Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.60 page 1

# Developing optimal oil for grease for CVJ boots

**Greases for constant velocity joints (CVJs) need to be compatible with the construction material of the boots that protect the joints – a challenge facing developers of new base oils for such greases. Nynas Naphthenics' Valentina Sera-Holm explains how the naphthenic base oil S 150 was made suitable for this application, whilst fulfilling other requirements.**

## Introduction

Commonly used in drive-line applications, constant velocity joints (CJVs) are special types of universal couplings which can transmit drive from the final reduction gear to a road wheel axle at constant rotation velocity. Constant velocity joints are protected by sealing boots made of chloroprene rubber or thermoplastic elastomer (TPE) which are usually bellows-shaped. The primary functions of the boot are to retain the lubricating grease in the joint and keep out contaminants. Two of the main requirements on the grease for CVJs are optimal compatibility with the boot material and very good low temperature properties.

When it comes to grease compatibility with the boot material and risk of deterioration of the boots, base oils have a relevant impact. In fact, all mineral and synthetic base oils extract the plasticisers from the elastomers. Some base oils diffuse very little into the elastomer, causing shrinkage, and others diffuse extensively, causing excessive swelling. Both shrinkage and excessive swelling are undesired as they compromise the stability of the sealing boot, ultimately resulting in failure of the CVJ. Paraffinic base oils and polyalphaolefins are examples of oils that cause shrinking of chloroprene rubber and TPE, while standard naphthenic oils cause swelling. Naphthenic oils are typically included in grease formulations in order to ensure good low temperature properties. The combination of the excellent low temperature properties of naphthenic base fluids with optimal elastomer compatibility in a single oil would make this material a very interesting candidate to be a base fluid for CVJ greases.

Such oil can be produced by very severe hydrotreatment of a naphthenic distillate. The resulting oil will have a very low aromatic content and therefore a higher aniline point than standard naphthenic oils. The aniline point can be optimised in order to achieve optimal elastomer compatibility, meaning a limited degree of swelling which ensures an improved sealing of the boot, without affecting the elastomer stability.

## Experimental

### Materials

The newly developed naphthenic oil (designated with the letter S 150) was compared to a paraffinic and several naphthenic base oils. The naphthenic base oils S 150, BNS 150 and BT 150 are manufactured by severe hydrotreatment of naphthenic distillates. The naphthenic base oil SR 130 is produced by solvent refining. All the oils tested had a polyaromatic content, measured by IP 346[1], lower than 3 %, which is the carcinogenicity limit according to the EU legislation[2,3]. The paraffinic base oil was produced by solvent refining. The main difference between the naphthenic base oils is the severity of the hydrotreatment process, which in turn affects the oil's solvating power. The solvating power can be measured with different methods, the most common ones being Aniline Point (AP) and Viscosity Gravity Constant (VGC). The aniline point method (ASTM D611) involves measuring the temperature at which aniline dissolves in the oil. The higher the solvating power, the lower the aniline point. Viscosity Gravity Constant (VGC) is a dimensionless constant that is based on a mathematical processing of the viscosity and density values according to ASTM D2501 and provides a weighted value between the viscosity effect on the solvating power and the chemical nature of the oil. The higher the solvating power, the higher the value of VGC. In Table 1 the main properties of the oils tested are summarised.

*Table 1. Base Oils Main Properties*

| Characteristics | Test method (ASTM) | Base Oils | | | | |
|---|---|---|---|---|---|---|
| | | Naphthenic base oil S 150 | Naphthenic base oil SR 130 | Naphthenic base oil BNS 150 | Naphthenic base oil BT 150 | Paraffinic base oil SN 700 |
| Density @ 15°C (59°F), g/cm3 | D4052 | 0.905 | 0.908 | 0.914 | 0.922 | 0.889 |
| Viscosity 40°C (104°F), $mm^2/s$ (SUS) | D445 | 152 (704) | 144 (667) | 150 (695) | 152 (704) | 151 (700) |
| Viscosity 100°C (212°F), mm2/s (SUS) | D445 | 11.7 (65.3) | 10.7 (62.0) | 11.2 (63.5) | 11.1 (63.1) | 14.5 (76.0) |
| Flash point PM, °C (°F) | D93 | 228 (442) | 225 (437) | 222 (432) | 220 (428) | 251 (484) |
| Pour point, °C (°F) | D97 | -30 (-22) | -27 (-17) | -27 (-17) | -27 (-17) | -12 (10) |
| Viscosity Index | D 2270 | 48 | 29 | 36 | 31 | 94 |
| Aniline point, °C (°F) | D611 | 106 (223) | 95 (203) | 96 (205) | 89 (192) | 113 (235) |
| VGC | 2501 | 0.837 | 0.841 | 0.850 | 0.860 | 0.814 |
| $C_A$ % | D2140 | 3 | 5 | 7 | 13 | 4 |
| $C_N$ % | D2140 | 44 | 37 | 42 | 38 | 27 |
| $C_P$ % | D2140 | 53 | 58 | 51 | 49 | 69 |

