

## Synthetic Basestocks - Synergy with Greases

### Summary

The continuing debate on how to describe or define lubricating grease has not prevented it from becoming an important component of modern automotive and industrial machinery. Between 80-90% of all rolling element bearings are now grease lubricated [1]. This is easily explained if we look at the numerous reasons for employing grease. Similarly synthetic basestocks offer numerous advantages over conventional mineral basestocks. Comparing the benefits of both grease and synthetic basestocks we can see a natural fit that encourages grease manufacturers to make tailored, high performance synthetic lubricants.

Recent developments in polymer thickener technology which extends grease life significantly [2] make the use of synthetic basestocks such as Polyalphaolefins and Alkylated Naphthalenes highly desirable for manufacturing high performance greases.

This paper will look at these specific synthetic basestocks and the benefits they offer the grease manufacturer whether that be long life, improved film thickness, energy saving, NSF registration or solvency.

### Introduction

It seems strange that despite the long history of grease utilization, debates still continue about its definition. Derived from the Latin word "Crassus" meaning fat [3], simple descriptions for greases have included "a thick-ened lubricant" [4], "thinned down soaps" [5], "a plastic fluid" [6], and less commonly "an elusive butterfly"[5].

A typical description of a grease is that of a three dimensional matrix of thickener particles with the spaces in the matrix filled with a lubricating oil. As the matrix is compressed under load, the oil is released to provide its lubricating function. Based on this, it is easy to see how the common analogy of a sponge full of oil became standard teaching (Figure 1).

Figure 1.  
the 'Grease sponge'

However, as we now know, things are not as simple as that and greases are really "a complex, physical, multi-phase system" [7]. The films that separate moving surfaces are a combination of the thickener and lubricant. Logically, this should not be a surprise - it is the properties given by the combination of thickener and oil which makes grease so useful.

In general, greases stay where they are put. Imagine trying to lubricate a vertical slide way with oil or the bouncing wheel bearing on a car. The thickener acts as a seal, keeping oil in and contamination out. This of course also has the negative effect of keeping internal wear debris within the grease. However, the fact that the grease remains in place is vital in helping reduce the effects of corrosion, especially on standby equipment where oil films drain away. Noise reduction and the ability to deal with shock loading are also features of grease lubrication.

The lack of fluidity does reduce the ability of grease to provide a cooling function but in the majority of applications temperatures are relatively low and cooling can be implemented through suitable design features i.e. electric motor fans. We can of course make semi fluid greases which act like thick oil. These will flow under gravity (slump) and get splashed about by mechanical motion which helps with heat transfer but still have the ability to provide a sealing function. In comparison to oils, greases require less maintenance and, even when replenishment is required, this can be achieved automatically either individually per



bearing or via a central pumped multiple discharge system.

In general, the benefits of grease lubrication far outweigh the disadvantages and it is therefore no surprise that between 80-90% of all rolling element bearings are now grease lubricated [1].

### Thickeners

The thickener is used to create a 3 dimensional matrix with which to hold the lubricant. The final properties of the grease can be adjusted by using different types of thickeners of which there are many different options offering certain advantages and/or disadvantages. They are generally classified as soap based (e.g. lithium, sodium or calcium) or non soap based (clay or polymer). The thickener needs a good affinity with the lubricant and the ability to create a stable matrix with a uniformly dispersed lubricant.

The thickener, so often thought of as just a "sponge", has, in fact, an extremely difficult balancing act:

- It needs to be mechanically and thermally stable.
- It needs to be able to flow at low temperatures,
- It needs to hold the lubricant in its structure but allow some oil bleed at all temperatures,
- It needs to have an affinity for the surface in order to remain where it is put even under arduous conditions such as high pressure water spray,
- It needs to protect that surface from the environment whilst not interfering with the surface active additives,
- It needs to provide part of the lubricant film thickness under ElastoHydroDynamic (EHD) lubrication conditions [10].

Due to their properties, lithium complex thickeners are very popular offering the ability to create high performance multi-purpose greases. For electric motor bearings requiring long life at relatively high operating temperatures and low loads, polyurea thickeners have become

very popular. With increasing temperatures, polyurea thickeners combined with synthetic base oils seem to offer the best grease life [8].

Recent developments in thickener technology [9] indicate that a polymer thickener based on polypropylene can offer significant benefits such as:

- Longer life and extended re-lubrication intervals
- Improved low temperature performance
- Increased film thickness reducing noise, vibration, friction and wear
- Improved additive efficiency

As we move on to look at synthetic base oils, we will see that the benefits of this new thickener type highly complement the benefits of synthetic greases and has the ability to make truly high performance greases.

## Synthetic Base Oils

In a similar way that greases offer a benefit over oils, synthetic base oils offer a benefit over conventional paraffinic or naphthenic base oils in lubricants.

