High Temperature Performance with Alkylated Naphthalene

The 2nd Asian Industrial Lubricants Conference
Singapore
November 12 – 13, 2019

KING INDUSTRIES
SPECIALTY CHEMICALS

environ

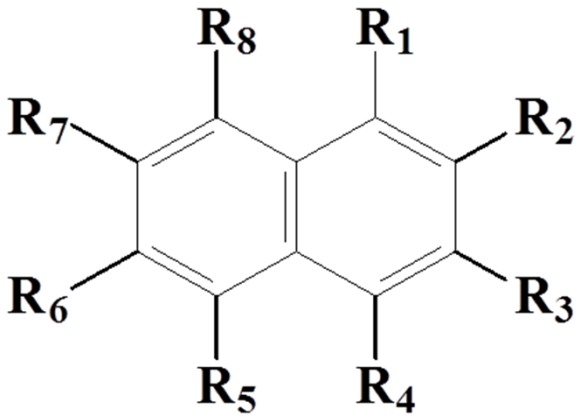
Presentation Outline

- Alkylated Naphthalene Background
- Physical/Chemical Properties
- Performance Evaluations
- 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

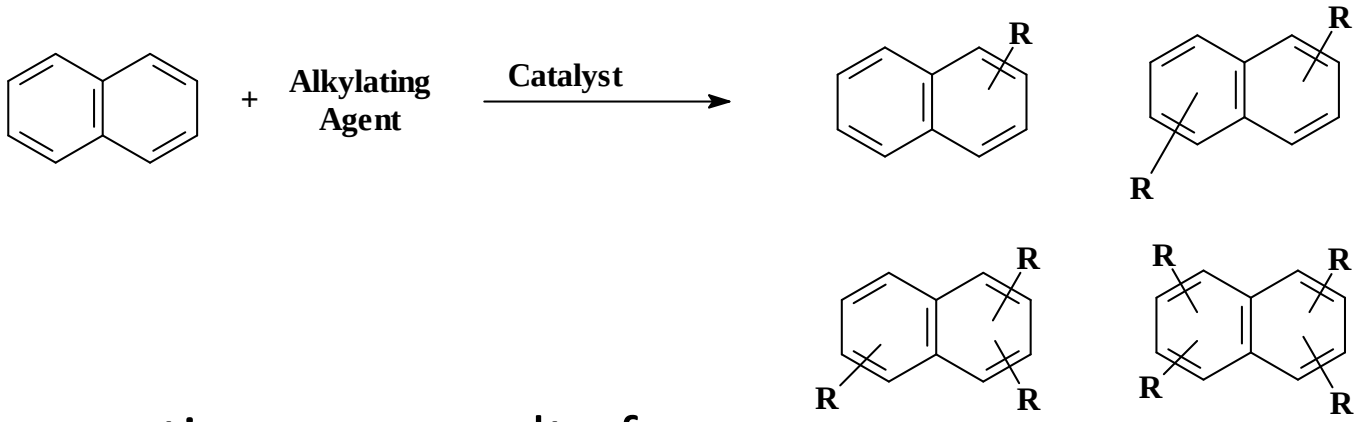
Alkylated Naphthalene Structure



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 an electron rich conjugated π system.

Alkylated Naphthalene Synthesis

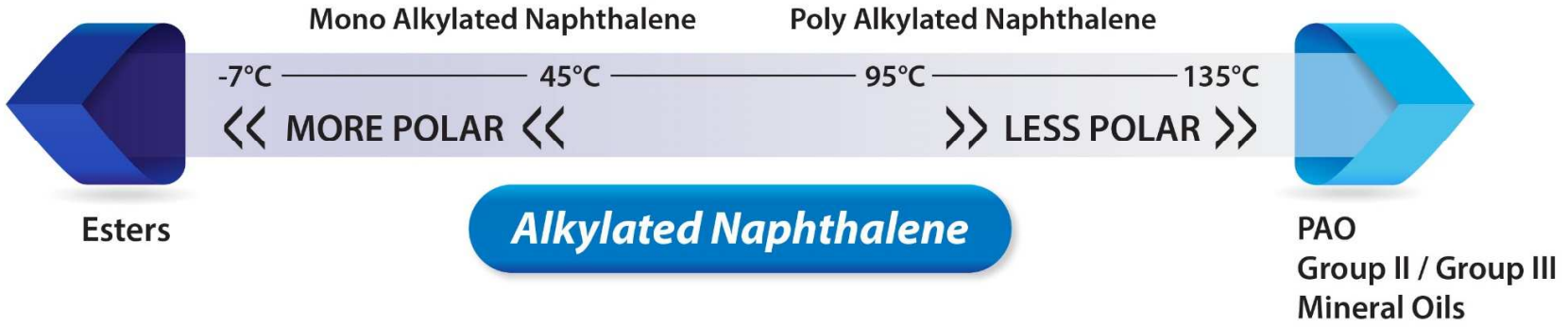


- Physical properties are a result of:
  - Number of carbons in the alkyl group (controlled by raw material selection)
  - Degree of branching of alkyl groups (controlled by raw material selection)
  - Number of alkyl groups on naphthalene ring (controlled by chemical processing)

Presentation Outline

- Alkylated Naphthalene Background
- Physical/Chemical Properties
- Performance Evaluations
- Summary

Aniline Point



- Alkylated naphthalenes can aid in solubilizing additives in non-polar base stocks
- Varying balances of Mono Alkylates and Poly Alkylates impart a variety of properties including, but not limited to:
  - Aniline point
  - Viscosity Properties
  - Volatility
  - Flash Point

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	90	42°C	12 wt%	-33°C	236°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

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
- Viscometrics and VI
  - A variety of viscosities with low pour points and good VI

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
- Base oil modifying properties
  - Excellent compatibility with other base stocks to achieve balanced and enhanced performance
- Hydrolytic stability
  - No functional groups that can hydrolyze

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 Applications

- 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
- Performance Evaluations
- Summary

Performance Evaluations

- Thermo-oxidative stability
  - Panel Coker
  - Rotating Pressure Vessel Oxidation Test (RPVOT)
  - Pressure Differential Scanning Calorimetry (PDSC)
- Hydrolytic Stability
  - Beverage Bottle Test
- Volatility
  - Thin Film

Performance Evaluations

- Friction
  - FZG
- Seal Swell
  - Volume Change
- High Temperature Chain
  - Evaporation
  - Varnish Control
- Plywood Manufacturing
  - Varnish Control

Performance Evaluations

- Grease
  - Lithium 12-Hydroxystearate
  - Lithium Complex
  - Polyurea
  - Aluminum Complex

Thermo-oxidative Stability

Panel Coker (FTM 791-3462)

	100% PAO (ISO VG 220)	**10% AN-8** 90% PAO	**10% AN-15** 90% PAO	**10% AN-19** 90% PAO
Coking Value (mg)	9.0	1.0	3.0	2.0

Temperature Conditions: Test Panel: 200°C; Oil Sample: 140°C

Grp III (ISO VG 46) vs. Grp III Modified with AN

Tests	0.7% R&O Package 99.3% Group III	0.7% R&O Package **15.0% AN-8** 84.3% Group III
RPVOT ASTM D2272 Lifetime, minutes	1339	1926
CM Thermal Stability ASTM D2070 Condition of Steel Rod: Color Condition of Copper Rod: Color Total Sludge (mg/100 ml)	 2 5 10.75	 2 5 5.30

