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Development and Testing of a Novel Oxidatively Stable Ester

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Introduction

Sulphur limits and the desire for lower viscosity oils for passenger car and heavy-duty diesel lubricants has reduced total global demand for Group I base oils. Manufacturers are moving towards Group II and III which have multiple advantages but are lower in viscosity than Group I base oils.

Because automotive applications represent about 50% of total finished lubricant demand, they define what types of base oils are produced. Pressure to reduce emissions, especially sulphur, improve fuel economy and increase time between drain intervals is driving demand for Group II base oils, as illustrated in Fig.1.

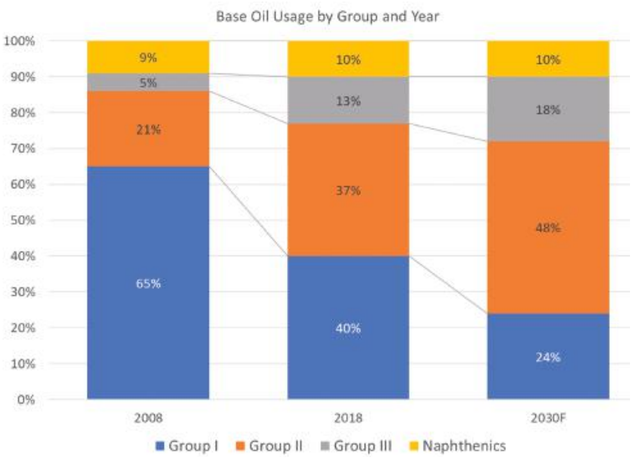


Fig 1: *Base oil Group and usage by year.*

Group I demand is falling and plants that produce it are closing, reducing total global capacity. From 2007 to 2014, Group I capacity declined by 6.5 million tonnes[1]. Group II is expected to make up about half of the total worldwide base stock demand by 2030[2].

Characterisation of Bright Stock

Bright stock is sourced from Group I base oils and is used as a viscosity modifier/ thickener for Group I and II base oils, with a viscosity of around 500Cst at 40°C and 32Cst at 100°C. It has a high sulphur content, giving it excellent oxidation stability. Alternative high viscosity naphthenic oils have poor oxidation stability unless sulphur is added back into the formulation. The reduction in supply of Group I base oils is reducing the supply of bright stock. Supply is becoming tighter and prices are going up. Users of Group I and II Based lubricants are looking for replacements for bright stocks.

Croda was approached by multiple customers to investigate and develop a product that could be used as a bright stock replacement with equal or superior viscosity modification characteristics and oxidation stability. We created a complex ester-based thickener with multiple advantages over bright stock. In this article, it is called Croda BSA (bright stock alternative).

Development Challenges

We used our knowledge of bio-based chemistries to create a product that matched both the thickening

[1] *https://www.nynas.com/en/product-areas/base-oils/knowledge-tank/closing-time-for-group-i-refineries/*
[2] *https://www.infineuminsight.com/en-gb/articles/base-stocks/exxonmobil-on-global-base-stocks*

power of bright stock but also had comparable oxidation stability without the addition of sulphur. Croda BSA is 85% biobased. The following piece outlines the results of our testing of the product's performance in comparison to bright stock alternatives.

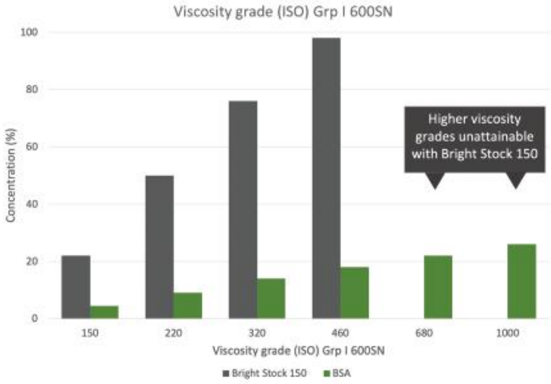


Fig 2: *Viscosity Impact ISO Grades.*

The improved thickening power of the BSA is evident in Fig. 2. Approximately one fifth of the concentration is needed to achieve the equivalent (ISO*) viscosity and far in excess of the limitation of the standard bright stock.

