTM D5293	1750	2900	5400	17,100	29,100	n/d	n/d	n/d
Pour point, °C	ASTM D97	-57	-57	-53	-37	-34	-37	-35	-30
Fire point, °C	ASTM D92	242	240	258	258	258	260	265	270
Density at 25°C, g/ml	ASTM D7042	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	n/d	n/d	n/d	n/d

The polymers span many of the classical ISO viscosity grades but it is possible to design even lower and higher viscosity grades using the same synthesis approach. These OSP base oils have higher viscosity indices than mineral oils, excellent low temperature properties with pour points as low as -57°C and very low aniline points. Details of their performance benefits of such polymers will be discussed.

Oil Solubility

The oil solubility of OSP-32 to 680 was assessed in API Group I to Group III mineral oils (ISO-46) and three API Group

IV polyalphaolefins. These PAO's have been labelled in Tables 2 and 3 as Group IV-H (PAO-40), Group IV-M (PAO-8) and Group IV-L (PAO-4). Blends containing 10 and 50% by weight of OSP base oil in each of the hydrocarbon oils were prepared and assessed for solubility at ambient temperature for 1 week. The visual appearance of the fluids was assessed before and after the test. Blends which appeared homogeneous throughout the test were characterised as being soluble (green) and those which were not homogeneous were characterised as non soluble (red). Tables 2 and 3 show the results.

Table 2 – Typical oil solubility for 10% OSP base oils in API Group I-IV hydrocarbon oils

	PO/BO	PO/BO	PO/BO	PO/BO	PO/BO	BO	BO	BO
	OSP-32	OSP-46	OSP-68	OSP-150	OSP-220	OSP-320	OSP-460	OSP-680
Group IV -L	Green	Green	Green	Green	Green	Green	Green	Green
Group IV-M	Green	Green	Green	Red	Red	Green	Green	Green
Group IV-H	Green	Green	Green	Red	Red	Red	Red	Red
Group III	Green	Green	Green	Red	Red	Green	Green	Green
Group II	Green	Green	Green	Red	Red	Green	Green	Green
Group I	Green	Green	Green	Red	Red	Green	Green	Green

Green = fully soluble at ambient, red = not soluble.

Table 3 – Typical oil solubility for 50% OSP base oils in API Group I-IV hydrocarbon oils

	PO/BO	PO/BO	PO/BO	PO/BO	PO/BO	BO	BO	BO
	OSP-32	OSP-46	OSP-68	OSP-150	OSP-220	OSP-320	OSP-460	OSP-680
Group IV -L	Green	Green	Green	Green	Green	Green	Green	Green
Group IV-M	Green	Green	Green	Red	Red	Green	Green	Green
Group IV-H	Green	Green	Green	Red	Red	Red	Red	Red
Group III	Green	Green	Green	Red	Red	Green	Green	Green
Group II	Green	Green	Green	Red	Red	Green	Green	Green
Group I	Green	Green	Green	Red	Red	Green	Green	Green

Green = fully soluble at ambient, red = not soluble.

Generally excellent solubility is seen for the lower viscosity OSP grades (OSP-32, 46 and 68) and the higher viscosity grades (OSP-320, 460 and 680) in all the Group I-IV base oils except the high viscosity PAO. OSP-150 and 220 are less miscible in Group II and III oils.

One macro trend in the base oil industry is the transition of many lubricant formulations from Group I to Group II and III base oils. Newer hydrocarbon base oils are much more iso-paraffinic with significantly lower aromatic content and lower sulphur levels. In Group I base oils these components often provide a degree of solvency which helps to impart solubility for performance enhancing additives. The absence of these unwanted polar compounds in Group II, III and also Group IV base oils has made it more challenging for formulators to develop compositions using many conventional types of performance enhancing additives. The excellent low aniline points of the polar OSP base oils means their addition to hydrocarbon oils can overcome this barrier and also provide additional benefits described below.

Deposit Control

The excellent deposit control characteristic of conventional PAG lubricants is well known [3]. In some applications controlling deposits and varnish formation is a critical concern [4]. PAGs have been used extensively in some applications such as rotary screw air compressor lubricants to essentially eliminate this problem. The deposit control behaviour of blends of OSP-46 in a Group I solvent neutral 150 (S.N.150) mineral oil was evaluated using a modified ASTM D-2893B test method. To S.N.150 base oil was added 10, 5 and 1% by weight of OSP-46 and a phenolic antioxidant (0.5% w/w). The fluids were heated to 121°C with dry air blown through the fluid at a flow rate of 10L/hour for an extended period of 50 days. The visual appearance of each product was assessed and any deposits observed and reported. Results are visually shown in Figure 2.

The inclusion of an oil soluble PAG significantly improves oil cleanliness and deposit control. Heavy deposits were formed in the mineral oil fluid that did not contain any OSP base oil and yet all fluids which contained the OSP base oil were clear translucent and deposit free at 10 and 5%. Even at 1% evidence of improved cleanliness was observed. One plausible explanation for the absence of deposits is that the oxidation by-products of mineral oils are more polar compounds. These are not soluble in hydrocarbon base oils and lead to deposit formation. However they are soluble in the more polar OSP polymers. Conceptually this is a significant observation since it is well known that hydrocarbon lubricants are prone to deposit formation in engine oils, turbine fluids, compressor oils and gear lubricants. The inclusion of an oil soluble PAG to hydrocarbon oils, could upgrade them, providing longer fluid life and greater equipment reliability. In the automotive industry specifications pertaining to deposit control continue to tighten and solutions are desired that minimise this impact.