Grp III vs. Grp III Mod with Ester and AN

Tests	0.6% Add Pack*	0.6% Add Pack	0.6% Add Pack	0.6% Add Pack	0.6% Add Pack
	100% Group III*	78% Group III 22% Ester***	78% Group III 11% Ester **11% AN-8**	78% Group III **22% AN-8**	**100% AN-8**
RPVOT ASTM D2272 Lifetime, minutes	1194	1023	1179	1288	1689

*Ashless package based on nitrogen-phosphorus-sulfur

**Group III ISO VG 46

***Saturated Polyol Ester

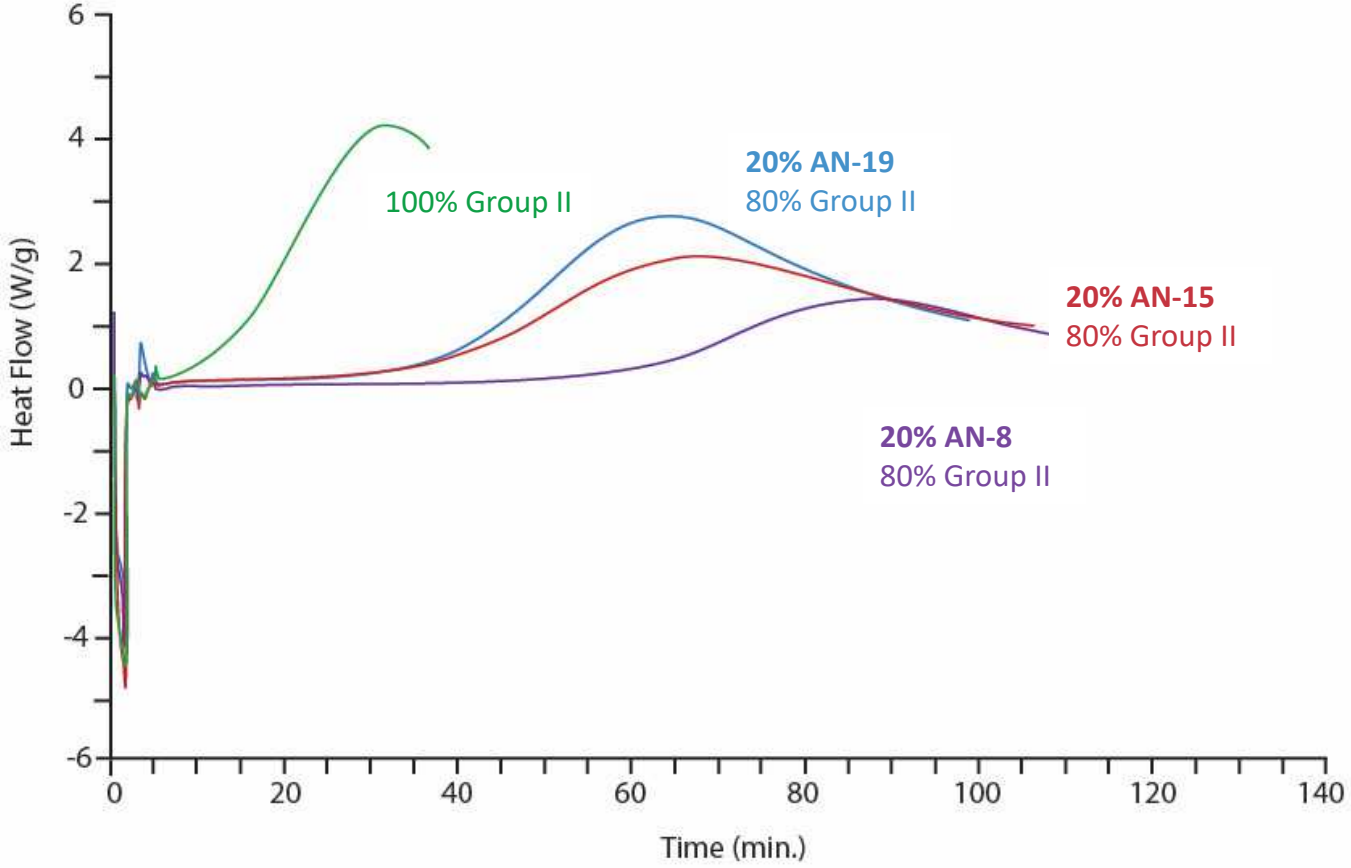
Alkylated Naphthalene Synergy with ADPA AO

HX-1 Base Oils	PAO 10	White Oil	PAG	**AN-19 Food Grade**	Ester
RPVOT, ASTM D2272 Lifetime (Minutes)					
Control (no AO)	55	31	15	76	115
+0.2% ADPA*	268	141	40	**905**	470

* Alkylated diphenylamine

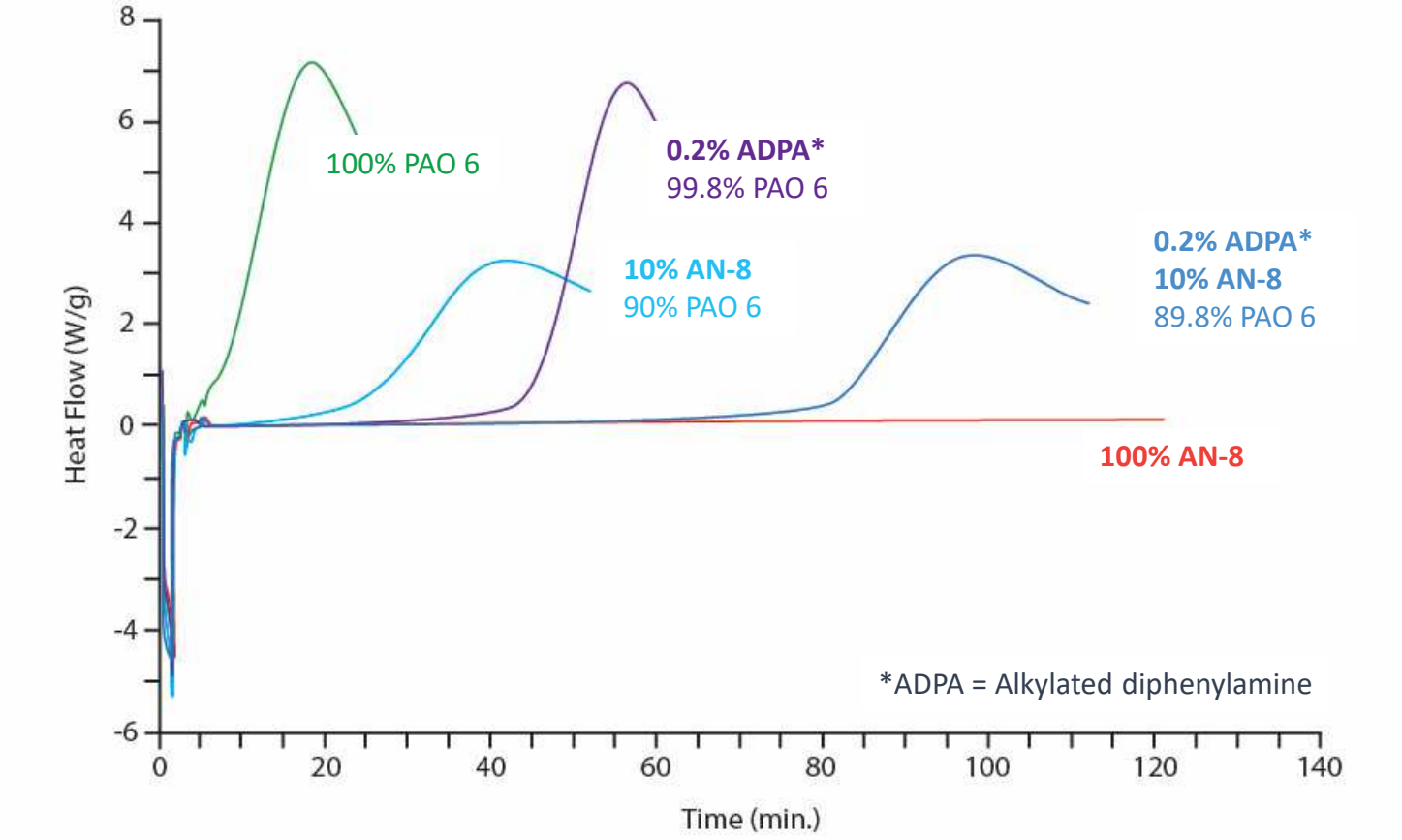
PDSC Performance of AN Modified Group II

