Alkyalted Naphthalenes for High Temperature Applications

71 | Synthetics and Hydraulics

Maureen E. Hunter, Ph.D.
Presentation Outline

• Alkylated Naphthalene Background
• Physical / Chemical Properties
• Lubricant Trends
• Performance data focusing on High Temperature Applications
• Summary
**Alkylated Naphthalenes**

- High Performance Group V Base Oils
- Co-Base Oil
  - with other synthetics or Group II and Group III oils
  - to enhance thermal and oxidative stability, varnish control and additive response
  - to extend the lifetime of high performance lubricants
Alkylated Naphthalene Structure

R1 to R8 are independently a linear or branched alkyl group or hydrogen.

The core naphthalene system consists of two fused six-membered rings with a electron rich conjugated π system.
Alkylated Naphthalene Synthesis

Physical properties depend on:

- **Number of carbons** in the alkyl group
  (Controlled by raw material selection)

- **Degree of branching** of the alkyl group
  (Controlled by raw material selection)

- **Number** of alkyl groups on the naphthalene ring
  (Controlled by chemical processing)
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Aniline Point

More Polar
-7 – 5°C
Monoesters
Diesters
Polyol Esters

40 – 55°C
MAN

85 – 105°C
PAN

Less Polar
115 – 135°C
PAO
Group II
Group III
Mineral Oils

Alkylated naphthalenes can aid in solubilizing additives in non-polar base stocks
## Alkylated Naphthalene Properties

<table>
<thead>
<tr>
<th></th>
<th>Viscosity @ 40°C ASTM D445</th>
<th>Viscosity @ 100°C ASTM D445</th>
<th>Viscosity Index Calculated</th>
<th>Aniline Point ASTM D611</th>
<th>Noack Volatility CEC L40 ASTM D6375</th>
<th>Pour Point ASTM D97</th>
<th>Flash Point ASTM D92</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-7</td>
<td>22 cSt</td>
<td>3.8 cSt</td>
<td>22</td>
<td>40°C</td>
<td>39 wt%</td>
<td>&lt;-48°C</td>
<td>206°C</td>
</tr>
<tr>
<td>AN-8</td>
<td>36 cSt</td>
<td>5.6 cSt</td>
<td>65</td>
<td>42°C</td>
<td>12 wt%</td>
<td>-33°C</td>
<td>236°C</td>
</tr>
<tr>
<td>AN-9</td>
<td>37 cSt</td>
<td>5.7 cSt</td>
<td>90</td>
<td>50°C</td>
<td>8 wt%</td>
<td>-36°C</td>
<td>240°C</td>
</tr>
<tr>
<td>AN-15</td>
<td>114 cSt</td>
<td>13.5 cSt</td>
<td>115</td>
<td>94°C</td>
<td>2.2 wt%</td>
<td>-39°C</td>
<td>260°C</td>
</tr>
<tr>
<td>AN-19</td>
<td>177 cSt</td>
<td>18.7 cSt</td>
<td>119</td>
<td>103°C</td>
<td>1.4 wt%</td>
<td>-26°C</td>
<td>285°C</td>
</tr>
<tr>
<td>AN-23</td>
<td>193 cSt</td>
<td>19.8 cSt</td>
<td>118</td>
<td>N/A</td>
<td>&lt;1.0 wt%</td>
<td>-21°C</td>
<td>310°C</td>
</tr>
</tbody>
</table>
General Performance Features of Alkylated Naphthalenes

• Thermo-oxidative stability
  – Excellent performance because of the electron-rich naphthalene ring

• System Cleanliness
  – Excellent Varnish Control

• Volatility
  – Low volatility as compared to other base stocks
General Performance Features of Alkylated Naphthalenes

• **Solvency**
  – An intermediate aniline point that has the right balance of polarity
  – Good additive response
  – No surface competition with the additives

• **Viscometrics and VI**
  – A variety of viscosities with low pour points and a good VI

• **Base Oil Modifying Properties**
  – Excellent compatibility with other base stocks to achieve balanced and enhanced performance

• **Hydrolytic stability**
  – No functional groups that can hydrolyze
General Performance Features of Alkylated Naphthalenes

