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Base oil blends to meet the new demands of the lubricant industry

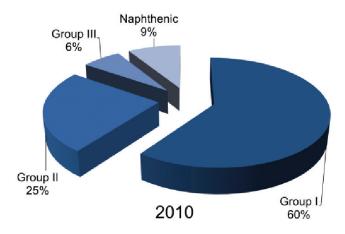
The base oil industry has been going through fundamental changes in the last years. These changes have been marked by the rapid growth in capacity for Group II and Group III base oils, while the availability of Group I oils has decreased considerably.[1-3] By looking at base oil production statistics for the last two years, it can be appreciated how paraffinic Group I production went from being 60% of the total in 2010 down to 54% in 2012, a difference of more than 52000bpd in only two years, while Group II and Group III base oils experienced an increment of more than 41000bpd and 19000bpd respectively during the same period. Projections over the demand-supply situation of the base oil industry to 2020 reveal that new Group II, III and GTL capacity will largely exceed the global demand, which is expected to grow at an average of 0.5-1.5%. This will result in more consolidations in the base oil industry in the

future, and with higher production costs and a shrinking market, more Group I refineries will likely close to compensate for new Group II and III capacity.[4]

A consequence of these changes is that the offering of the base oil industry is no longer optimised for the industrial lubricant industry requirements. These requirements are generally defined in terms of products that have high viscosity and/or high solvency. One look at the maximum viscosity that can be obtained from a Group I, II and III refinery, shows that Group II refineries can produce products with a maximum viscosity of around 100cSt at 40°C or what is known as heavy neutrals; and that the yield on those products is much lower than that in Group I refineries (20% for Group II as opposed to 33% for Group I).[4] Moreover, neither Group II nor Group III refineries can produce Bright stocks.

Another consequence of the shift from Group I to Group II and III base stocks is a loss in solvency of the products, by reducing the aromatic content from around 10% for paraffinic Group I oils to <1% for the hydrocracked paraffinic oils (Group II and Group III), the solvency power of the oils is drastically reduced.

This has serious consequences in industrial applications where high solvency is required either because of a high additive load in the formulation, or because the lubricant is expected to keep the machinery free from deposits and to dissolve contaminants. It is important here to remember that the use of the aromatic content as an indication of solvency works only between similar oils (like in this case paraffinic based), and that naphthenic oils are available at different refining degrees and aromatic contents ranging also from around 10% to below 1%,



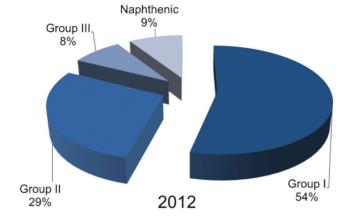


Figure 1. Base oil production 2010 -2012. (Source: Lubes'N'Greases)

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but their solvency is invariable higher than paraffinic oils having the same aromatic content and viscosity, the reason for that is the higher amount of naphthenic molecules in the oil. The lubricant industry is understandably reacting to these changes. Traditionally, lubricant and lubricating grease formulations have been based in one or two base oils. For instance, it is an extended practice in the lubricating grease industry, especially in Western Europe and the United States, to use two different base oils, usually paraffinic Group I and naphthenic oils in grease manufacturing. These traditional formulations were created in a market where the availability of raw materials was given for granted, something that resulted in a conservative culture within the industry, where the main drivers for change of the formulations were price reduction of the raw materials, fulfilling certain

In recent years, due in part to the added complexity of sourcing traditional raw materials, together with the ever increasing demands on performance and the environment, lubricant producers have started to change the way they look at base oils, from being simply commodities, to being part of a more complex formulation where they have an active role in achieving a desired performance. This complexity has resulted in the widespread use of base oil blends in lubricant formulations. According to some reports, up to 80% of modern commercial formulations are based on two or more base oils. [5]

specification, or environmental, health

and safety aspects.

These base oil blends are used to improve different properties in the formulations. In recent studies done at Nynas, it was found that by blending naphthenic oil with a paraffinic Group III oil, it is possible to modify the low temperature behaviour (beyond the pour point) of the formulation. In Figure 1, it can be seen how the rheological behaviour of the paraffinic base oil and the naphthenic one (all having the same kinematic viscosity at 40°C), is very different, with a clear increment on the viscosity of the paraffinic base oil at temperatures around 0°C, well below the measured pour point of that oil (-15°C).

Characteristics	Unit	Test method, ASTM	S1 S2		S3
Base oil type			Naphthenic	S1+S3	API Gr III
Density at 15 °C	kg/dm ³	D 4052	0.903	0.871	0.840
Viscosity at 40 °C	mm²/s	D 445	29.3 30.2		32.2
Viscosity at 100 °C	mm²/s	D 445	4.3 5.1		5.9
Viscosity index	-	D 2270	5.3 95		131
Flash point	°C	D 93A	176 186		221
Pour point	°C	D 97	-46 -23		-15
Aniline point	°C	D 611	77.6 102.4		121.4
Sulphur content	ppm	D 2622	600 320		0
Hydrocarbon Type Analysis		IR			
C _A (aromatic)	%		16	8.7	0.9
C _N (naphthenic)	%		38.3	29.3	20.9
C _P (paraffinic)	%		45.7	62.0	78.2

Table 1. Typical properties of a naphthenic and a paraffinic Group III base oil and a blend of them.

