

Alkylated Naphthalenes for High Temperature Applications

71 | Synthetics and Hydraulics

Maureen E. Hunter, Ph.D.



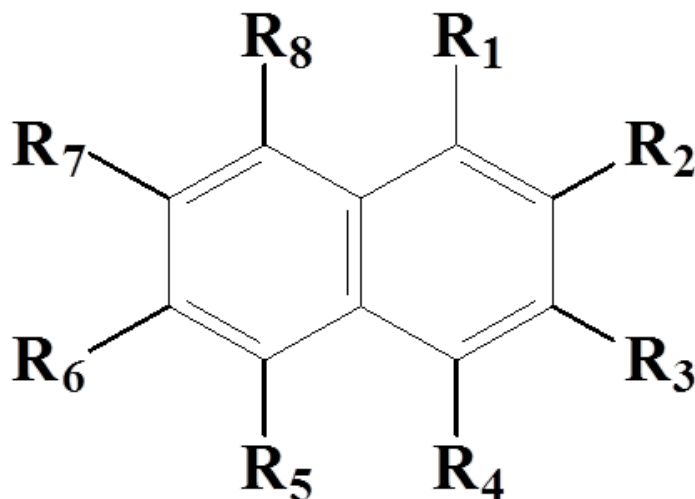
Presentation Outline

- **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

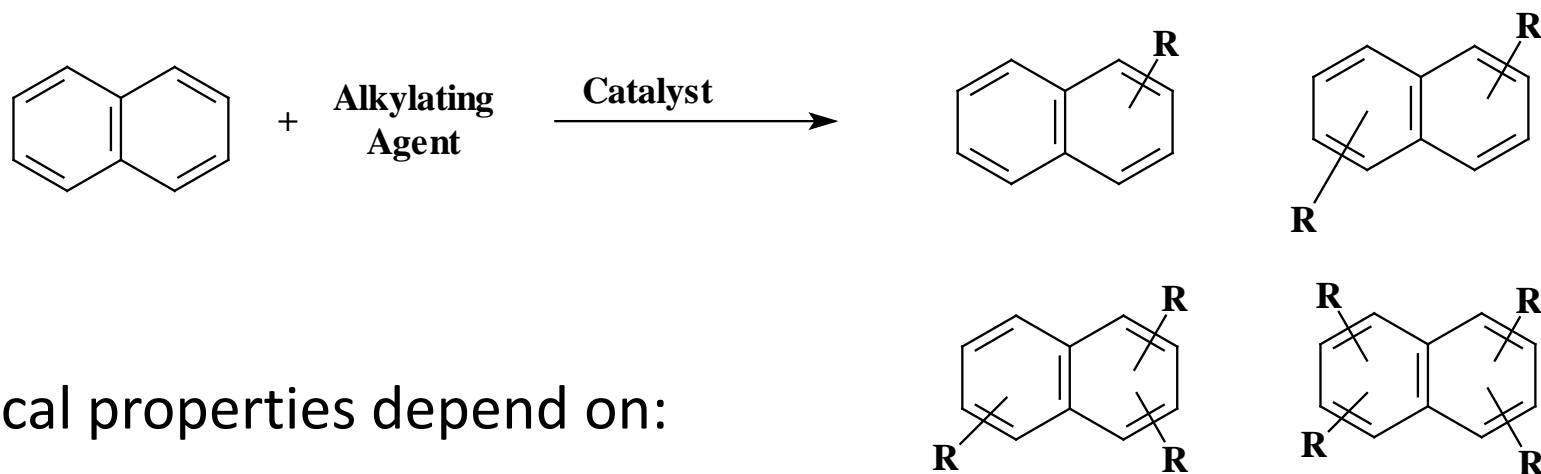
Alkylated Naphthalene Structure



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)