• Good Lubricity / film thickness / reduced friction
• Good seal swelling properties
• Nuclear radiation resistance
• Good air release properties
• HX-1 Approvals – “Food Grade”
Main Application Areas

- Automotive and Stationary Engine Oils
- Automotive and Industrial Gear Oils
- High Temperature Chain Lubricants
- Paper Machine Oils
- Hydraulic Oils
- Circulating Oils/Turbine Oils/R&O Oils
- Screw Compressor Oils
- Heat Transfer Oils
- Windmill Oils and Greases
- Automotive and Industrial Greases
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General Lubricant Trends
Industrial, Auto Engine & Driveline, Greases

- Higher operating speeds & temperatures
- Longer life lubricants; extended drain intervals
- Reduced lubricant volumes
- Sealed-for-life systems

Lead to the requirements for:
- Improved thermo-oxidative stability
- Improved thermal stability
- Improved additive response
- Improved compatibility with seals & housings
Meeting the demanding trends in industrial lubricants, automotive engine oils, driveline fluids, and greases is the driver to the growth of optimized combinations of highly refined petroleum oils and synthetic base stocks:

- Group II hydrotreated mineral oils
- Group III severely hydrocracked oils
- Group IV polyalphaolefins (PAO)
- Esters
- Alkylated naphthalenes
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New Results for High Temperature Applications

- High Temperature Chain
- Plywood Manufacturing
- In-house Panel Coker
High Temperature Chain Lubricants
Alkylated naphthalenes extend fluid lifetime by:

- Reducing the volatility to retain the fluid longer
- Imparting thermal and thermo-oxidative stability to inhibit viscosity increase and varnish formation
# Chain Lubricant Market

## Application and Base Fluid By Temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Application</th>
<th>Suitable Base Fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;150°C</td>
<td>Transport, agriculture, and mining equipment</td>
<td>Mineral Oil, Vegetable Oil, Diester, PAO, PAG</td>
</tr>
<tr>
<td>150 – 220°C</td>
<td>Bakeries</td>
<td>Water Soluble PAG, PAO, Ester, Alkylated Naphthalene</td>
</tr>
<tr>
<td>180 – 250°C</td>
<td>Automobile &amp; beverage can painting</td>
<td>Trimellitate / Dimer Esters, PAO, Alkylated Naphthalenes</td>
</tr>
<tr>
<td>220 – 300°C</td>
<td>Plywood/textile/ceramic/plastic film manufacturing</td>
<td>Dimer / Polyol Esters, Alkylated Naphthalenes</td>
</tr>
<tr>
<td>&gt;600°C</td>
<td>Pottery/brick/cement kilns</td>
<td>PAGs as carrier for solid lubricants (e.g. graphite)</td>
</tr>
</tbody>
</table>

### Alkylated Naphthalenes for High Temperature Applications
Typical Chain Lubricant Formulation

- **Base fluid with:**
  - **0 – 20% Thickener / Tackifier / Adhesion Improver**
    - Polymerics: PIB, VI improvers
  - **1 – 5% Antioxidant(s)**
    - Combinations of aminics and phenolics
  - **0 – 5% Extreme Pressure / Antiwear**
    - Phosphates, amine phosphates, S/P type (triphenyl ZDP, thiophosphate)
  - **0 – 1% Corrosion Inhibitor**
    - Ferrous: organic acids, partial esters, amides, sulfonates
    - Copper: triazoles, thiazoles
  - **0 – 0.1% Defoamer**
    - Organics, silicones, modified siloxanes
Test Procedure

• Testing was conducted to determine if the addition of alkylated naphthalene to chain lubricant formulations would help with the high temperature performance.

• Test Method:
  – 3 g of test fluid are place in an aluminum pan
  – Sample is heated at 260°C for 8 hours
  – Report:
    • % Evaporation Loss
    • Condition of fluid
POE is an ISO VG 68 polyol ester recommended for high temperature chain lubricants (180–300°C).

AO Blend is a 50:50 mixture of alkylated diphenylamine with phenyl-alpha naphthylamine.

AN-19 has a viscosity of 177 cSt at 40°C.