This increment in viscosity is believed to be caused by the waxes present in the oil, which start to crystallize at those temperatures. It can also be appreciated in the same figure how the viscosity of the wax-free naphthenic sample (S1) did not present that sudden increment in viscosity in this temperature range, but instead the viscosity of the oil increased gradually down to the lowest temperature studied (-20°C).[6]

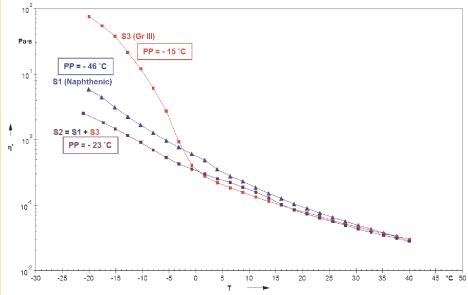


Figure 1. Viscosity as a function of Temperature for the base oils and a blend of them.

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Figure 1 illustrates further how by blending this Group III oil (S3) with an equal amount of the naphthenic oil (S1) the low temperature behaviour of the oil blend follows more closely the behaviour of the "pure" naphthenic sample, and that the sudden increment in viscosity at 0°C is no longer observed. This has deep implications in the flexibility of using the formulation based on these base oils at low temperatures; with the formulation based on Group III oil requiring higher energy to be pumped at these conditions than the formulations based on the naphthenic oil or on the naphthenic/paraffinic blend.

The tribological behaviour of the samples at low temperatures has been studied by using a "tribo-cell" device that may be attached to a rotational rheometer.[6] This "tribo-cell" consists of a steel ball which slides with respect to the contact points on three plates. This instrument permits the study of the friction curves as a function of sliding speeds at different temperatures. In this study a steel ball on bronze plates were used. The contact pressure has been calculated to 144 MPa and the sliding speeds were varied from 10⁻⁶ to 1.4m/s. In Figure 2 it can be seen that the frictional behaviour of S3 at -20°C is very unstable, with the friction coefficient decreasing and increasing several times at low sliding speeds, before reaching a more stable value at higher sliding speeds. This unstable friction behaviour might be due to reduced flow of the oil into the lubricating zone at this temperature. On the other hand, the same figure shows how the tribological behaviour of the blend S2 is more stable, which can be correlated with the rheological data described above.[7]

Furthermore, it can also be observed in Table 1, how S2 besides presenting a lower pour point, it also has a lower aniline point than the one of S3 (the Group III oil), the difference being almost 20°C. It is known that the oil's aniline point is one of the parameters used to measure its solvency, the lower the aniline point, the higher the solvency of the oil towards both additives and deposits. This means that a formulation based on S2 would be able to have a higher additive load or better ability to keep deposits or other contaminants in

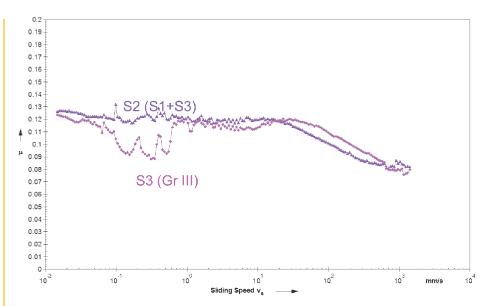


Figure 2. Frictional behaviour of Group III base oil and blend with the naphthenic oil at -20°C.

Characteristics	Unit	Test method ASTM	N	PII	B1
Base oil type			Naphthenic	Paraffinic Gr II	50% N + 50% PII
Density at 15 °C	kg/dm ³	D 4052	0.920	0.859	0.887
Viscosity at 40 °C	mm²/s	D 445	114	90.2	99
Viscosity at 100 °C	mm²/s	D 445	8.5	11.3	9.6
Flash point	°C	D 93A	212	240	222
Pour point	°C	D 97	-25	-12	-21
Aniline point	°C	D 611	85	122	105
Sulphur content	ppm	D 2622	600	50	300 ppm

Table 2. Typical properties of the base oils used for preparation of lubricating greases.

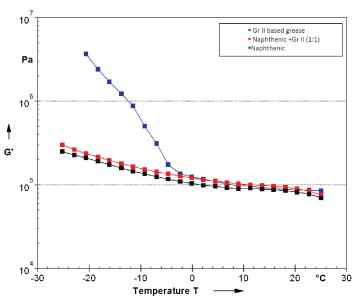
solution, while still having a high viscosity index (the VI for the blend is 95). It has also been reported that the aniline point affects the oil compatibility with different elastomers, so the change in the aniline point of the Group III base oil by blending it with a naphthenic one could also improve the compatibility of this oil with some elastomers.[8]

The different properties of the base oils or their blends have also a big effect on the production parameters and the properties of the lubricants based on them. If one takes the case of lubricating greases where the base oil content is between 80-95% of the formulation; it can be expected that the choice of the base oil would have a profound impact both in their manufacturing and final properties. In another study done at Nynas, NLGI grade 3 greases were produced in an open kettle. Different base oils were used to produce these greases, one naphthenic (N), one paraffinic Group II (PII), and a blend of equal volume of both oils (B1), see Table 2.