The oils S 150, BNS 150, BT 150 and SN 700 were used to prepare NLGI grade 2 lithium greases. The recipes of the greases and their main properties are reported in Tables 2 and 3.

*Table 2. Grease Composition*

| | |
|---|---|
| 12-hydroxy stearic acid | 292.5 g |
| Stearic acid | 24.6 g |
| Oil | 1080 g |
| Lithium hydroxide | 44.55 g |
| Oil | 3*300 g for cooling |
| More oil added until correct NLGI grade was reached | |

*Table 3. Grease Main Properties*

| Grease | Paraffinic base oil SN 700 | Naphthenic base oil S 150 | Naphthenic base oil BNS 150 | Naphthenic base oil BT 150 |
|---|---|---|---|---|
| ASTM D217 Worked Pen 60 1/10 mm | 284 | 284 | 290 | 291 |
| NLGI grade | 2 | 2 | 2 | 2 |
| IP 396 Dropping point °C | 203 | 199 | 200 | 199 |

The elastomers used for the compatibility tests were chloroprene rubber and thermoplastic elastomers (TPE). The chloroprene rubber was supplied by Forsheda AB and it contained dioctyl adipate (DOA) (8 phr) as plasticiser. The TPE used was Arnitel EB463 from DSM Engineering Plastics.

## Test Methods

The tests for studying rubber interactions with grease and base oil were conducted through total immersion of the rubber samples in the base oils and greases. The ageing was performed at a 100°C and the test duration was 168 hours. The change in hardness and weight for the rubber samples were measured. Hardness is a measurement of a rubber's ability to resist penetration of a specified cone. The two most common methods for hardness determination are Shore A and IRHD (International Rubber Hardness Degrees). In both methods the rubber's resistance to indentation is measured by pressing a rounded steel peak connected to a calibrated spring towards the material. The scale runs from 0 to 100 degrees where 0 is an extremely soft material and 100 is an extremely hard material. Common rubber values are 30-85 degrees.[4] The desired hardness is given by added fillers and plasticisers. The method used for the measurements in this study was IRHD.

The low temperature pumpability of the greases was determined by the flow pressure test DIN 51 805. The test setup consists of a standard conical nozzle which is filled with deaerised grease. The nozzle is placed in the measuring instrument, equilibrated for 2-3 hours at a desired temperature, and then an increasing pressure is applied to the nozzle. The threshold pressure at which grease starts to flow through the nozzle is recorded as the flow pressure of the grease at the actual temperature.

The oil separation was measured by ASTM D1742 test, which determines the amount of oil likely to bleed out of a grease stored at room temperature in a 15,9 kg pail. The grease sample is supported on a sieve and is subjected to an air pressure of 1.72 kPa for 24 h at 25°C. The oil that separates from the grease drains into a beaker and is weighed. The amount of oil separation is determined as a percentage value of the initial grease weight.

The ageing of the naphthenic oils was carried out in a circulated oven in air at 150°C for 6 hours. The weight, the color and the total acid number were measured before and after the ageing.

The oxidation stability was determined by IP 280. 25 g of inhibited oil were blended with 0.25 g of soluble metal catalyst (iron and copper). An oxygen flow was passed through the oil for 164 hours at 120°C. After the test the volatile acids, the acidity of the oil and the precipitated sludge were measured and their value was used in a correlation to calculate the total oxidation products (TOP). Because of its duration, the presence of soluble catalysts and the use of oxygen, this test is particularly severe.