Presentation Outline

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

Aniline Point

More Polar

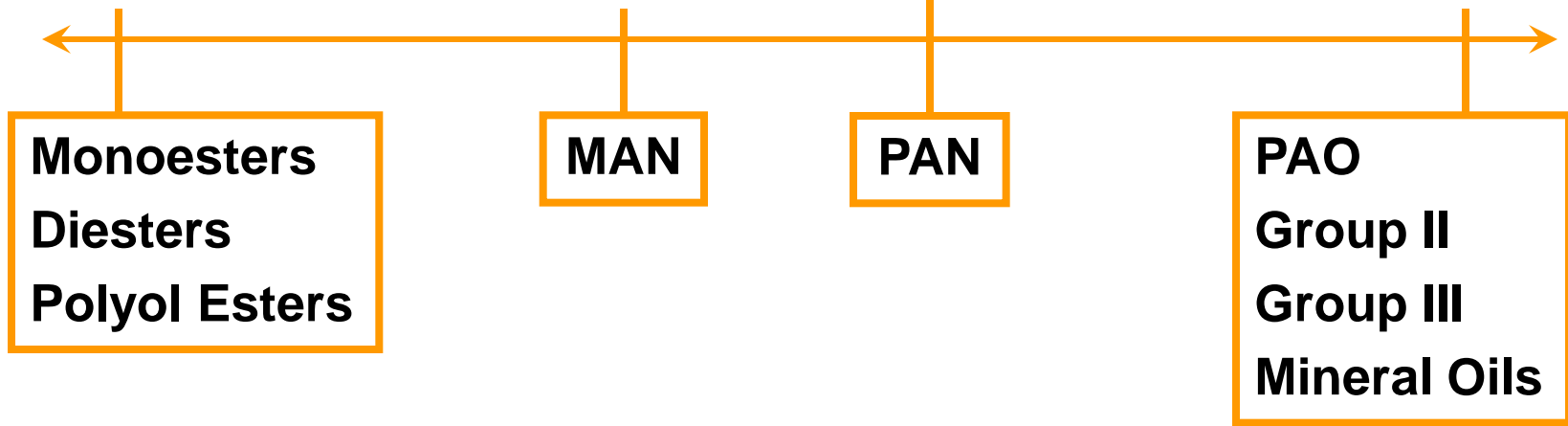
Less Polar

-7 – 5°C

40 – 55°C

85 – 105°C

115 – 135°C



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

Alkylated Naphthalene Properties

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

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

Presentation Outline

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

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

Fluids Evolve to Meet These Trends

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

Presentation Outline

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

New Results for High Temperature Applications

- High Temperature Chain
- Plywood Manufacturing
- In-house Panel Coker

High Temperature Chain Lubricants

Alkylated Naphthalenes for High Temperature Applications

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

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

Typical Chain Lubricant Formulation

- Base fluid with:
 - 0 – 20% Thickener / Tackifier / Adhesion Improver
 - Polymeric: 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

Evaporation Loss Reduction to Retain Fluid

	POE*	97% POE 3% AO Blend**	80% POE 20% AN-19***	77% POE 20% AN-19 3% AO Blend
Blend Number	1	2	3	4
Evaporation Loss 8 Hours @ 260°C	94%	94%	71%	68%

* 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.

Evaporation Loss Reduction to Retain Fluid

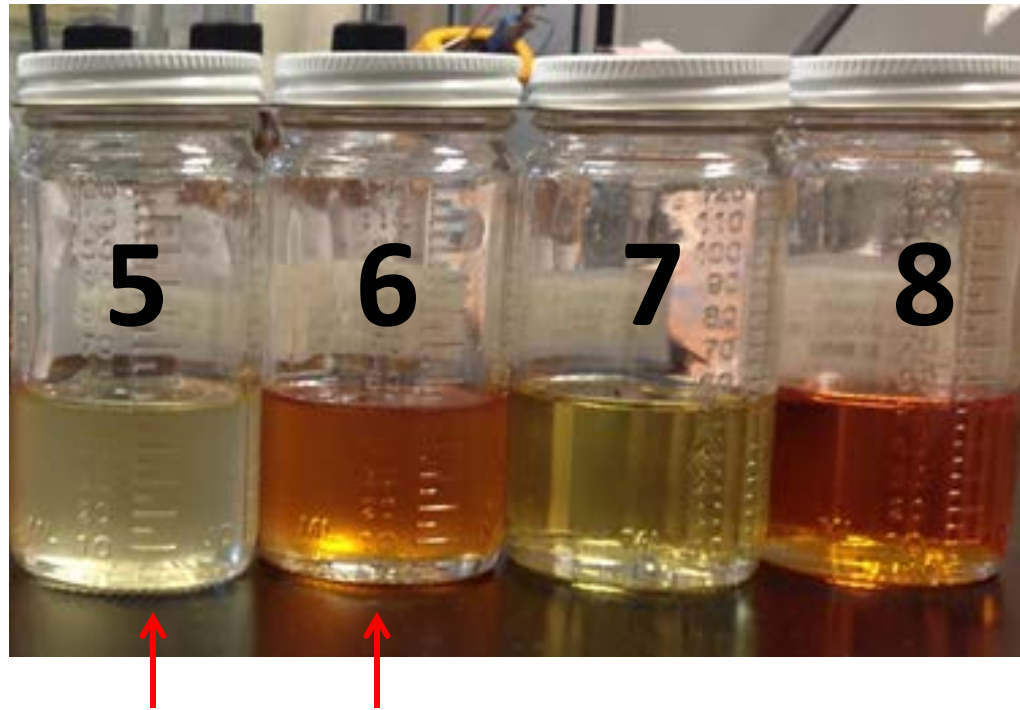
	POE	AN-19	80% POE 20% AN-19
Evaporation Loss 8 Hours @ 260°C	94%	43%	Theoretical: 84% Observed: 71%