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### Evaporation Loss Reduction to Retain Fluid

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>POE*</th>
<th>97% POE 3% AO Blend**</th>
<th>80% POE 20% AN-19***</th>
<th>77% POE 20% AN-19 3% AO Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Evaporation Loss 8 Hours @ 260°C</td>
<td>94%</td>
<td>94%</td>
<td>71%</td>
<td>68%</td>
</tr>
</tbody>
</table>

* POE is an ISO VG 68 polyol ester recommended for high temperature chain lubricants (180–300°C).

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*** AN-19 has a viscosity of 177 cSt at 40°C.
### Evaporation Loss Reduction to Retain Fluid

<table>
<thead>
<tr>
<th></th>
<th>POE</th>
<th>AN-19</th>
<th>80% POE 20% AN-19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation Loss</td>
<td>94%</td>
<td>43%</td>
<td>Theoretical: 84%</td>
</tr>
<tr>
<td>8 Hours @ 260°C</td>
<td></td>
<td></td>
<td>Observed: 71%</td>
</tr>
</tbody>
</table>
### Evaporation Loss Reduction to Retain Fluid

<table>
<thead>
<tr>
<th>Blend Number</th>
<th>88% POE* 12% PIB</th>
<th>85% POE 12% PIB 3% AO Blend</th>
<th>68% POE 12% PIB 20% AN-19</th>
<th>65% POE 12% PIB 20% AN-19 3% AO Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Hazy</td>
<td>95%</td>
<td>96%</td>
<td>69%</td>
<td>69%</td>
</tr>
</tbody>
</table>

*POE alone has an evaporation loss of 94%.

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**Alkylated Naphthalenes for High Temperature Applications**
Appearance of Blends

- Blends 5 and 6 containing PIB with no alkylated naphthalene are hazy.
- Blends 7 and 8 are the same formulations with 20% alkylated naphthalene. These blends show no haziness.
Samples Before Aging
Samples After Aging at 260°C for 8 Hours

- The lighter brown samples do not contain AN-19 and resulted in thin, hard varnish.
- The darker samples contain AN-19 and resulted in less evaporation leaving thicker/viscous but still liquid samples.
The viscosity of the samples that contain AN-19 increased after being heated, but the remaining samples were self-healing when scratched.
The samples that contain AN-19 flow after oxidation.
Varnished Blend Without Alkylated Naphthalene

- The samples without AN-19 created a hard varnish on the metal surface and were not self-healing when scratched.
**Extended Service Life of a AN Modified POE**

100% Polyol Ester ISO VG 68

- Solid Varnish
- No Extension
- Chain Seized

80% Polyol Ester ISO VG 68
20% AN-19

- Viscous Liquid
- Coated and baked for 8 hours @ 260°C
- Post-bake hanging performance
- Full Extension - 2 Seconds

*Alkylated Naphthalenes for High Temperature Applications*
High Temperature Chain Lubricants

• The addition of AN-19 resulted in:
  – less evaporation loss
  – sample clarity
  – superior varnish control

• The samples containing AN-19 remained liquid:
  – retaining lubrication
  – avoiding varnish flake off
Plywood Manufacturing
Conveyor Belt Oil for Plywood Manufacturing

Alkylated naphthalenes:

- When used for the first time in a press, dissolved the deposits on drive roller friction liners that had formed from an oil previously used.
Plywood Manufacturing – Hot Presses

240°C – 260°C

Alkylated Naphthalenes for High Temperature Applications
Cleaning of Equipment

High Temperature Belt Oil for Plywood Manufacturing

• Prior to using the oil containing the AN-19, pictures were taken of the friction liners showing heavy deposits from oxidation products of the previously used oil.

• After 6 months of using the oil containing the AN-19, it was observed that the oil was very dark and the friction liners were completely clean.