## Test Results and Discussion

The properties measured were: elastomer compatibility (chloroprene rubber and TPE), low temperature pumpability of greases, bleeding at storage of greases, response to oxidation inhibitors of base oils, and behavior at ageing of the naphthenic base oils.

### Elastomer Compatibility

The compatibility of the newly developed naphthenic oil with elastomers was measured both with chloroprene rubber and with TPE, which are the most commonly used elastomers in CVJ boots. The ageing of chloroprene rubber was carried out both in contact with the base oils and with the greases. The naphthenic base oils S 150, BNS 150, BT 150 and the paraffinic base oil SN 700 were used. Rubber pieces were placed in 100 ml containers filled with oil or grease. The containers were thermostated at 100°C and the ageing experiment was run for 7 days. At the end of the ageing, the weight and hardness of the rubber samples were measured and compared with the weight and hardness of the fresh samples. The results of the ageing tests on chloroprene rubber are reported in Figures 1 and 2.

*Figure 1. Weight Change in Chloroprene Rubber in Oil and Grease*

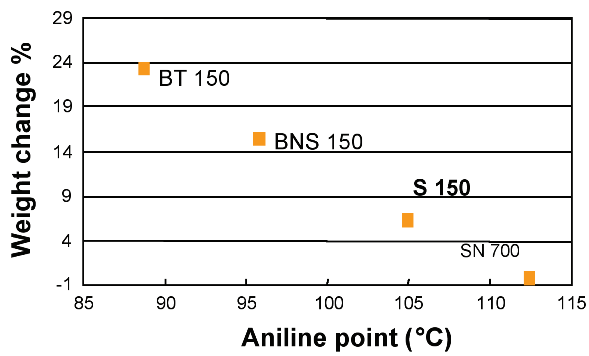
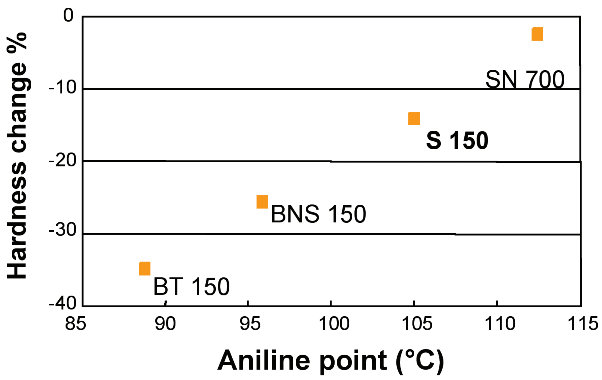


*Figure 2. Weight Change in Chloroprene Rubber in Oil and Grease*




As expected, the contact with lubricants causes swelling in the chloroprene rubber, the swelling being more marked the higher the solvating power and therefore the lower the aniline point of the base fluids. Consequently, the elastomer softens. The highest compatibility is displayed by the paraffinic oil SN 700 and by the newly developed naphthenic oil S 150. Compared with the paraffinic oil, the naphthenic oil S 150 provides some degree of swelling, which may be desired, as it improves the sealing performance of the boot.

As the results of the ageing of chloroprene rubber show a good accordance between the values obtained from ageing in grease or in the corresponding base fluid, which is confirmed also by other previously performed tests[5], the ageing of TPE was carried out only in contact with the base fluids. The results obtained with TPE (Figures 3 and 4) confirm the same trend observed for chloroprene rubber. The oils with a high solvating power (low aniline point) are too aggressive towards the elastomer and cause an excessive swelling. Again, the oils that perform best are the naphthenic oil S 150 and the paraffinic oil SN 700.

*Figure 3. Weight Change in TPE in Oil*

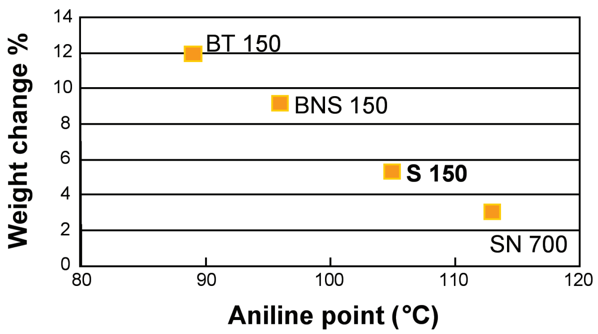
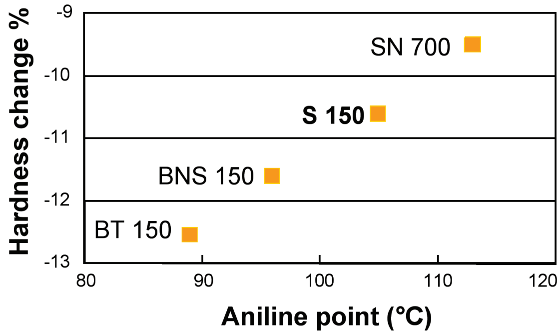