Oxidation

Bright stock is inherently oxidatively stable due to the residual sulphur content acting as an antioxidant, so part of the brief for an alternative was to compare directly with bright stock. We also extended the testing to include Group II base oil as the natural replacement to the reducing Group I stocks. The screening used the Rapidoxy static oxidation tester, manufactured by Anton Paar under ASTM 7545.

The test comprises of a pressurised chamber at an elevated temperature, observing oxygen consumption as a function of time; consumption of 10% oxygen denotes the rapid onset of oxidation or the oxidation induction time (OIT).

Initial test results (Fig 3) show the extent of the protection against oxidation that can be achieved with bright stock without the use of an antioxidant package. When compared to the BSA there is a slight reduction in overall oxidation stability, but this is not the whole story; further analysis highlights the deficiencies of the higher sulphur Group I base oils which is clearly demonstrated in Fig 4. Oxidation deposits (sludge) are reduced when used in Group I base oils compared to bright stock. This is also highlighted in oven tests showing a reduction in deposits and reduced colour change in a test of the neat products (Fig 5).

The same can be seen when tested in Group II. Fig 6 shows that the BSA increases the OIT time compared to the neat material. Fig 7 shows that the sludge/ deposit formation is not as evident in Group II but there is an improvement in colour change compared to bright stock.

Oxidation stability at 180°C: 10% in Core ™* 100 Group I base oil

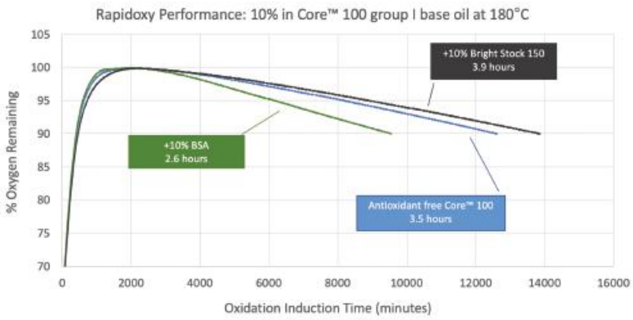


Fig 3: *Comparative oxidation protection.*

Colour, deposit and sludge formation

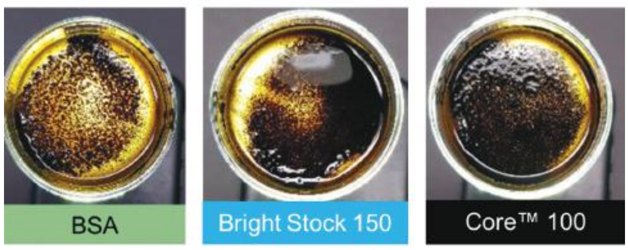


Fig 4: *Residue formation Rapidoxy test – 10% in Core 100.*

**Core is a trademark of Exxon Mobil Corporation*

Oven test at 180°C: Differences in colour, deposit and sludge formation, 10% in Group I

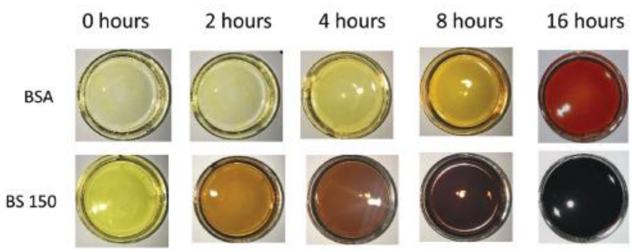
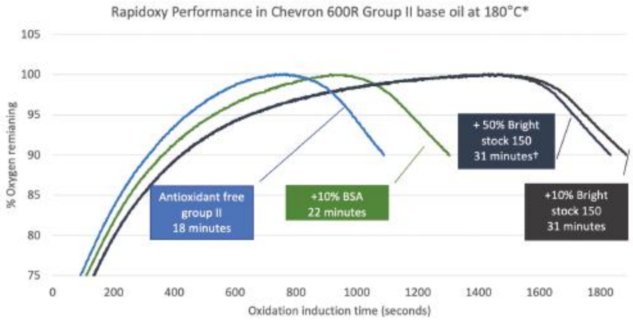