The aim of this study was to explore the low temperature behaviour of the greases. One way of doing this is by measuring the elastic modulus of the greases. As it can be seen in Figure 3, the greases become thicker (more elastic) as the temperature is reduced from +25°C to -25°C at an applied shear stress of 30Pa. This shear stress was within their linear viscoelastic region/range (LVER) where the grease is regarded to be shear stable. It can be observed in Figure 3 how at temperatures below -4°C, the elastic modulus of the grease based on 100% paraffinic Group II oil (PII) increases quite rapidly, most likely due to the waxes present in that oil, which start to crystalize at around that temperature. This higher elastic modulus indicates that higher energy would be required in order to pump this grease, in comparison to the other two greases (N and B1 based). In a separate study, the same base oils, N and PII, and a blend of them (58% PII and 42% N) were used in order to produce lithium greases. The goal of this study

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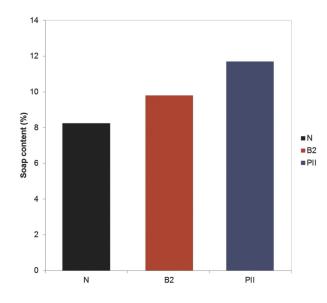


Figure 3. Elastic modulus as a function of temperature.

Figure 4. Soap content in NLGI 3 Lithium greases based on N, PII and B2

was to optimize the formulation of the greases in terms of thickener content; i.e. to use the minimum percentage of thickener possible in order to obtain a NLGI 3 grease. It is a well-known fact that the higher polarity of naphthenic oils contributes to a better soap-oil interaction which results in both a more homogeneous grease structure and a lower soap consumption in order to obtain a grease with the same consistency compared to if paraffinic base oils are used.[9] As it can be seen in Figure 4 the grease made with 100% paraffinic Group II oil (PII) required around 11.7% of thickener to achieve that consistency, but by blending 48% of naphthenic oil with the paraffinic one, the soap content was reduced to 9.8%, effectively reducing the soap consumption with 16%. Finally it can be seen how the "pure" naphthenicbased grease required only 8.2% soap to reach the same consistency than the other two greases, a reduction in soap consumption of 16% with respect to the naphthenic/ paraffinic blend- based grease and of almost 30% in soap consumption with respect to the "pure" paraffinic- based grease.

Today, modern lubricants are regarded more and more as "high end construction parts" that form part of the equipment where they are used. This has spurred a fundamental change in the lubricant industry, especially in Europe, which is moving away from generic to application specific products (products

formulated for a specific application). These higher demands on the lubricants performance are being met by the use of more complex formulations that require different base oils and additives. In this article it has been demonstrated how by blending different base oils one can affect several properties in a formulation. Moreover, it has been seen the positive effects that those changes can have in the production and performance of that formulation. It is important to remember that by blending base oils one is affecting several properties at the same time, as they are all connected to the final composition of the formulation.

The use of blends, very often means compromising between different properties. That is why there are many parameters which should be taken into consideration by product developers while creating a new formulation such as the environmental impact, raw material availability (long term, short term), solvency power, viscosity, viscosity index, film thickness, rheological and tribological behaviour under different conditions, polarity, seal compatibility, labelling, thermal stability, corrosion inhibiting, low and high temperature behaviour, colour, etc.

It is obvious that by making the right choice of base oils, one might not only improve the overall performance of the formulation, but might also potentially have an overall positive effect on its cost as some properties can be obtained without or at a lower additive load. Last but not least, the roll of the technical support offered from the oil suppliers shouldn't be underestimated when, a better and faster optimization of the blends for a certain application is required.

References

- DeMarco, N., New capacity redraws base-oil map. Lube report, 2012.
- DeMarco, N., Bracing the base oil wave. Lube report, 2012.
- Sullivan, T., Tighter base oil supply expected in Europe. Lube report, 2012.
- Serra-Holm, V., The collateral damage of the shift in paraffinic base oil pool, in LUBE Magazine. 2011, UKLA: UK.
- Sullivan, T., Supply chain in chains, in Lubes'N'Greases Europe-Middle East-Africa, 2013.
- Fathi-Najafi, M., et al., Low temperature tribology. A study of the influence of base oil characteristics on friction behaviour under low temperature conditions. EUROGREASE, 2012. 4.
- Fathi-Najafi, M., et al., Low temperature tribology: A study of the influence of base oil chraracteristics on friction behaviour under low temperatue conditions, in 18th International Colloquium Tribology 2012: Esslingen-Germany.
- Salomonsson, L., G. Stang, and B. Zhmud, Interaction of chloroprene and nitrile-butadiene rubber with lubricating greases and base oils. Lubricating oil, 2006. 21(54).
- Salomonsson, L., G. Stang, and B. Zhmud, Oil/thickener interactions and rheology of greases. Tribology transactions, 2007. 5(3)

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