Friction Properties

Traction measurements were performed using a Mini-Traction Machine (MTM). The MTM is a computer controlled precision traction measurement system. The test contact is formed between a polished 3/4 inch steel ball and a 46-mm diameter steel disc, each independently driven to produce a sliding/rolling contact. Traction measurements on blends of a polyalphaolefin base oil (PAO-8) and OSP-46 at concentrations of 5 and 8% were recorded at a contact pressure of 0.75GPa, a temperature of 80°C and a slide roll ratio of 10% over a 30 minute period. Traction data is shown in Figure 3.

Simplistically the polar nature of the OSP polymer appears to have good surface affinity and provides a film that lowers and stabilises friction. Under these test conditions, excellent stability is observed at a level of 8% OSP-46. Friction begins to increase when it is used at 5%. In some applications such as automotive engine oils, synthetic esters are used as friction modifiers or indeed boundary

friction additives. However it is widely known that many esters are susceptible to hydrolysis [6]. Since PAGs are hydrolytically stable, oil soluble PAGs may provide another tool to formulators that wish to improve friction control.

Noack Volatility

Volatility measurements were made for OSP-32 to 68 using method CEC-L-40. Measurements were made on the virgin base oil (no anti-oxidant). Measurements were also made for OSP-32, 46 and 68 when 1 and 2% w/w of an alkylated diphenylamine antioxidant was added. Results are shown in Figure 4.

The NOACK volatility test is conducted at 250°C. At this temperature lower molecular weight oligomers are volatilised. Since the composition of the lower molecular weight oligomers decreases as the average polymer molecular weight and viscosity increases, volatility decreases accordingly as is shown. Furthermore the addition of anti-oxidant to the base oil suppresses the volatility since it reduces the rate of oxidation of the polymers. PAGs form lower molecular weight oligomers on oxidation which are more volatile than their parent polymer.

Rotary Pressure Vessel Oxidation Test

The Rotary Pressure Vessel Oxidation Test (ASTM D2272) was used to measure the oxidation stability of one model polymer – OSP-46 – and its response to aminic and phenolic anti-oxidants. The anti-oxidants were screened at levels of 2% w/w. Included in the assessment are a dialkylated diphenylamine (DADP), alkylated phenylanththylamine (APNA) and an alkylated phenolic (AP) antioxidants. Results are shown in Table 4.

Table 4

	RPVOT, minutes
OSP-46	15
OSP-46 + DADP (2%)	834
OSP + APNA (2%)	966
OSP-46 + DADP (1%) + AP (1%)	623
OSP + proprietary AO package (2%)	1530

The virgin OSP-46 base oil showed a low value of 15 minutes. However, addition of aminic anti-oxidants and a combination of aminic and phenolic anti-oxidants yield significantly higher values.

A proprietary anti-oxidant package shows values above 1500 minutes are possible through simple experimentation.

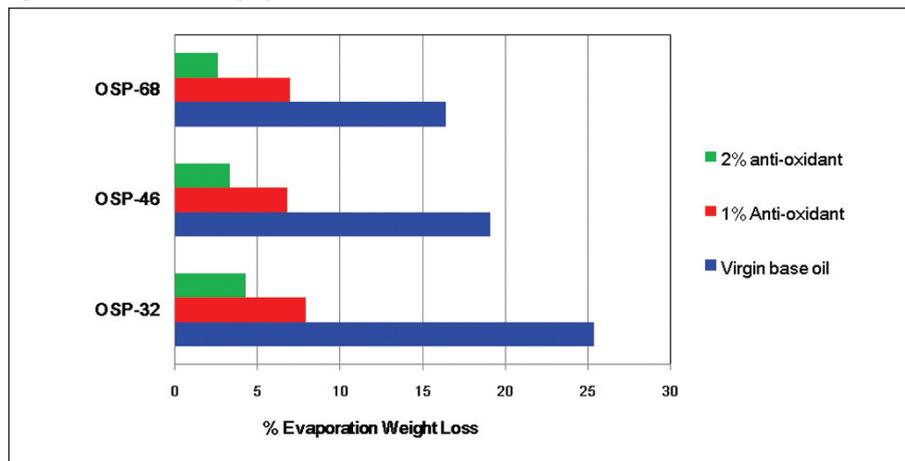
Practical Uses of OSPs

The new oil soluble polyalkylene glycols provide additional functionality over traditional PAGs. Simplistically they can be used as a primary base oil, co-base oil and as a performance enhancing additive. As a primary base oil, it is envisioned that new industrial lubricant products can be formulated such as gear lubricants, greases and compressor fluids. One practical advantage is that equipment conversions from a hydrocarbon oil to an oil soluble PAG lubricant will be much simpler. Furthermore the new OSP polymers are kinder to elastomers and seals and are also less hygroscopic than conventional PAGs.

Their use as a co-base oil in mineral oil to form semi-synthetic lubricants or as a performance enhancing additive in hydrocarbon oils will open up the application envelope for PAGs. For the first time hydrocarbon oils and PAGs are compatible. As deposit control additives, OSPs can help solve many of the challenges of varnish formation in the gas turbine industry or eliminate challenges with servo-valve sticking or filtration blockages in hydraulic systems. In recent years there has been a proliferation of specifications for automotive engine oils around deposit control. Oil soluble PAGs provide an additional tool to formulators to meet these specifications and also provide benefits in friction control as film forming additives.

Finally, the high polarity and low aniline points of OSPs will help formulators to solubilise critical additives in newer Group II and III base oils which are more iso-paraffinic and less polar in nature. But also macro-changes in the dynamics of the base oil industry and the reduced availability of bright stock has created a shortage of high viscosity base fluids. The inclusion of an OSP as a bright stock replacement may offer formulators an alternative approach to boosting a lubricants viscosity and also provide some of the additional functionality described above.

Figure 4 – NOACK volatility by CEC-L-40



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