Evaporation Loss Reduction to Retain Fluid

	88% POE* 12% PIB	85% POE 12% PIB 3% AO Blend	68% POE 12% PIB 20% AN-19	65% POE 12% PIB 20% AN-19 3% AO Blend
Blend Number	5 Hazy	6 Hazy	7 Clear	8 Clear
Evaporation Loss 8 Hours @ 260°C	95%	96%	69%	69%

*POE alone has an evaporation loss of 94%.

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.

Alkylated Naphthalene Blends After Aging



- The viscosity of the samples that contain AN-19 increased after being heated, but the remaining samples were self-healing when scratched.

Alkylated Naphthalene Blends After Aging



- The samples that contain AN-19 flow after oxidation.

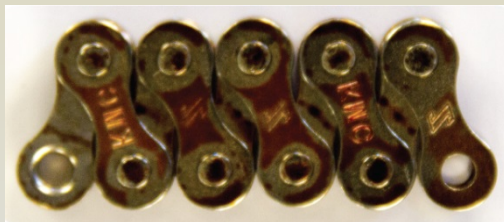
Varnished Blend Without Alkylated Naphthalene



- 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



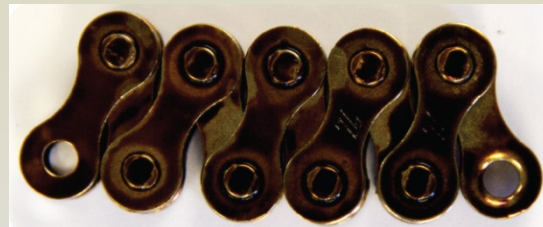
No Extension
Chain Seized

Coated and
baked for
8 hours
@ 260°C

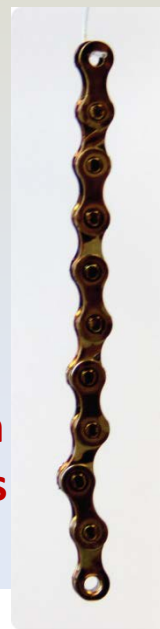


Post-bake
hanging
performance

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



Viscous Liquid



Full Extension
- 2 Seconds

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

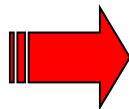
Cleaning of Equipment

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 darkened 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

