A naphthenic specialty oil as an alternative to brightstock in grease formulations

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Nynas AB
Sweden
Outline

- Introduction
  - Impact of base oil market on greases
  - Naphthenic oils properties

- Experimental work
  - Properties of the oils and greases
  - Results

- Summary and conclusions
Impact of base oil market on grease industry

2010
- Group III: 62430bpd; 6%
- Naphthenic: 84650bpd; 9%
- Group II: 234760bpd; 25%
- Group I: 574950bpd; 60%

2012
- Group III: 82160bpd; 8%
- Naphthenic: 88140bpd; 9%
- Group II: 276260bpd; 29%
- Group I: 522360bpd; 54%

2013
- Total BAO production up to more than 1M bpd
- API Group I has slipped under 50%

Deficit on high viscosity and high solvency products

* Source Lube’N’Greases
Properties of Naphthenic oils

- Higher solvency power than paraffinics (while having low aromatic content, low toxicity)
- Good emulsion stability
- Good low temperature properties
- Low viscosity index, compared to paraffinics
- Good heat transfer capacity, effective cooling effect
- Higher volatility than paraffinics
- Large viscosity range (3 – 4000cSt at 40°C)
Existing product, new application

- Nynas Nytex 4700
  - Residue oil blend from the vacuum distillation process
  - Used predominantly in tyre oils
  - Can be used in low speeds, high loads applications

<table>
<thead>
<tr>
<th>Tests (all ASTM)</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, 15°C kg/dm³</td>
<td>0.94</td>
</tr>
<tr>
<td>Viscosity, 40°C mm²/s</td>
<td>710</td>
</tr>
<tr>
<td>Viscosity, 100°C mm²/s</td>
<td>29</td>
</tr>
<tr>
<td>Flash Point, PM °C</td>
<td>220</td>
</tr>
<tr>
<td>Pour point °C</td>
<td>-15</td>
</tr>
<tr>
<td>Aniline Point °C</td>
<td>90</td>
</tr>
</tbody>
</table>

A Naphthenic speciality oil as an alternative to brightstock in grease formulations
According to the REACH legislation Nytex 4700 has the following listings:

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Residues (petroleum), vacuum</td>
<td>REACH #: 01-2119498291-32, EC: 265-057-8, CAS: 64741-56-6</td>
<td>30 - 60</td>
<td>Not classified.</td>
<td>Not classified.</td>
<td>-</td>
</tr>
</tbody>
</table>

Annex I Nota L applies to the base oil(s) in this product. Nota L - The classification as a carcinogen need not apply if it can be shown that the substance contains less than 3 % DMSO extract as measured by IP 346.

**Type**
- [1] Substance classified with a health or environmental hazard
- [2] Substance with a workplace exposure limit

Complies with polycyclic aromatic hydrocarbons (PAH) limits specified in EU directive 1907/2206/EC, Annex XVII, entry 50 (REACH)
## Experimental work: Characterisation of oils

<table>
<thead>
<tr>
<th>Test Method (ASTM)</th>
<th>BS200+SN500</th>
<th>Nytex 4700+SN500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity, 40°C, mm²/s</td>
<td>D 445 235 370 505</td>
<td>235 370 505</td>
</tr>
<tr>
<td>Viscosity, 100°C, mm²/s</td>
<td>D 445 17.9 24.6 30.4</td>
<td>16.2 20.8 24.8</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>D 2270 81 86 88</td>
<td>60 56 54</td>
</tr>
<tr>
<td>Flash Point, PM °C</td>
<td>D 93 229 239 247</td>
<td>223 223 223</td>
</tr>
<tr>
<td>Pour point °C</td>
<td>D 97 -12 -12 -12</td>
<td>-24 -24 -15</td>
</tr>
<tr>
<td>Aniline Point °C</td>
<td>D 611 105 110 110</td>
<td>94 93 92</td>
</tr>
<tr>
<td>Cu-Corrosion, rating</td>
<td>D 130 1a 1b 1b</td>
<td>1a 1a 1a</td>
</tr>
</tbody>
</table>
Grease Production : NLGI Grade 2