PDSC (ASTM D6186) 160°C, 500 psi oxygen



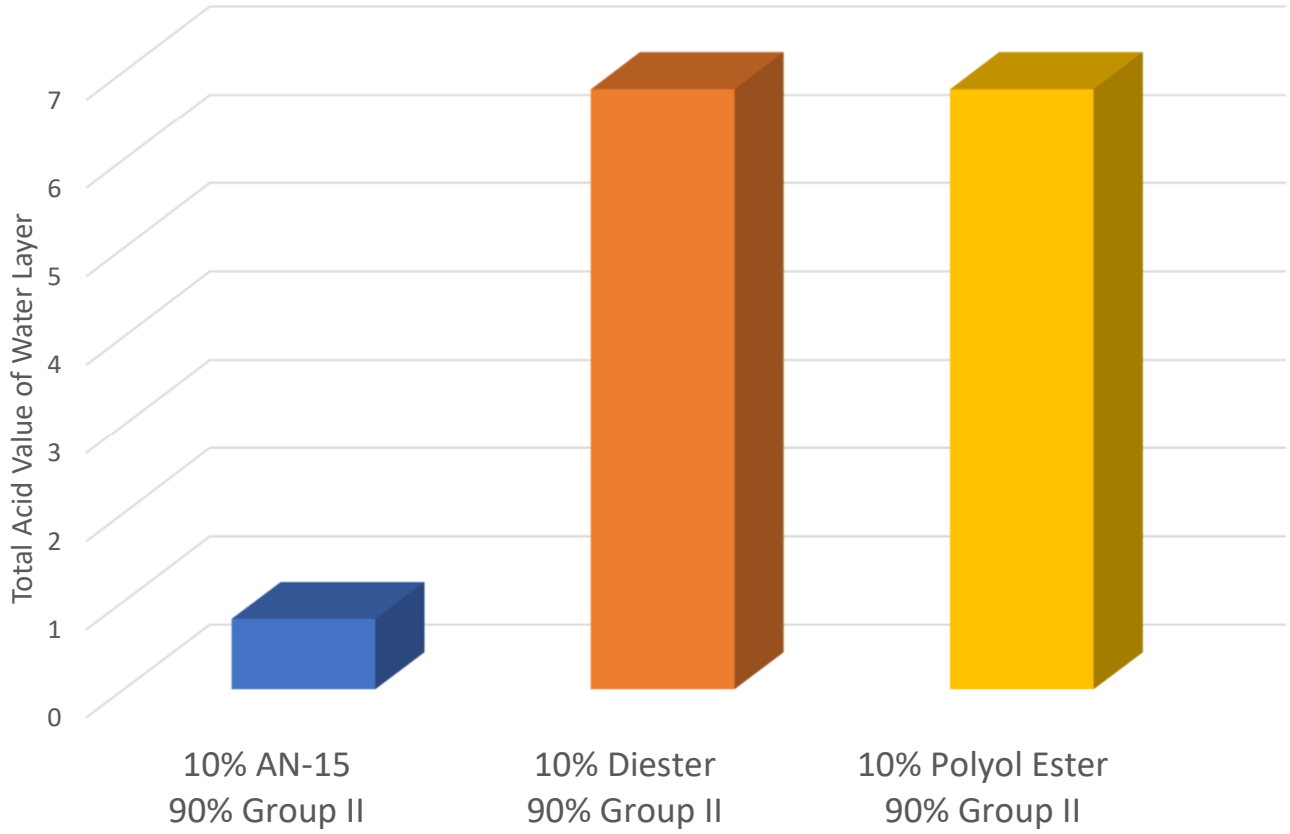
PDSC Performance of AN Modified PAO

PDSC (ASTM D6186) 170°C, 500 psi oxygen



Hydrolytic Stability

Hydrolytic Stability (ASTM D2619)



Group II Base Oil (ISO VG 46) modified by adding 10% of different Group V Base Stocks