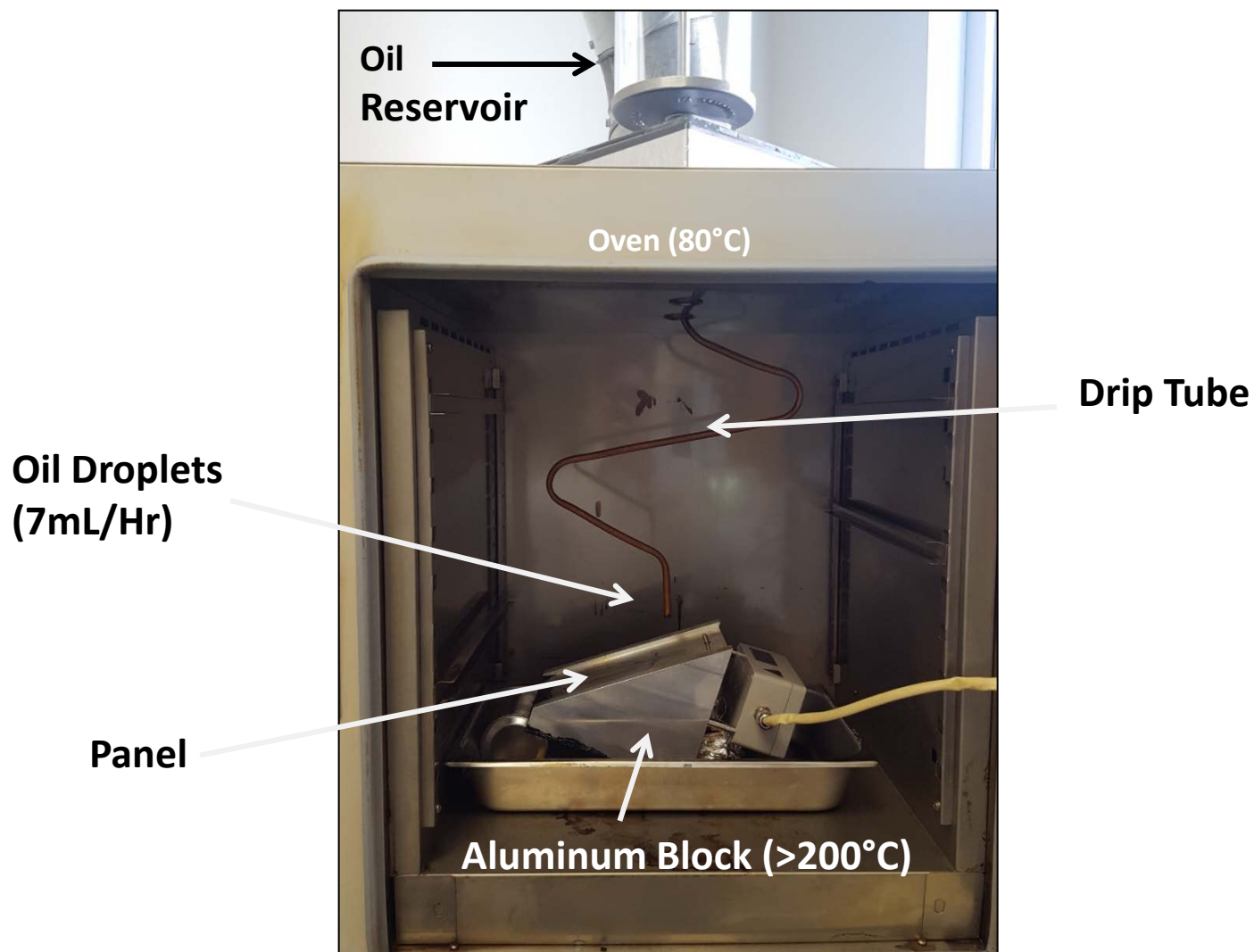
Cleaning of equipment by AN-19

- reduced unwanted noise, vibration and wear of the equipment
- greatly reduced maintenance cost