*Figure 4. Hardness Change in TPE in Oil*

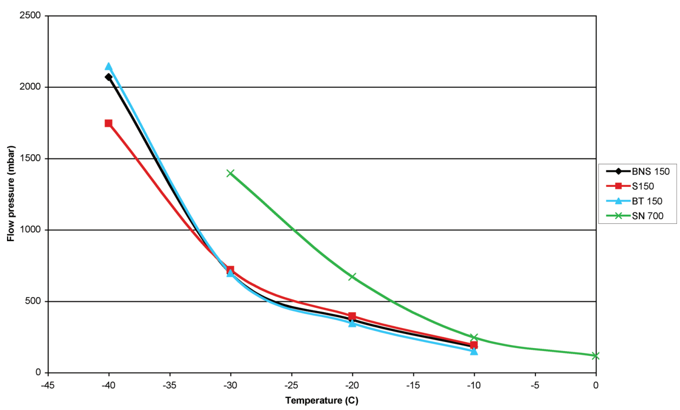



Thanks to its relatively high aniline point compared to standard naphthenic oils, the newly developed oil displays a better elastomer compatibility towards chloroprene and TPE compared to the other naphthenic oils tested, its compatibility being comparable with that of the paraffinic oil. But, as mentioned earlier, another parameter needs to be included in the picture and that is the low temperature behavior of the base fluids and of the greases produced thereof.

### Low Temperature Pumpability

As reported in Table 1, all the naphthenic base oils have a lower pour point than the paraffinic oil. This results in a superior pumpability at low temperature. In order to verify the influence of the oil on the behavior of the grease at low temperature, a flow pressure test was performed on the greases based on the naphthenic base oils S 150, BNS 150, BT 150 and on the paraffinic base oil SN 700. The results are illustrated in Figure 5.

*Figure 5. Flow Pressure for the Paraffinic and Naphthenic Greases at Low Temperatures*




As can be observed, at temperatures above 0°C there is no noticeable difference between the paraffinic- and the naphthenic-based greases, but already at -10°C the flow pressure for the paraffinic-based grease is about 30% higher than that of the naphthenic-based ones. This difference is increasing when the temperature decreases, and at -30°C the pressure needed for the paraffinic grease to flow is almost twice as high as that for the naphthenic greases. At -35°C some differences between the naphthenic greases start to show up and it is the grease based on the novel severely hydrotreated naphthenic oil S 150 that shows the best result. At -40°C there is a difference of 400 mbar between the grease based on the naphthenic base oil S 150 and that based on the naphthenic base oil BT 150.

The low temperature behavior of naphthenic- and paraffinic-based greases was investigated as well by rheological measurements. Parameters such as storage modulus, yield stress, rheology intersection stress, and critical stress were measured over a wide temperature range and confirmed the results obtained in the flow pressure test[6].

### Ageing of Base Oils

Last but not least, the stability of the oil is also of importance when formulating CVJ greases. 150 g of the naphthenic base oils S 150, SR 130, BNS 150, BT 150 and the paraffinic base oil SN 700 were placed in open beakers and heated for 6 hours at 150°C in a circulating air oven. The evaporation loss, and the changes in total acid number and color are reported in Figures 6-8. It can be observed that the newly developed naphthenic oil A is more stable and less volatile than standard naphthenic oils.