The potential benefits on offer are;

- Wider operating temperature range through better high and low temperature properties.
- Longer life and reduced deposit formation through improved oxidation resistance and lower volatility at high temperatures.
- Improved flow and lower bearing torque at low temperatures.
- Energy savings through the ability to use lower base oil viscosity or oils with reduced traction.
- Improved wear protection through thicker oil films or improved oil film formation.
- Biodegradability and/or low bio-toxicity.
- The ability to make incidental contact food grade lubricants.

Traditional synthetic base oils are fluids chemically created using selected feed stocks that have uniform structures and properties. For the lubricant developer, this means they can choose precisely the constituents wanted in the oil, rather than having to make do with the

hydrocarbon mix that traditional mineral oils provide. The finished lubricants can have specific characteristics that can be matched to an application.

Having said that, highly refined mineral oils such as API Group III oils are being manufactured using feedstock and methods which allow them to be categorised as synthetic oils. Although limited in viscosity range and lacking the low temperature properties of PAO or esters, they nevertheless have proven very popular, particularly in the engine oil market.

Of all the synthetic base oils, Polyalphaolefins (PAO) have a long history of use in greases (~40years) and are probably the most widely used due to their;

- Wide range of viscosities (2-1000 cSt @100°C)
- Wide operating temperature range
- Good oxidative stability when inhibited with antioxidants
- Low traction coefficients offering energy savings
- Compatibility with mineral oils and other base oils
- Negligible effect on most paints, elastomers or plastics
- meeting FDA requirements for technical white mineral oil (21CFR178.3620(b))

For grease formulators, the complications of compliance with REACH legislation might be reduced by the use of PAO and polymer thickeners since polymers are generally exempt from the regulations.

Esters are also widely used due to their good thermal stability, low temperature properties, lubricity and, in most cases, high levels of biodegradability. In addition they have good solvency which is one of the most important factors in the choice of base oil for greases. It affects how the grease is made and how the thickener structure is formed. This can have a dramatic effect on the mechanical stability and lubricating ability of the grease. However the high solvency of esters can often lead to problems with excessive seal swell or material compatibility. In addition, esters can be subject to hydrolysis in the presence of water which is an all too often contaminant in

industrial lubricants and greases.

Combinations of PAO with some ester are thus often used with the solvency effect of the ester offsetting the poor solvency of the PAO.

Alkylated Naphthalene (AN) is another synthetic basestock which not only offers good solvency but is thermally, oxidatively and hydrolytically stable and can replace esters in lubricant formulations. In combination with PAO or other basestocks, it offers a synergistic boost to the oxidative stability of the formulation.

As both the Alkylated Naphthalene and PAO products from ExxonMobil Chemical are registered in the NSF White Book™ as acceptable as lubricants with incidental food contact (H1), they can be combined to make high performance "food grade" greases.

Other synthetic base oils such as polyglycols, silicones and polyethers are also used but their specific properties mean that they are generally limited to specialist lubricant greases.

## Putting it all together

So let's look how the benefits of PAO and Alkylated Naphthalene can help work together with the properties of the polymer thickener mentioned before:

1. Longer life and extended re-lubrication intervals.
2. Improved low temperature performance
3. Increased film thickness reducing noise, vibration, friction and wear
4. Improved additive efficiency

## 1. Longer life and extended re-lubrication intervals

Product	Mineral Oil Group II	6 cSt PAO	40 cSt PAO	100 cSt PAO
% Vis Change @ 100°C	215.7	3.5	2.6	1.8
TAN change, mg	14.5	0.1	0.08	1.1
Lead loss, mg	160.7	0.9	0.1	0.2
Sludge	moderate	nil	nil	trace

Test Conditions: 163°C (325°F), 72 hours

Figure 2. Oxidative stability of PAO in an oxidation corrosion test

The thermal and oxidative stability of PAO when inhibited with antioxidants, typically offer 4 to 5 times the life of mineral basestocks. Figure 2 shows the comparative stability of various PAO's versus a group II mineral oil in an oxidation-corrosion test.

It is clear that the PAO grades show much less deterioration at the end of the test in comparison with the Group II oil.

Alkylated Naphthalene is also thermally and oxidatively stable. An additional feature is that, when combined with PAO (or other basestocks) and antioxidants, it helps to boost the oxidation resistance beyond expected levels (see figure 3).