In-House Panel Coker Test

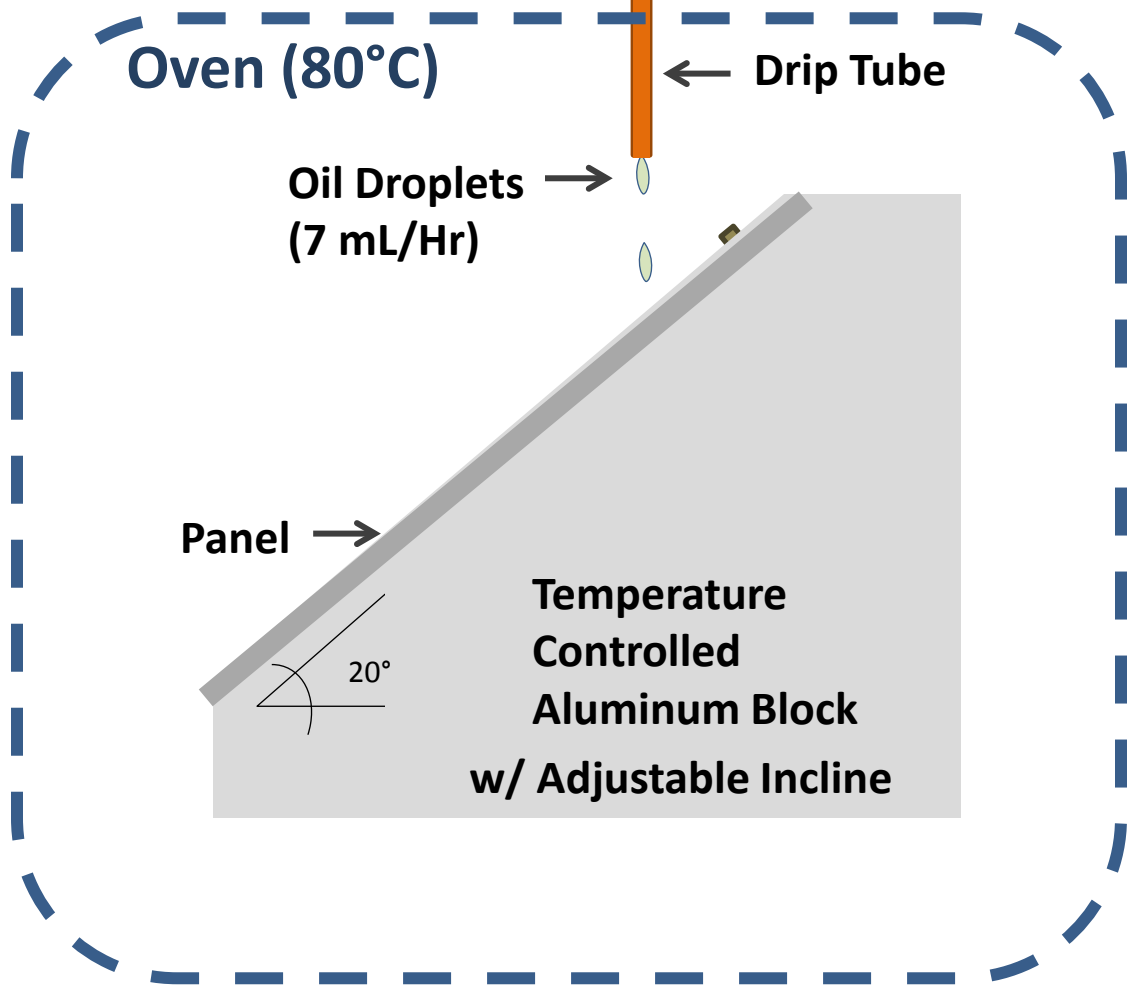
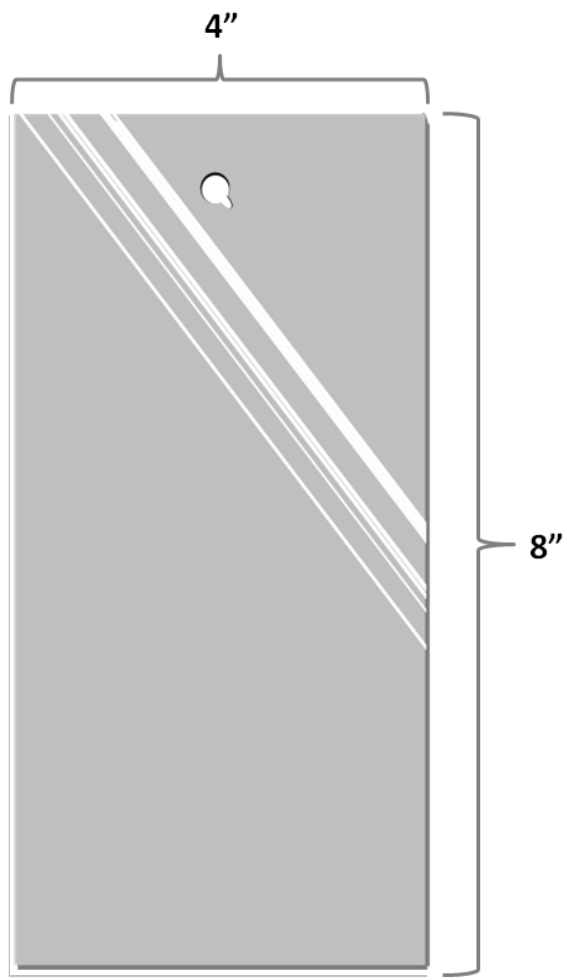
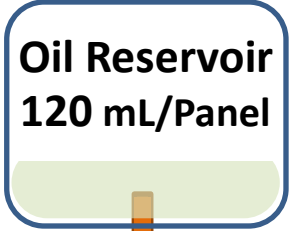
To determine tendencies of oils to form coke in a moving system when in contact with a hot metal surface.