Fig 5: *Residue formation Rapidoxy test – neat.*

Oxidation and thermal stability at 180°C: 10% in Chevron 600R* Group II base oil



**Solubilised in 10% polyol ester*
† 50% bright stock to give equivalent viscosity to 10% Croda BSA

Fig 6: *Comparative oxidation stability*

Oven test at 180°C: Differences in colour, deposit and sludge formation, 10% in Group II +10% solubuliser

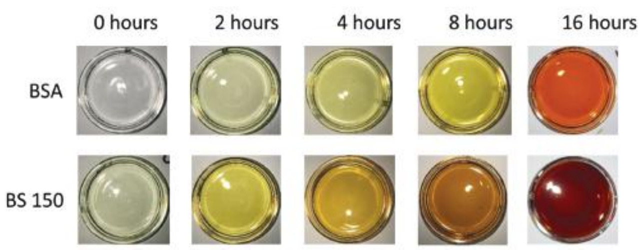


Fig 7: *Oven test at 180°C*

Lubrication

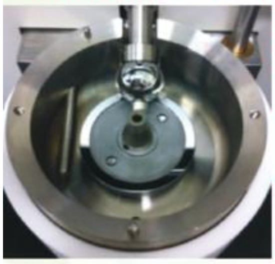
To test the lubricating nature of the BSA we initially tested it in a model Group I based industrial gearbox formulation using Afton's Hitec® 317 gear oil additive package. (See fig 8.).

Component	Purpose	Composition (w/w %)							
		ISO 150 (150cSt at 40°C)		ISO 220 (220cSt at 40°C)		ISO 320 (320 cSt at 40°C)		ISO 460 (460cSt at 40°C)	
		A	B	A	B	A	B	A	B
BSA	Oxidatively stable complex ester	4.5	-	9	-	15	-	20	-
BS150	High viscosity Group I base oil	-	22	-	50	-	76	-	98
600SN	Group I base oil	93.5	76	89	48	83	22	78	N/A
Hitec™ 317	Industrial gear oil additive package	2	2	2	2	2	2	2	2
	KV 40°C	162	154	238	220	348	338	-	-
	KV 100°C	16.9	14.7	23.3	19.7	31.7	24.7	-	-
	VI	111	94	121	94	128	94	-	-

Fig 8: *Model gear oil formulations.*

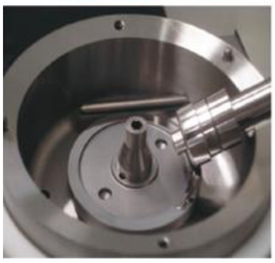
These formulations were tested using a PCS mini traction machine (MTM) using the following parameters. (See Fig 9).

Ball-on disc – Traction Curves



Parameter	Value
Speed	0.5mm/s
Temperature	100°C
Contact Pressure	1.24Gpa (70N)
Slide/Roll Ratio	Variable
Specimens	AISI 52100 steel

Barrel-on-disk - Variable Load Test



Parameter	Value
Speed	0.050m/s
Temperature	100°C
Contact Pressure	1.25 – 3.2 Gpa 5 – 75 N
Slide/Roll Ratio	50%
Specimens	AISI 52100 steel

Fig 9: *MTM parameters.*

Initially utilising the barrel on disk, higher contact pressures can be achieved than using ball on disc. The results observed in fig. 10 showed a consistent reduction in friction coefficient up to approximately 2.1 Gpa, demonstrating that in addition to the thickening effect of the ester based BSA, there is a positive effect on lubrication.