Volatility

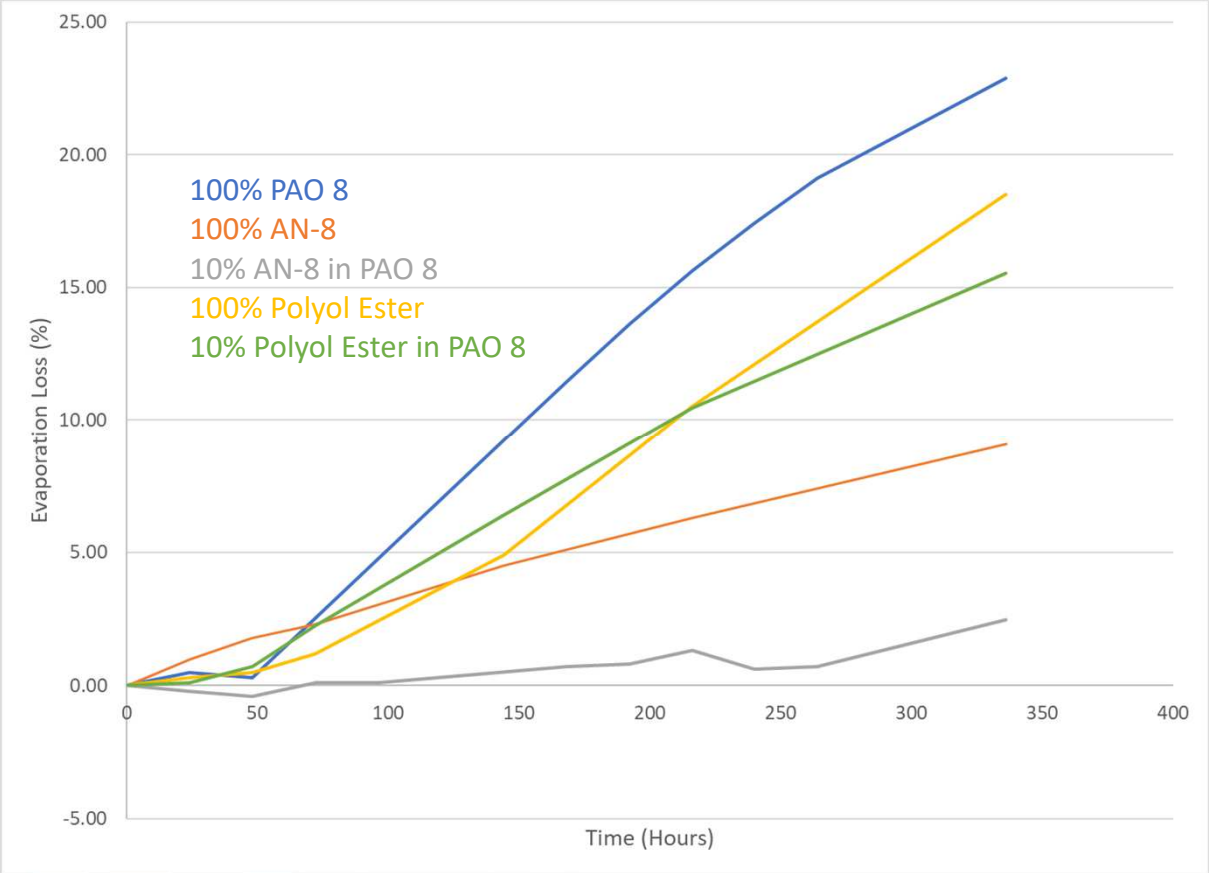
Thin Film Volatility

2 grams in aluminum pan for 24 hours

	Weight Loss, %		
	200°C	225°C	250°C
AN-19	8.5	19.7	41.6
PAO 40 cSt	17.9	29.8	45.4
20% AN-19 80% PAO 40 cSt	9.4	20.2	39.6
20% Ester 80% PAO 40 cSt	28.5	43.1	56.7

Volatility Results

10 grams in aluminum pan for 2 weeks at 120°C

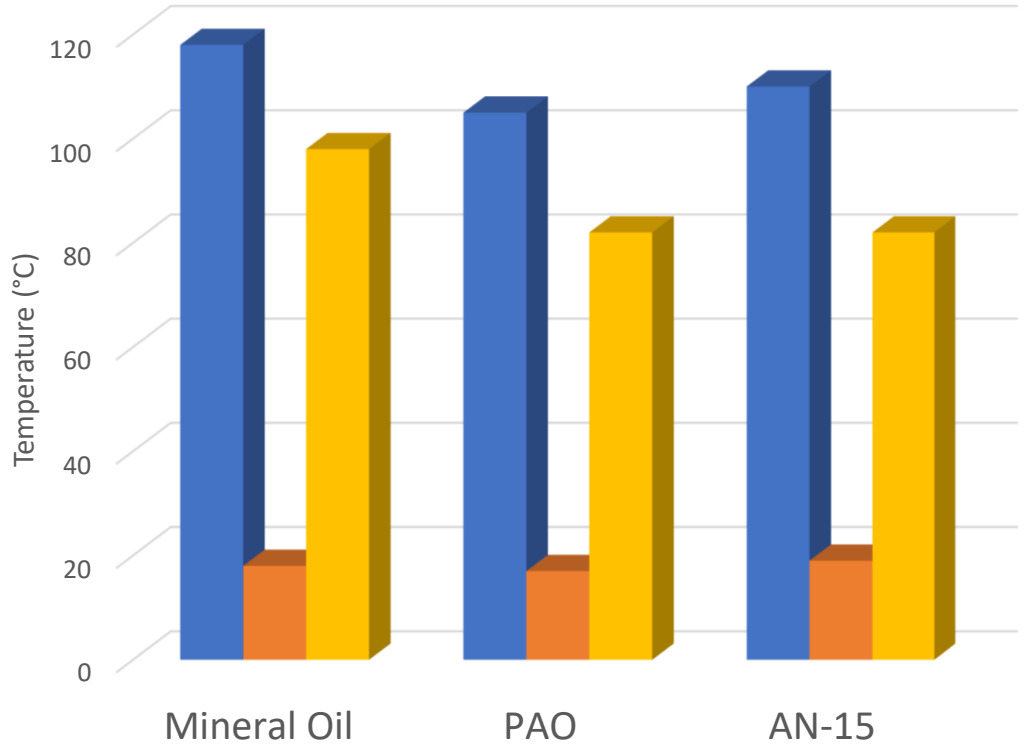


	Weight Loss, % (2 weeks)
100% PAO 8	22.89
100% AN-8	9.08
10% AN-8 90% PAO 8	2.46
100% Polyol Ester	18.52
10% Polyol Ester 90% PAO 8	15.53

Friction Testing

FZG (ASTM D5182 Modified), Temp/Friction Study

Test Oils with 0.3% Antiwear Additive



Load Stage 1-6 are run in accordance to ASTM D5182. Load Stage 7 is applied for an 8-hour duration.

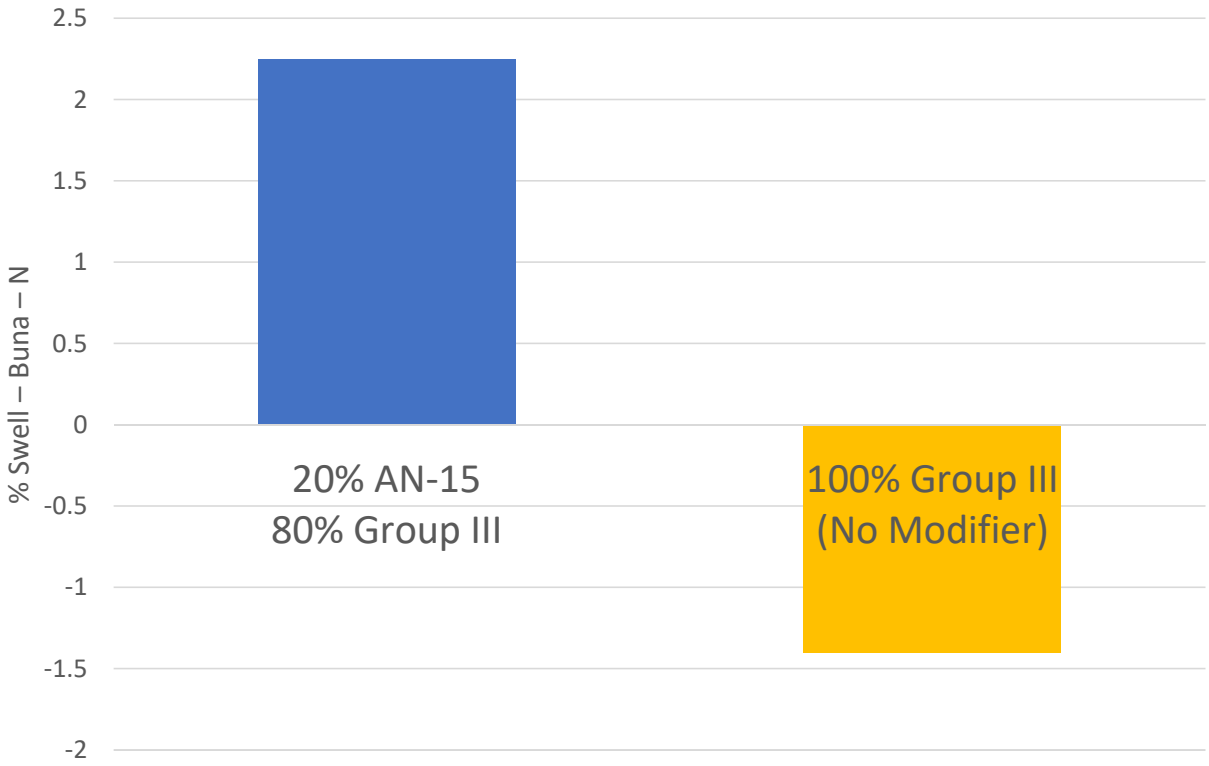
Viscosity @ 40°C (cSt):	117.5	124.1	114.5
Viscosity @ 100°C (cSt):	12.6	16.9	13.5
V.I.	98	148	110