In-house Panel Coker



Panel Coker Setup

17 Hour Run Time



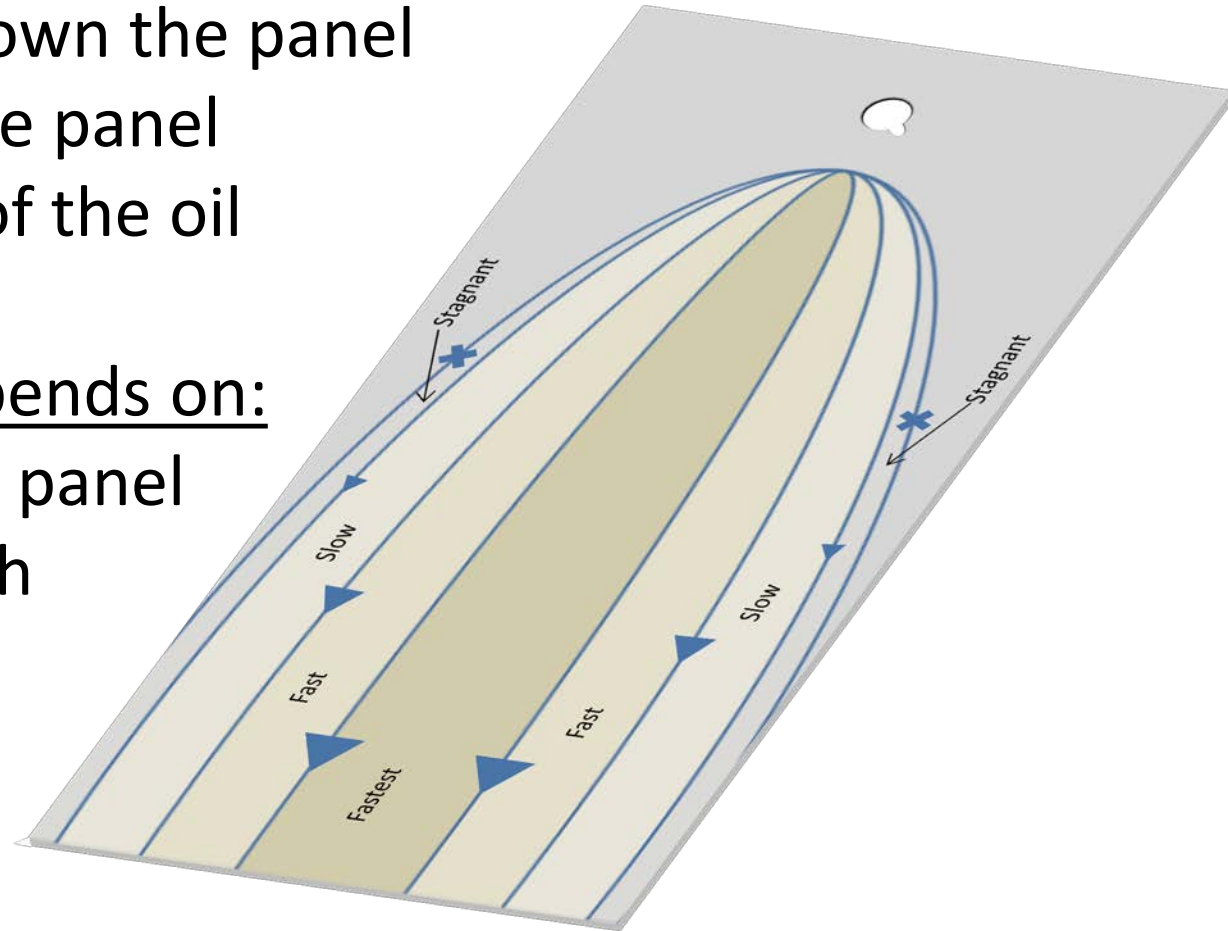
King Panel Coker Test

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.