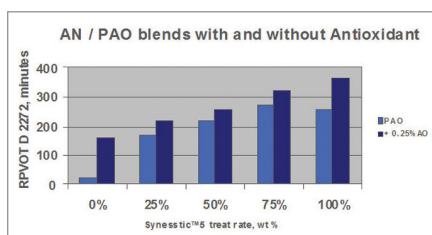


Figure 3. Oxidation boost by adding Alkylated Naphthalene to PAO

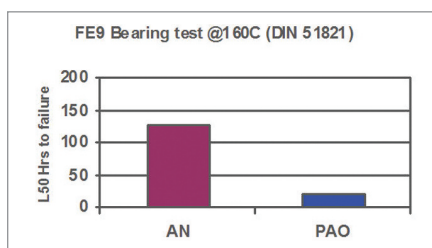


Figure 4. Improvement in high temperature bearing wear using Alkylated Naphthalene (NLGI#2 greases, 110cSt, same additive pack)

In recent testing, #2 lithium thickener greases were made using the same generic additive package and 110cSt base oils - one using PAO and the other Alkylated Naphthalene. The grease made using Alkylated Naphthalene showed a significant increase in bearing life in the FE9 test versus the same grease made with PAO base oils. (figure 4)

As with lubricants, greases made with synthetic base oils last longer than mineral base oil greases using the same thickener type under the same elevated temperature conditions [8].

## 2. Improved low temperature performance

PAO and ester have very low pour points in comparison to mineral oils. This means that greases can be made which will still lubricate under very cold applications (e.g. refrigerated warehouses, Arctic/Antarctic operations, aircraft equipment, etc). Figure 4 shows how synthetic base oils, and particularly PAO and adipate esters, have much better pour points than mineral oils and Kemble [8] showed that PAO/ester-lithium special/complex greases tend to operate at lower temperatures than other grease types.

Whilst the pour point of Alkylated Naphthalene is somewhere between PAO and mineral oils (figure 5), its good solvency allows lower levels of thickener to be used whilst still maintaining good stability. This contributes to improved pumpability at low temperatures (within the operating range of AN) as shown in the US Steel Mobility tests shown in figure 6.

The polymer thickener was reportedly developed to help overcome the low oil bleed encountered with conventional thickeners at low temperature [9]. The use of Synthetic base oils with very low pour points means that the oil bled from the thickener will still have the ability to flow where it is required.

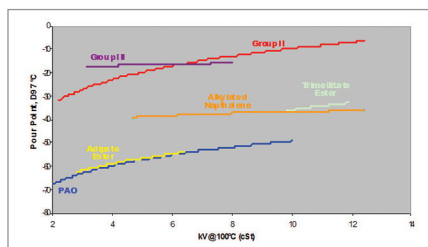


Figure 5. Typical pour point ranges of base oils

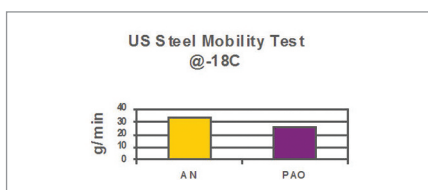


Figure 6. Comparison of low temperature pumpability using Alkylated Naphthalene versus PAO (NLGI#2 greases, 110cSt, same additive pack)

## 3. Increased film thickness reducing noise, vibration, friction and wear

The additional film created by the thickener

helps to increase the lubricant film thickness in EHD lubrication regimes [10].

High Viscosity Index (HVI) PAO's can also help to improve EHD film thickness. Figure 7 shows the addition of only 2% of a 150cSt HVI PAO to ISO 46 Synthetic oil. Tested on a ball on disk traction machine, the blue line shows the theoretical film thickness that the lubricant should generate. The blue squares show that the actual lubricant film decreases with speed. The addition of the HVI PAO provides improves the film thickness and maintains it down to low speeds delaying the transition to boundary conditions.

Increased specific film thickness ( $\lambda$ ) correlates with improved component life. Figure 8 shows how component life in EHD lubricated components can be extended as the specific film increases. Beyond a  $\lambda$  of 4, we have effectively separated the surfaces and see no further benefit in component life.

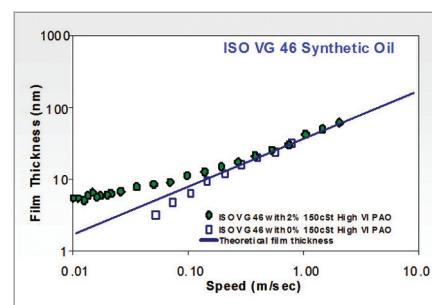


Figure 7. improved oil film thickness using HVI PAO

Under EHD lubrication conditions, the two contact surfaces, separated by a very thin film of lubricant, are generally moving at different speeds which requires shearing of the oil film.