*Figure 6. Evaporation Loss*

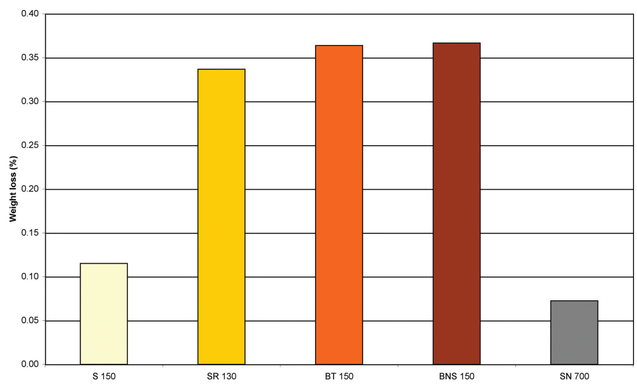



*Figure 7. Change in Total Acid Number*

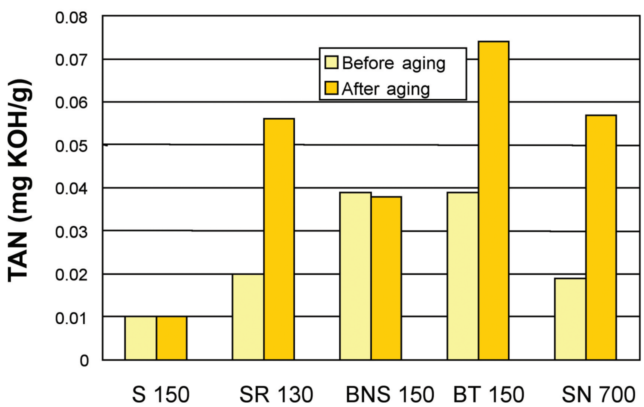
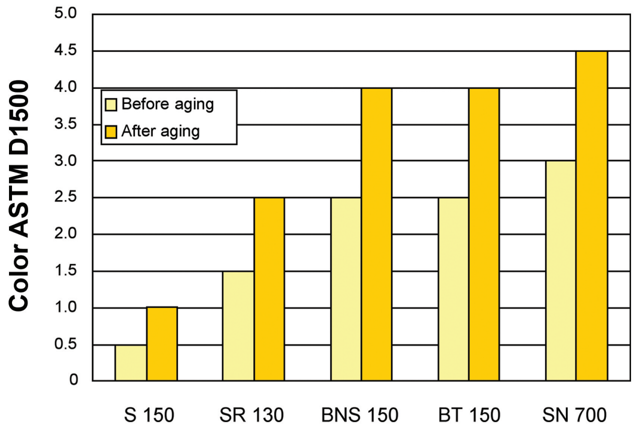



*Figure 8. Change in Color*




## Conclusions

A naphthenic oil (S 150) was developed for application in CVJ greases. The new oil combines the advantages of a severely hydrotreated oil, such as very good compatibility with chloroprene rubber and TPE and very good response to oxidation inhibitors, with the advantages of a typical naphthenic oil such as excellent low temperature properties. In this sense, the new naphthenic oil represents an upgrade from standard paraffinic oils as it provides comparable elastomer compatibility, but superior low temperature pumpability. Moreover, the newly developed oil shows a lower volatility and higher stability compared to standard naphthenic oils.

**Valentina Serra-Holm**
*Nynas Naphthenics*
*Nynashamn, Sweden*

**LINK**
**www.nynas.com**

***References***

1. *IP 346, the Institute of Petroleum, Methods IP 282-409, IP, London, 1995*
2. *European Union: Commission Directive 93/21/EEC of 27 April 1993 Adapting to Technical Progress for the 18th Time Council Directive 67/548/EEC on the Approximation of the Laws, Regulations and Administrative Provisions Relating to the Classification, Packaging and Labelling of Dangerous Substances. Official Journal of the European Communities No. L 110 04.05.1993 (1993).*
3. *CONCAWE: The Use of the Dimethyl Sulphoxide (DMSO) Extract by the IP 346 Method as an indicator of the Carcinogenicity of Lubricant Base Oils and Distillate Aromatic Extracts. Report No. 94/51. CONCAWE, Brussels (1994).*
4. *SS-ISO 37:1994, "Rubber, vulcanised or thermoplastic – Determination of tensile stress-strain properties".*
5. *Stang G. and Salomonsson L., Rubber interactions with grease and base oil, NLGI Spokesman, Vol. 69, N. 1, 2005, pp.20-34.*
6. *Salomonsson L., Stang G. and Zhmud B., Oil/Thickener Interactions and Rheology of Lubricating Greases, presented at the STLE's 61st Annual Meeting and Exhibition 7-11 May 2006, Calgary*