- Manufactured in an open kettle (pilot plant of 10kg capacity)
- Lithium hydroxide and 12-hydroxystereate thickener system
- Cooked to a maximum temperature of 205°C for 10 min
- The base oil mixture was used for cooking and cooling
- 54-57% of the total oil used in the cooking stage

**NB:** Base greases – do not contain any additives
Experimental work: Characterisation of greases

<table>
<thead>
<tr>
<th>Specifications</th>
<th>BS200 + SN500</th>
<th>Nytex 4700 + SN500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Base oil viscosity (mm²/s)</td>
<td>235</td>
<td>370</td>
</tr>
<tr>
<td>Penetration, 60 str (0.1mm)</td>
<td>276</td>
<td>268</td>
</tr>
<tr>
<td>Thickener content (%)</td>
<td>6.2</td>
<td>6.6</td>
</tr>
</tbody>
</table>

A Naphthenic speciality oil as an alternative to brightstock in grease formulations
Homogeneous soap structure

- Cryo-TEM tests on naphthenic and paraffinic lithium greases
- Soap fibers more uniform in shape and size in the naphthenic grease

Naphthenic-based

Paraffinic-based
Solvent power / Solubility

Solvent power = The ability to solvate other molecules
Solubility = The ability of being dissolved by other molecules

In the oil’s PDS the solvent power is found in:

- Measurements:
  - Aniline point
  - VGC

- Properties:
  - Aromatic content \( (C_A) \)
  - Naphthenic content \( (C_N) \)
  - Viscosity

- At equal viscosity naphthenic oils have higher solvent power than paraffinic oils
Lower thickener consumption

Higher solvency power contributes to a more dense and thicker fibrous structure

Lower thickener content is needed to reach the required consistency (NLGI grade)
**Results : Mechanical Stability**

<table>
<thead>
<tr>
<th>Specifications</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A’</th>
<th>B’</th>
<th>C’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration - 60str (0.1mm)</td>
<td>276</td>
<td>268</td>
<td>272</td>
<td>277</td>
<td>268</td>
<td>274</td>
</tr>
<tr>
<td>Penetration - 100,000 str (0.1mm)</td>
<td>296</td>
<td>291</td>
<td>294</td>
<td>275</td>
<td>278</td>
<td>277</td>
</tr>
<tr>
<td>Difference in penetration</td>
<td>20</td>
<td>23</td>
<td>22</td>
<td>-2</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

Greases produced from blends of Nytex 4700 show better mechanical stability despite lower thickener content.
Results: Load carrying capacity

- Four ball test analyses were carried out (ASTM D 2666)
- Test conditions
  - Load: 140kg
  - Running time: 60sec
  - Speed: 1440 rpm

<table>
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<th>B</th>
<th>C</th>
<th>A'</th>
<th>B'</th>
<th>C'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil viscosity (cSt)</td>
<td>235</td>
<td>370</td>
<td>505</td>
<td>235</td>
<td>370</td>
<td>505</td>
</tr>
<tr>
<td>Wear Scar (mm)</td>
<td>2.3</td>
<td>2.71</td>
<td>2.77</td>
<td>2.73</td>
<td>2.7</td>
<td>2.67</td>
</tr>
</tbody>
</table>

- Nytex 4700 based greases show equal load carrying capability despite lower thicker content and lower viscosity index
Results: Water resistance

- Water Wash Out (ASTM D41264)
  - 79°C/60min
- Water Spray Off (ASTM D4049)
  - 38°C/276kPa