To investigate this further additional testing took place using the ball on disk and carrying out a traction test. This was completed on all viscosity variants to establish how a change in viscosity grade would affect the potential for lubrication.

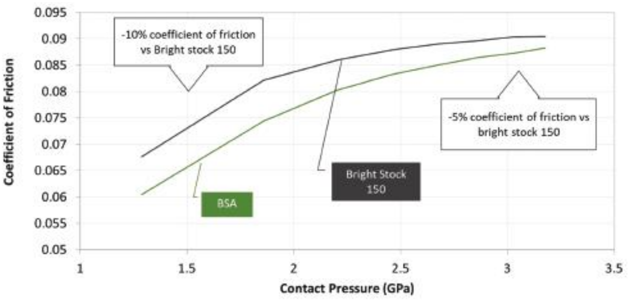


Fig 10: *Barrel on Disk – Variable Load Test, ISO 150, 50% SRR.*

The traction curve is a test at a constant speed and an increasing slide roll ratio (SRR). This test shows the potential for oil entrainment between two surfaces and in this case, a rotating ball and disk. As the SRR increases,the shear rate increases for that specific load and speed and a constant friction is attained which is related to the ability of a fluid to form a lubricating film.

Typically, increasing viscosity will increase the traction coefficient due to the inability of the fluid to entrain into the gap between the surfaces (in essence drag). This is the case with the bright stock based formulation (fig 11): There is a step increase in friction as the viscosity increases through each ISO grade.

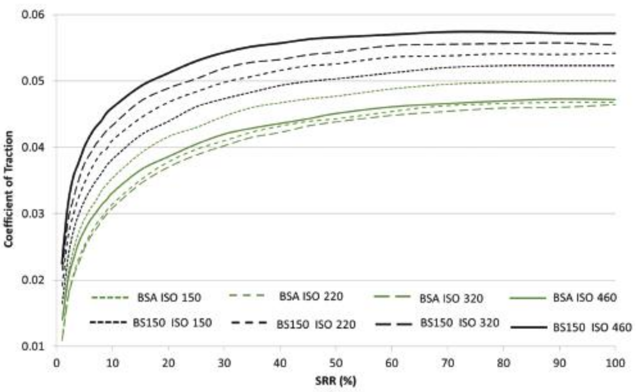


Fig 11: *Ball on Disk – Fixed speed and load variable SRR, Traction Curves 1.24 Gpa/70N, 500mm/s.*

This is the opposite for the BSA: Initially there is a slight reduction in the traction coefficient between the two ISO 150 grades but as the viscosity increases there is an initial drop in friction and then a constant friction, exhibiting the film forming potential of the BSA.

Further lubricity testing was centred around ASTM D5182, the industry standard, FZG Gear Load Wear test. There are 14 load stages used to categorise gear and hydraulic fluids with respect to their lubricating properties.

We utilised a method provided by Optimol Lubrication®, utilising the SRV lubricity tester (DIN 51834-4), which simulates the loading used on the FZG test.

Again, we utilised the model industrial gear formulations as shown in Fig. 8 and the results can be seen in Fig 12. The additive package is rated as an FZG load stage 12 pass in a Group I based formulation.

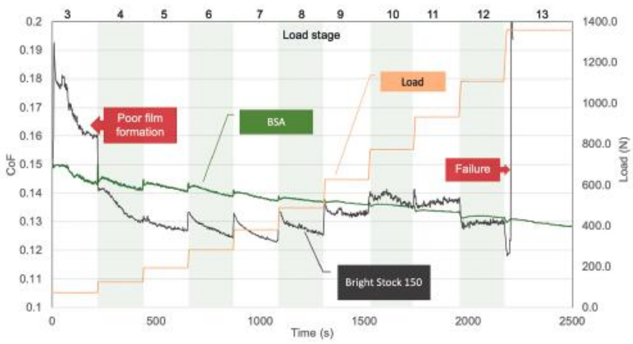


Fig 12: *FZG Gear Load test simulation at Load Stage 13.*

In this test we compared the lubricating nature of the bright stock against the BSA. The bright stock formulation reacted as expected with a pass at load stage 12, whereas the BSA has enhanced the capability of the additive package way beyond the prescribed and could be classified as a load stage 13+. The results clearly show the enhanced film forming properties achievable with the BSA.