• When the darken oil containing the AN-19 that had dissolved the deposits was exchanged for fresh oil, the deposit formation and oil darkening did not reoccur.
Removal of Deposits

Friction liners before and after 6 months of AN-19 containing product use.
Plywood Manufacturing

Cleaning of equipment by AN-19

• reduced unwanted noise, vibration and wear of the equipment

• greatly reduced maintenance cost
In-House Panel Coker Test

To determine tendencies of oils to form coke in a moving system when in contact with a hot metal surface.
**In-house Panel Coker**

- **Oil Reservoir**
- **Oven (80°C)**
- **Drip Tube**
- **Panel**
- **Aluminum Block (>200°C)**
- **Oil Droplets (7mL/Hr)**
Panel Coker Setup
17 Hour Run Time

Oil Reservoir
120 mL/Panel

Oven (80°C)

Drip Tube

Oil Droplets
(7 mL/Hr)

Panel

Temperature Controlled
Aluminum Block
w/ Adjustable Incline

Alkylated Naphthalenes for High Temperature Applications
King Panel Coker Test

Coking pattern depends on:
• Oil flow pattern down the panel
• Temperature of the panel
• Thermal stability of the oil

Oil Flow pattern depends on:
• Dimensions of the panel
• Panel surface finish
• Pitch of the panel
• Viscosity of the oil
King Panel Coker Test

If:
• all reasonable parameters are controlled
• the flow pattern of oil is understood

Then:
• the thermal stabilities of oils can be compared by qualitatively evaluating their coking patterns at various temperatures
King Panel Coker Test

After 2 drops of PAO 8 cSt at 230°C
Flow Pattern and Coke Pattern

Panel A
At surface temps below the *Coking Temperature*, the oil flows over the bottom edge and off of the panel.

Panel B
At surface temps at or above the *Coking Temperature*, the oil cokes before reaching the bottom edge of the panel.

An oil’s *Coking Temperature* is the lowest panel temperature at which a closed coke pattern is observed.
Coking Patterns at 220°C

Open Coke Pattern
100% PAO 8

Open Coke Pattern
80% PAO 8
20% AN-19
Coking Patterns at Different Temperatures

220°C
Open Coke Pattern

240°C
Open Coke Pattern
80% PAO 8 / 20% AN-19

250°C
Closed Coke Pattern

Alkylated Naphthalenes for High Temperature Applications
Coking Patterns at Different Temperatures

220°C

Open Coke Pattern

220°C

Open Coke Pattern

230°C

Closed Coke Pattern

100% ISO VG 46 Group III

Good Repeatability

Alkylated Naphthalenes for High Temperature Applications
Coking Patterns at 230°C

Closed Coke Pattern
100% ISO VG 46
Group III

Closed Coke Pattern
90% Group III
10% AN-19

Open Coke Pattern
80% Group III
20% AN-019
Coking Patterns at Different Temperatures

230°C
Open Coke Pattern
80% ISO VG 46 Group III / 20% AN-19

240°C
Open Coke Pattern

250°C
Closed Coke Pattern

In-house Panel Coker – Current Results

• For PAO 8:
  – The Coking Temperature was 230°C.
  – 20% AN-19 addition increased the Coking Temperature to 250°C.

• For ISO VG 46 Group III:
  – The Coking Temperature was 230°C.
  – 20% AN-19 addition increased the Coking Temperature to 250°C.
In-house Panel Coker – Future Testing

• Collect the fluid flowing off the panel and conduct analytical and performance testing.

• Evaluate the ability of alkylated naphthalene to dissolve deposits formed by other oils.

• Evaluate the coking patterns and temperatures of fully formulated high temperature fluids with and without alkylated naphthalene.
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Summary

Why Use Alkylated Naphthalenes

• Diverse viscosity range for flexibility in designing lubricants for a variety of applications
• Excellent thermal & thermo-oxidative stability
• Excellent varnish control
• Low volatility with higher viscosity
• Superior solubility characteristics than Group II, Group III, and Group IV (PAO)
Summary

Why Use Alkylated Naphthalenes

• Inherent hydrolytic stability
• Excellent additive response
• Good low pour point
• Good film thickness and film strength
• Good seal swelling
Acknowledgements – Lab Work

• Amanda Harris
• Dylan Robbins
King Industries Offers

- Alkylated Naphthalene Blends/Packages
- Friction Modifiers
- Antiwear
- Antioxidant
- Extreme Pressure
- Corrosion Inhibitors
- Rust Inhibitors
- Rust Preventive
- Technical Product Support