environ

KING INDUSTRIES SPECIALTY CHEMICALS

Seal Swell

Seal Swell (ASTM D471)



Alkylated naphthalenes will impart Seal Swell Properties to Non-Polar Base Oils.

High Temperature Chain Lubricants

High Temperature Chain Lubricants

Alkylated naphthalenes extend fluid lifetime by:

- Reducing 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 Naphthalenes**
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
    - 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 placed in an aluminum pan
  - Sample is heated at 260°C for 8 hours
  - Report:
    - % evaporation loss
    - Condition of fluid

Reduction of Evaporation Loss to Retain Fluid

	POE 1963*	97% POE 1963 3% AO Blend†	80% POE 1963 **20% AN-19**	77% POE 1963 **20% AN-19** 3% AO Blend
Blend Number	1	2	3	4
Evaporation Loss 8 hours @ 260°C	94%	94%	**71%**	**68%**

AN-19 alone has an evaporation loss of 43%.

* POE 1963 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

Evaporation Loss Results

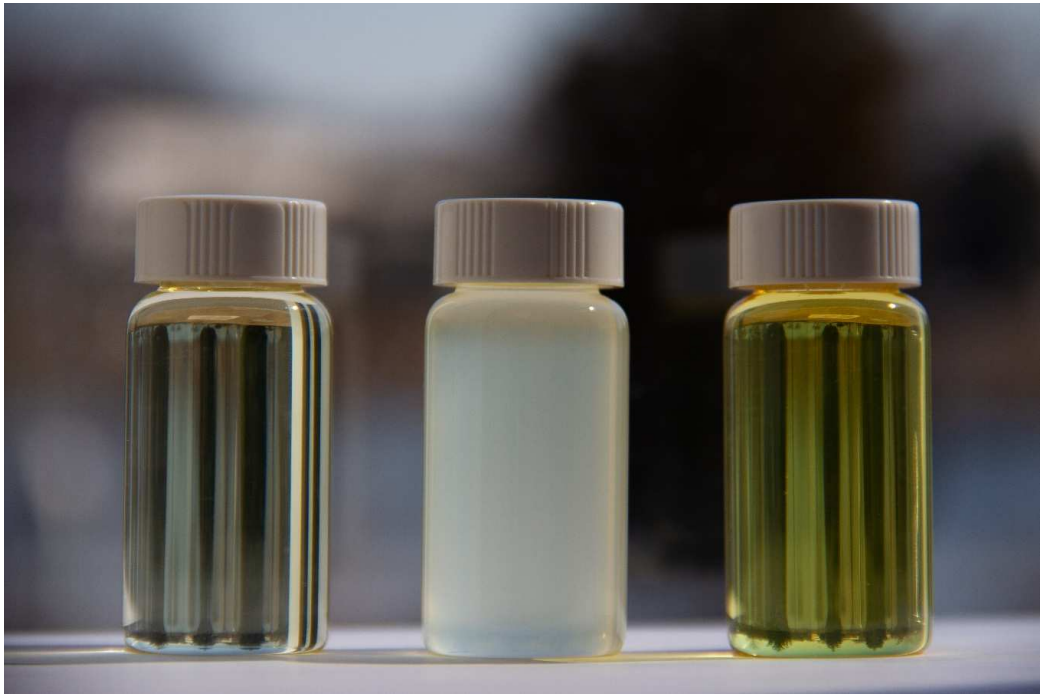
	POE 1963	**AN-19**	80% POE 1963 **20% AN-19**
Evaporation Loss 8 hours @ 260°C	94%	43%	Theoretical: 84% **Actual: 71%**

Reduction of Evaporation Loss to Retain Fluid

	88% POE 1963 12% PIB 950	85% POE1963 12% PIB 950 3% AO Blend	68% POE 1963 12% PIB 950 **20% AN-19**	65% POE 1963 12% PIB 950 **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 1963 alone has an evaporation loss of 94%.

Appearance of Blends



- The ester alone is clear (left). When 12% PIB was added to the ester the sample became hazy (middle); however, when 20% alkylated naphthalene was added in combination with PIB, the blend remained clear (right).

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

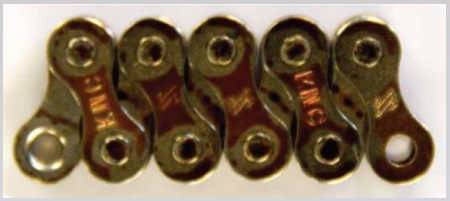
- The samples that <u>contain</u> AN-19 flow after oxidation.

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 an 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

Dark Viscous Liquid

Full Extension - 2 Seconds

environ

KING INDUSTRIES SPECIALTY CHEMICALS

High Temperature Chain Lubricants

- The addition of **AN-19** resulted in:
  - Sample clarity
  - Less evaporation loss
  - 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

Operating Conditions:

Temperature: 240°C to 260°C

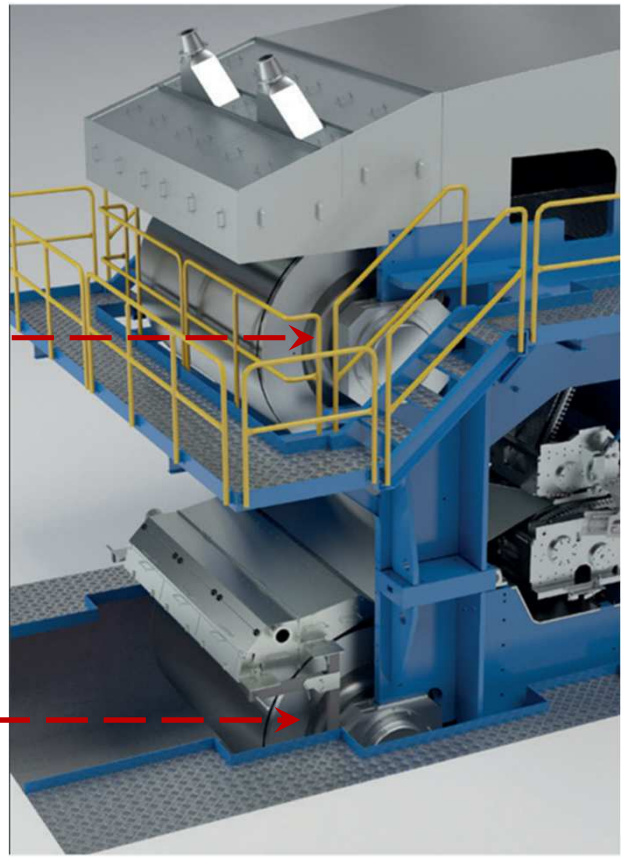
Production Speed: Up to 2 m/s

System Pressure: ~ 5000 kPa

Fluids Present: Lubricants, Release Agents and Adhesives

Plywood Manufacturing – Hot Presses

- Friction liners coated in heavy deposits from lubricant oxidation products and other contaminants