Croda BSA in HDD Engine Oil

	SAE40 monograde	Partial BS replacement
Bright Stock 150	20.70%	11.00%
600 SUS Grp II	74.35%	82.05%
Croda BSA		2.00%
CF-4 additive pack	4.85%	4.85%
ZDDP booster	0.10%	0.10%
KV@ 40	148.15	150.07
KV@ 100	15.16	15.48
VI	103	110

Fig 13: *SAE 40 monograde CF-4 engine oil formulations.*

The work carried out so far has been based on full replacement of the Bright Stock, but now we examine partial replacement performance. The formulations in Fig 13 are typical of a fully formulated Group I based mono grade heavy duty engine oil.

As well as viscosity modification, the BSA can improve the viscosity index of the formulation without the addition of viscosity index improvers. The effect can be seen in both gear and automotive formulations; even at lower concentrations there is marked improvement to the VI (Fig 13).

Testing carried out was again on the MTM with the conditions as set out in Fig 14.

Stribeck curve conditions	
Slide-roll ratio:	50%
Entrainment speed:	3 – 0.005 ms-1
Temperature:	135ºC
Load:	36N ~ 1GPa initial Hertzian Contact pressure
Slide-roll ratio:	50%

Fig 14: *Measured initially and after 2 hours rubbing at 0.5 ms-1.*

Friction Coefficient vs Log Speed (m/s) Conditions:

In this test we evaluated the capability of the fluid to protect the surface over a period of time through coefficient of friction (Fig 15) and subsequent wear characteristic (Fig 16). We do this by measuring an initial stribeck curve and then after rubbing the surface for 2 hours at a constant load.

This should activate any anti-wear additives in the formulation, such as Zinc dialkyldithiophosphate (ZDDP). It can be clearly seen that on the initial test there is very little difference between the Bright stock and the BSA enhanced formulation, exhibiting almost identical curves. After 2 hours rubbing, significant differences are now demonstrated: Whereas the