Equal or better performance on the napthenic based grease

<table>
<thead>
<tr>
<th>Specifications</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A´</th>
<th>B´</th>
<th>C´</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Wash Out (wt%)</td>
<td>1,37</td>
<td>1,61</td>
<td>2,00</td>
<td>2,73</td>
<td>1,38</td>
<td>2,12</td>
</tr>
<tr>
<td>Water Spray Off (wt%)</td>
<td>55,6</td>
<td>53,8</td>
<td>31,2</td>
<td>43,8</td>
<td>N/A</td>
<td>18,8</td>
</tr>
</tbody>
</table>
Results: Oil separation and Dropping point

<table>
<thead>
<tr>
<th>Specifications</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A´</th>
<th>B´</th>
<th>C´</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil separation</td>
<td>8.7</td>
<td>6.2</td>
<td>6.05</td>
<td>8.93</td>
<td>6.45</td>
<td>5.67</td>
</tr>
<tr>
<td>Dropping point</td>
<td>208</td>
<td>206</td>
<td>208</td>
<td>202</td>
<td>203</td>
<td>199</td>
</tr>
</tbody>
</table>

Results: Copper Corrosion

- Temperature: 100°C
- Running time: 24hrs

<table>
<thead>
<tr>
<th>Specifications</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>A´</th>
<th>B´</th>
<th>C´</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Corrosion – DIN 51811</td>
<td>2c</td>
<td>1b</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
<td>1a</td>
</tr>
</tbody>
</table>
Results : Oxidation analyses

- ASTM D6186 : Oxidation Induction Time of Lubricating Oils by PDSC
- ASTM D5483 : Oxidation Induction Time of Lubricating Greases by PDSC
- ASTM E2009 : Oxidation Onset Temperature of Hydrocarbons by DSC

Method : Oxidation Onset Temperature (OOT)
- Sample weights different for oils and greases
- Pressure – 35bar
- Oxygen flow rate 50ml/min
- One heating segment : rate of 10K/min

<table>
<thead>
<tr>
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<th>B</th>
<th>C</th>
<th>A´</th>
<th>B´</th>
<th>C´</th>
</tr>
</thead>
<tbody>
<tr>
<td>OOT oil (°C)</td>
<td>254</td>
<td>251</td>
<td>247</td>
<td>227</td>
<td>213</td>
<td>215</td>
</tr>
<tr>
<td>OOT grease (°C)</td>
<td>206</td>
<td>209</td>
<td>214</td>
<td>244</td>
<td>247</td>
<td>246</td>
</tr>
</tbody>
</table>
Results: Oxidation analyses

A Naphthenic speciality oil as an alternative to brightstock in grease formulations
Superior low temperature properties

Low pour point of the oil and oil-thickener interactions

Superior pumpability and rheological properties of the grease at low temperature

Paraffinic oil

Naphthenic oil

-20°C
Rheological measurements: Elastic modulus vs Temperature

- Temperature sweep at constant sheer stress (30Pa)
- Oscillation of the sample
- Plate on plate geometry
- Temperature range: +50 to -30 °C
Summary

- Nytex 4700 as an alternative to brightsocks in grease formations offers
  - Lower thickener content (better yield)
  - Better mechanical stability despite less thickener
  - Equal load carrying capacity, resistance to copper corrosion
  - Equal oil separation and dropping point
  - Better low temperature properties
  - Equal water wash out and better water spray off

Response to anti-oxidants be investigated
A Naphthenic speciality oil as an alternative to brightstock in grease formulations
Conclusions

- In lubricating greases naphthenic oils are:
  - Best for grease cooking
    - Lower soap consumption
    - Better soap structure (good texture)
    - Good affinity to the thickener system
  - Good low temperature properties
  - Good mechanical stability

- Compared with greases based on brightstock base oils
A Naphthenic speciality oil as an alternative to brightstock in grease formulations
Brazil

Santos depot
Aratu depot

- HP 12
- HP 2
- HP 4
- HP 6
- Nytex 4700
- Nytro 11GBXUS
- NYTRO ORION II
- S100B
- SR 130
- T 22
- T 4
- T 9

Volume total ~12 000 MT
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