Cleaning of Equipment

High Temperature Belt Oil for Plywood Manufacturing

- Prior to using the belt oil containing **AN-19**, pictures were taken of the friction liners showing heavy deposits from oxidation products of the previously used oil.
- After 6 months of use with the belt oil containing the **AN-19**, it was observed that the oil was very dark and the friction liners were completely clean.
- The darkened oil containing the **AN-19** that had dissolved the deposits was exchanged for fresh oil, and the deposit formation and oil darkening did not reoccur

Removal of Deposits Formed from a Previous Oil

Before Fluid Change

6-Months after Fluid Change
with **AN-19**

Plywood Manufacturing

Cleaning of equipment by **AN-19:**

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

Grease

Properties of AN Modified Li 12-OH Grease

	PAO 10 (88%) Li 12-OH **(12%)**	AN-15 (93%) Li 12-OH **(7%)**
Color/Appearance	Tan / Smooth	Amber / Transparent
Cone Penetration (ASTM D217)		
Unworked	275	285
60 Stroke	273	288
10,000 Stroke	309	335
100,000 Stroke	350	366
Oil Separation	4.10%	2.80%
Dropping Point	202°C	200°C
Viscosity @ -40°C	4.0×10^6 mPa.s	6.6×10^6 mPa.s
TGA	233°C	**304°C**
PDSC (500 psi O_2, 210°C)	400 W/g at 3.7 minutes	**5 W/g** at 5 minutes

Li 12-OH Grease – Color/Appearance

100% PAO Grease

100% AN-15 Grease

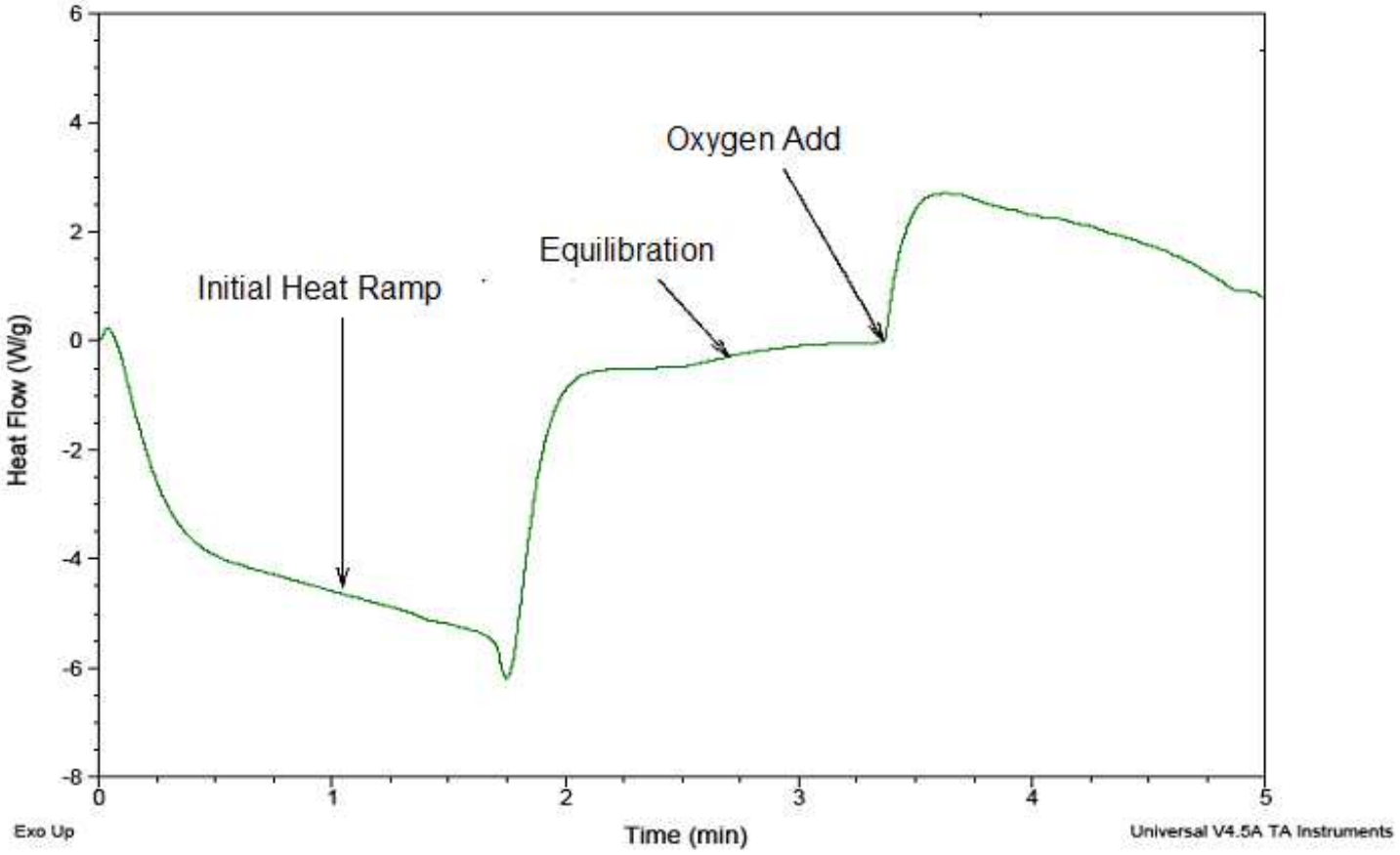
Less thickener = improved low temperature properties
Bridging solvent = reduced opaqueness
Effective dispersant = smooth grease

PDSC (ASTM D5483)