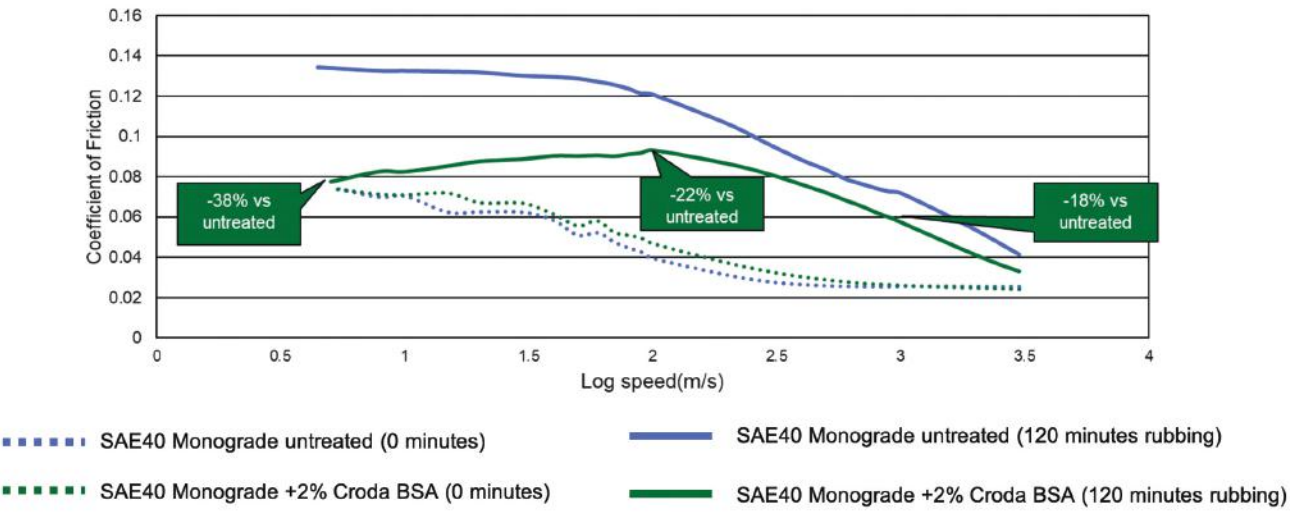


Fig 15: *Stribeck Curves, initial and after 2 hours.*

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untreated product increases in friction, the treated formulation maintained a lower friction coefficient throughout he stribeck curve (Fig. 15). The potential reduction in friction could be due to premature wear and change in the surface morphology.

Wear Volume Measurement

Wear volume was calculated using vertical scanning white light interferometry on disk surface and in this case the film forming properties of the BSA has had a dramatic reduction on surface wear, (fig. 16).

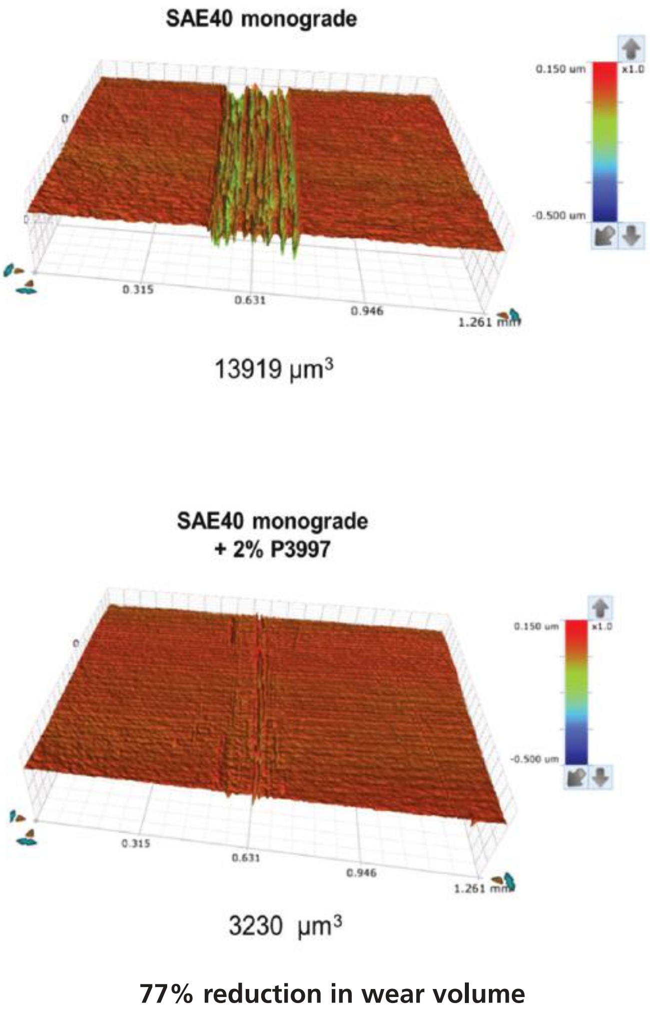

Fig 16: *Wear track disk data.*

Conclusion

We tested with industry standards for applications such as gear oils. We did physical and chemical testing, lubricity, FZG and oxidative stability.

As the industry evolves, it is important that there are viable alternatives to Group I and Group II based bright stocks are made available which offer the following characteristics and advantages:

- Viscosity index booster and thickener
- High lubricity and low wear
- Offers excellent oxidation stability
- Reduces deposits, varnishes and sludging
- Suitable for replacing bright stocks
- Soluble in Group I, II & III base oils

We found that Croda BSA is a viable alternative to bright stock, with additional properties to enhance the overall lubricant performance, and demonstrates the ways in which biobased alternatives can be utilised to equal or better commonly used bright stocks in formulations.

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