Panel A



Open Coke Pattern
Passed at 220°C

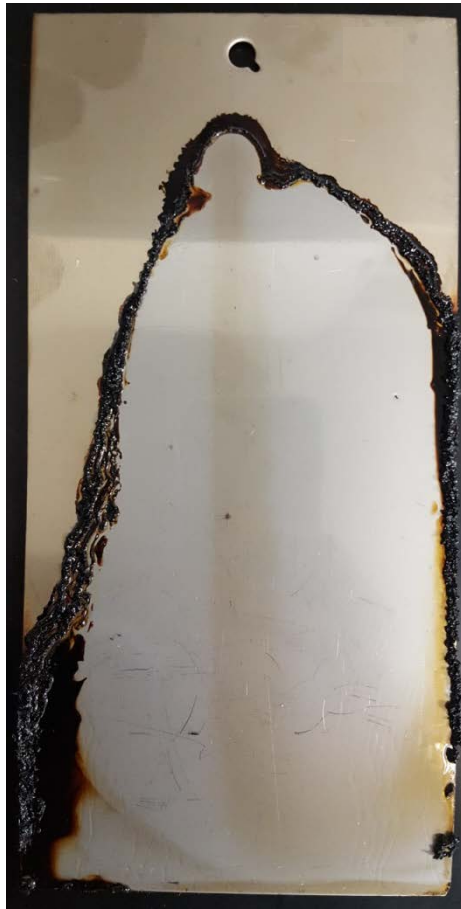
Panel B



Closed Coke Pattern
Failed at 230°C

100% PAO 8

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



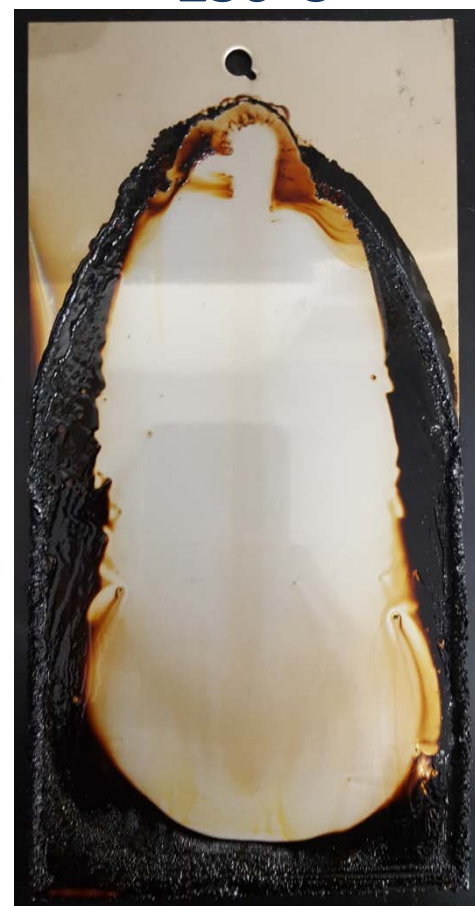
Open Coke Pattern

240°C



Open Coke Pattern

250°C



Closed Coke Pattern

80% PAO 8 / 20% AN-19

Coking Patterns at Different Temperatures

220°C



Open Coke Pattern

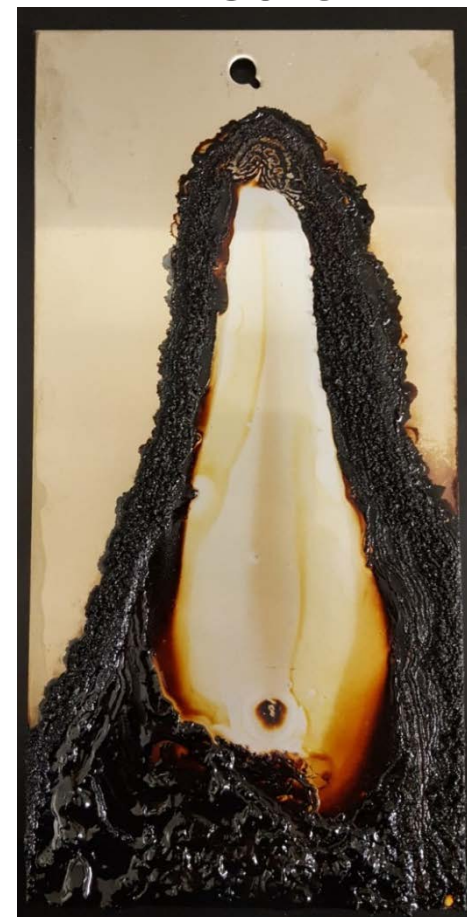
Good
Repeatability

220°C



Open Coke Pattern

230°C