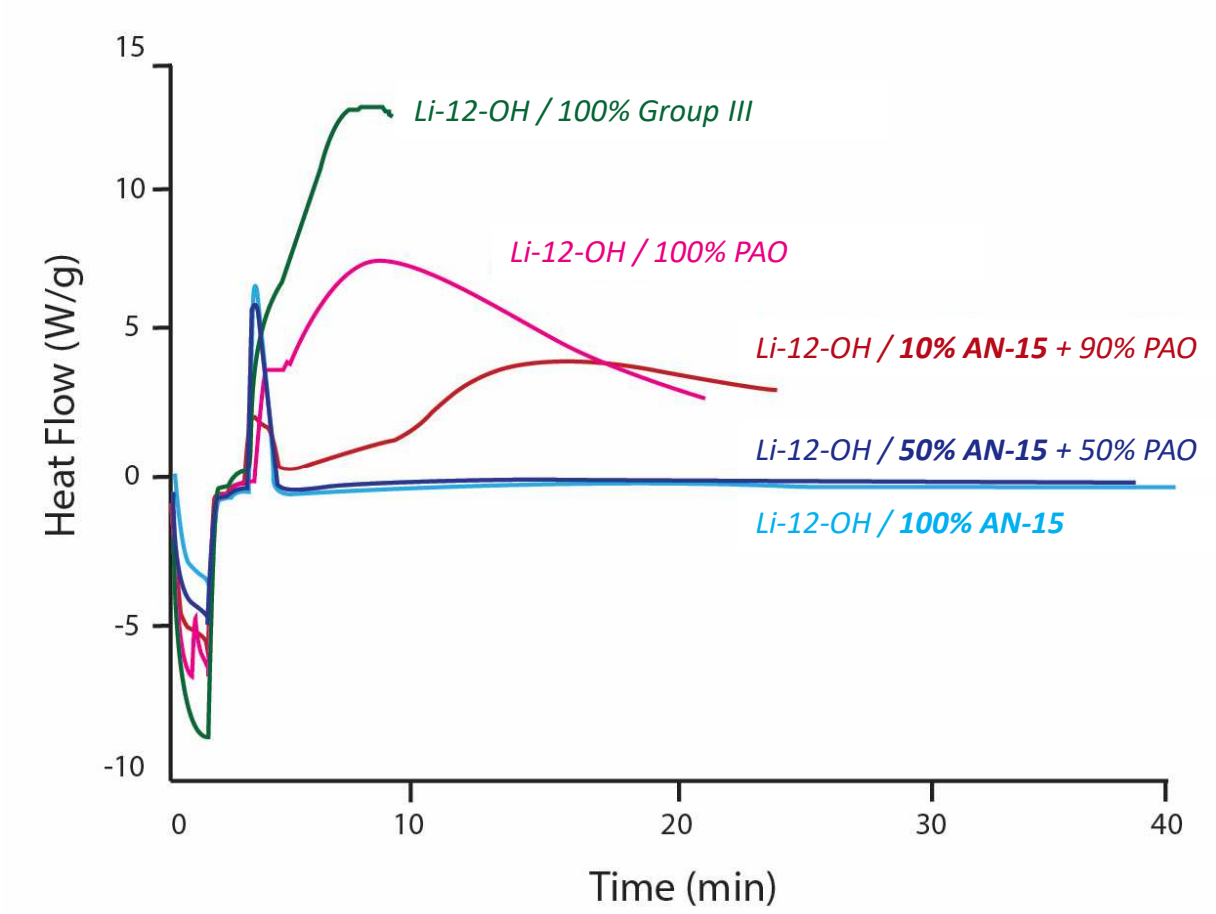
- Procedure:
  - Sample size 2.0 mg
  - Ramp 100°C/min to test temperature
    - 155 to 210°C
  - Equilibrate at test temperature
    - 2 minutes
  - Once equilibrated open O2 valve and pressurize to 500 psi
    - Within 2 minutes
  - Adjust O2 flow rate to 100 mL/min

Oxidation Induction time is calculated from when O2 valve is opened.

PDSC Explanation



PDSC (ASTM D5483) at 180°C



Grease Oxidation Stability (ASTM D942)

	Li 12-OH / 100% PAO 10	Li 12-OH / 90% PAO-10 ; **10% AN-15**	Li 12-OH / 50% PAO 10 ; **50% AN-15**	Li 12-OH / 100% Group III
Grease Oxidation Stability ASTM D942 Pressure Drop	38 psi @24 hours	9 psi @ 100 hours	0 psi @ 100 hours 2 psi @ 280 hours	16 psi @ 7 hours

Performance of AN Modified Li Complex Grease

Tests		3.35% Additive Package*		3.35% Additive Package*
Base Grease	Lithium Complex Grease with 100% PAO 10		Lithium Complex Grease with **30% AN-19** ; 70% PAO 10	
EMCOR (ASTM D6138) 10% Synthetic Sea Water, 1 week	2 (some stain)	0 , 0 (some stain)	0 (some stain)	0 , 0
PDSC (ASTM D5483) Onset Point, 500 psi, 200°C (min)	--	36	--	42
Grease Oxidation Stability (ASTM D942) 100 h, pressure drop (psi)	86	2	0	1
Cone Penetration (ASTM D217)				
Unworked	298	300	281	284
60 Strokes	299	310	282	294
10,000 Strokes	303	317	292	309

*Additive Package contains: calcium sulfonate, ADPA, sulfurized olefin/fatty oil, ZnDTP, and tolyltriazole derivative

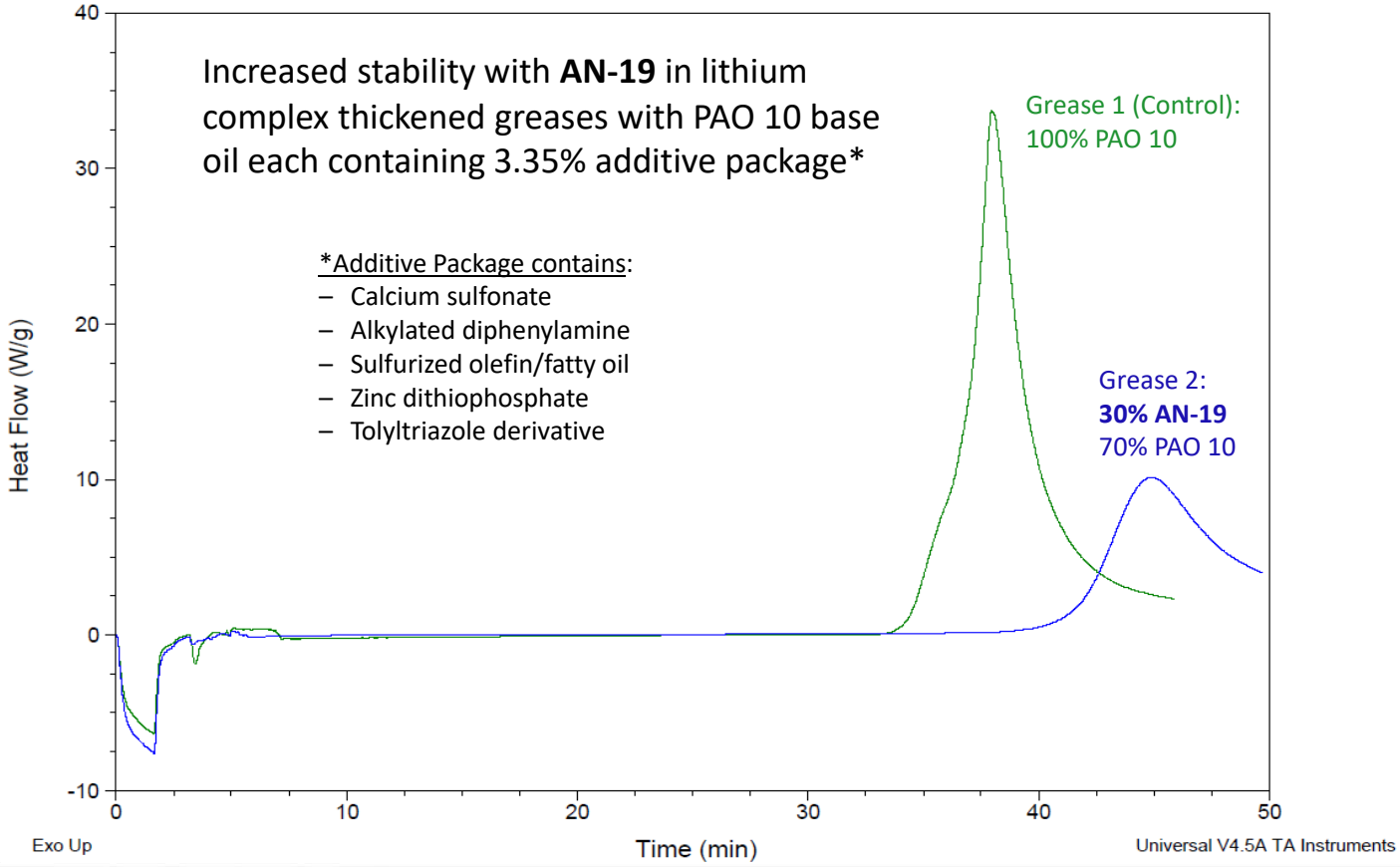
Performance of AN Modified Li Complex Grease