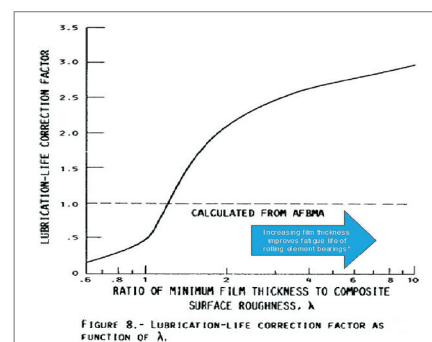


Figure 8. The influences of specific film thickness on component life [15]

Traction is the term given to the forces generated during shearing of the lubricant film. Under the extremely high contact pressures in EHD contacts, the lubricant behaves more like a solid than a liquid and the traction force is a function of the shear strength of the solidified lubricant rather than its viscosity [11].

The more uniform structure of PAO reduces the amount of internal friction created by the normal shearing of an oil film during operation. Lower traction forces are generated than for a mineral oil under the same conditions. The structure of HVI PAO offers a further reduction in traction force than conventional PAO as shown in figure 9. The lower friction can result in energy savings, lower oil temperatures and reduced scuffing.

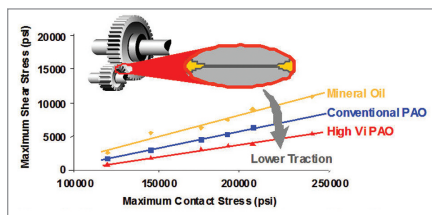


Figure 9. Comparison of traction forces between different base oils

Improved scuffing performance for gear / circulating oils was demonstrated by Jackson et al [12], who studied the influence of lubricant traction characteristics on the load at which scuffing occurs. Benefits of 25 - 220% were observed for low traction PAO-based lubricants at both high and low specific film thicknesses.

With respect to vibration and noise, the visco-elastic properties of the HVI PAO helped a customer to solve a problem with semi-fluid grease for a rack and pinion steering box. Not only was the wear and 10 year lifetime requirements achieved but noise from backlash was considerably reduced [13].

As previously mentioned, testing of #2 lithium thickener greases made using PAO and Alkylated Naphthalene was carried out. The improved solvency of Alkylated Naphthalene seems to provide a more homogeneous grease structure using approximately 30% less thickener. Despite the lower thickener content,

mechanical stability was improved slightly and the wear protection showed some improvement (figures 10 & 11)

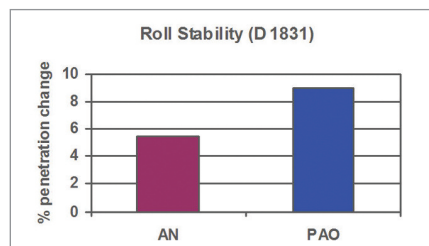


Figure 10. Improvement in mechanical stability using Alkylated Naphthalene (NLG#2 greases, 110cSt, same additive pack)

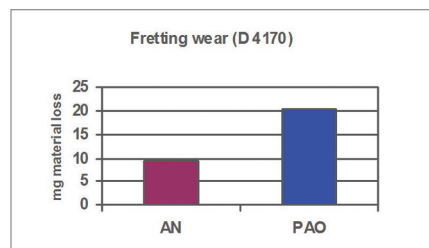


Figure 11. Improvement in fretting wear using Alkylated Naphthalene (NLG#2 greases, 110cSt, same additive pack)

#### 4. Improved Additive Efficiency

Conventional thickeners have an affinity for the surface which restricts access for the surface active additives in the lubricant such as anti-wear, rust inhibitors, extreme pressure, metal passifiers, etc.

The new polymer thickener is non polar and as such, claims have been made that there is less interference between it and the additives, making them more effective. In a similar manner, the use of Alkylated Naphthalene instead of esters can improve the efficiency of additives as seen in figure 12.

ISO VG 220	Ester Blend	AN Blend
40 cSt PAO	78 %	78 %
Adipate Ester	20 %	--
5cSt Alkylated Naphthalene	--	20 %
Additives	2 %	2 %
<b>4-Ball Wear Test (D 4472)</b>		
1800 rpm, 93 °C for 30 minutes		
60 kg load	0.822	0.739
80 kg load	2.094	0.822
Wear Scar, mm		

Figure 12. Improved wear performance replacing ester with AN

In the ester blend, increased loading in a four ball wear test creates severe wear whereas the same formulation with the

ester replaced by Alkylated Naphthalene shows little change as there is no interference with the additive performance. Several examples of significantly reduced cam wear have also been shown in engine tests when replacing esters with Alkylated Naphthalene [14].

#### Conclusion

We saw at the beginning of this paper that grease is much more than just a combination of thickener and lubricant. We also saw that synthetic lubricants can offer a better performance than mineral lubricants with properties that can tailored to a specific application.

Putting synthetic lubricants together with the correct thickener, matching the required properties, can make high performance greases for all types of applications.

As claimed in the title of this paper, synthetic basestocks such as PAO and Alkylated Naphthalene provide a good synergy for greases!

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#### LINK

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