Closed Coke Pattern

100% ISO VG 46 Group III

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

240°C



Open Coke Pattern

250°C



Closed Coke Pattern

80% ISO VG 46 Group III / 20% AN-19

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.

Presentation Outline

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

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

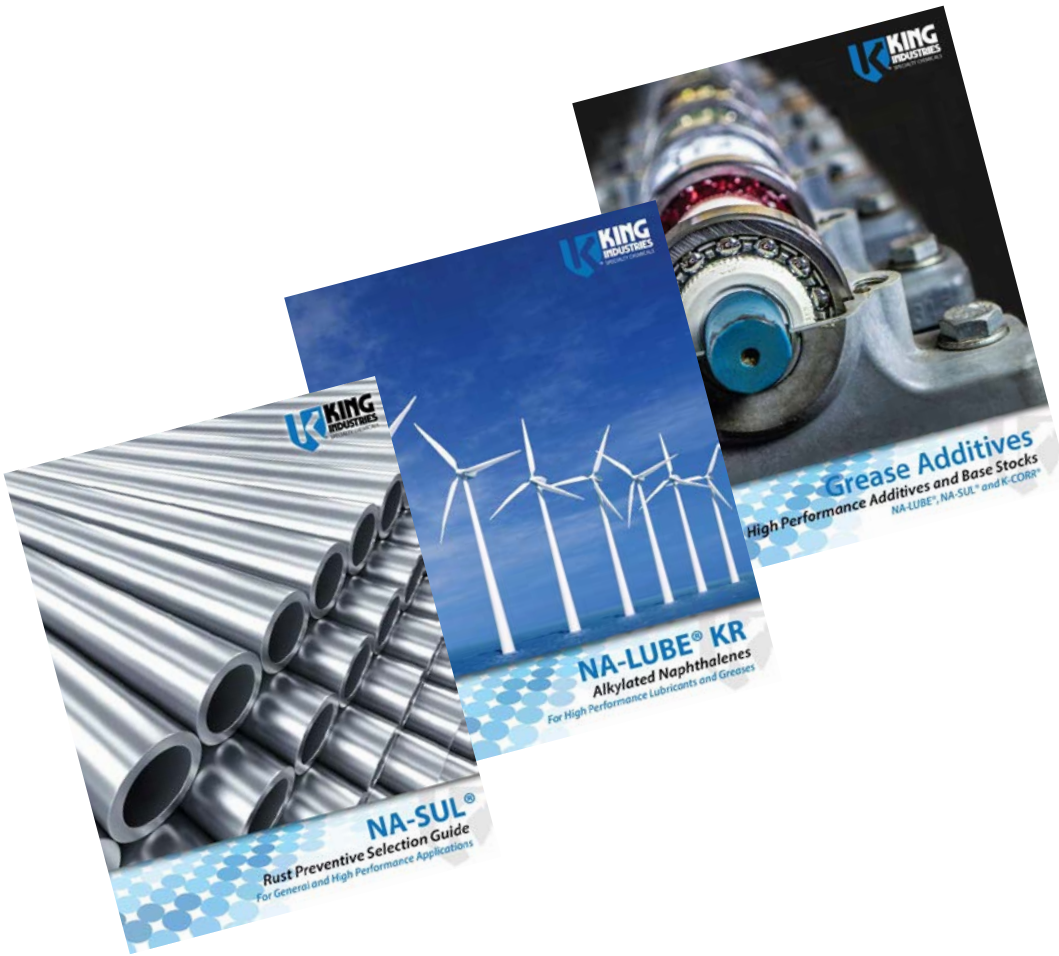
Why Use Alkylated Naphthalenes

- 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