Tests		3.35% Additive Package*		3.35% Additive Package*
Base Grease	Lithium Complex Grease with 100% PAO 10		Lithium Complex Grease with **30% AN-19** ; 70% PAO 10	
Four Ball Weld (ASTM D2596)				
10 seconds, 25°C, 1800 rpm				
OK Load (kgf)	120	240	140	280
Weld Load (kgf)	140	260	160	300
Four Ball Wear (ASTM D2266)				
1 hour, 75°C, 40kgf, 1200 rpm, (mm)	0.53	0.45	0.50	0.41
Copper Corrosion (ASTM D4048)				
24 hours, 100°C	2b	1b	1b	1a
Grease Water Stability (DIN 51807-1)				
3 hours, 40°C	0	0	0	0
3 hours, 90°C	2	2	2	2

*Additive Package contains: calcium sulfonate, ADPA, sulfurized olefin/fatty oil, ZnDTP, and tolyltriazole derivative

Performance of AN Modified Li Complex Grease

PDSC (ASTM D5483) 200°C, 500 psi oxygen



Performance of AN Modified Polyurea Grease

Tests		8.05% Additive Package*		8.05% Additive Package*
Base Grease	Polyurea Grease with 100% PAO 10		Polyurea Grease with **30% AN-19** ; 70% PAO 10	
EMCOR (ASTM D6138) 100% Synthetic Sea Water, 1 week	5	0 (some stain)	5	0
PDSC (ASTM D5483) Onset Point, 500 psi, 210°C (min)	17	51	27	>120
Grease Oxidation Stability (ASTM D942) 100 h, pressure drop (psi)	4	--	0	--

*Additive Package contains: synergistic rust inhibitor blend, ADPA, sulfurized fatty acid ester, ashless dithiocarbamate, and tolyltriazole derivative

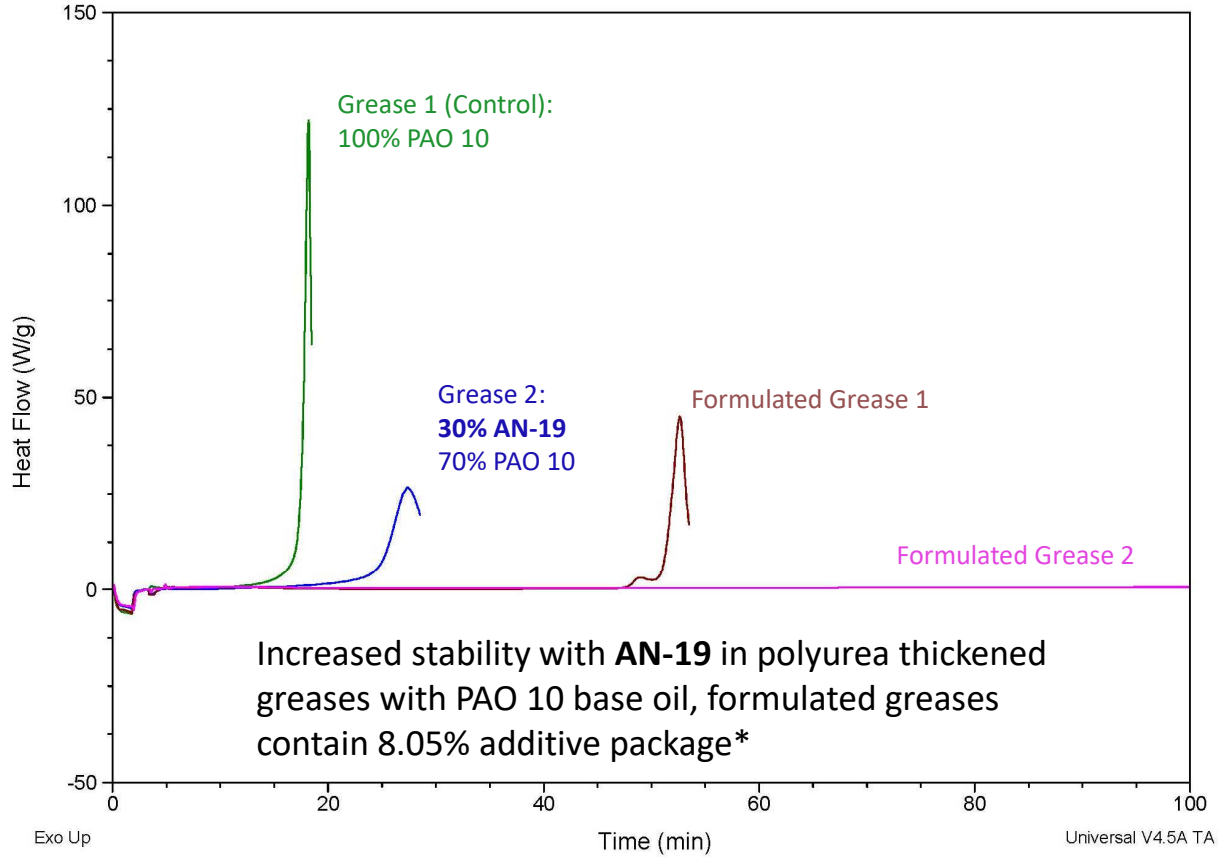
Performance of AN Modified Polyurea Grease

Tests		8.05% Additive Package*		8.05% Additive Package*
Base Grease	Polyurea Grease with 100% PAO 10		Polyurea Grease with **30% AN-19** ; 70% PAO 10	
Four Ball Weld (ASTM D2596)				
10 seconds, 25°C, 1800 rpm				
OK Load (kgf)	80	120	80	120
Weld Load (kgf)	100	140	100	140
Four Ball Wear (ASTM D2266)				
1 hour, 75°C, 40kgf, 1200 rpm, (mm)	0.60	0.52	0.58	0.49
Copper Corrosion (ASTM D4048)				
24 hours, 100°C	1b	1b/2a	1b	1b/2a
Grease Water Stability (DIN 51807-1)				
3 hours, 40°C	0	0	0	0
3 hours, 90°C	1/1.5	0	0	0

*Additive Package contains: synergistic rust inhibitor blend, ADPA, sulfurized fatty acid ester, ashless dithiocarbamate, and tolyltriazole derivative

Performance of AN Modified Polyurea Grease

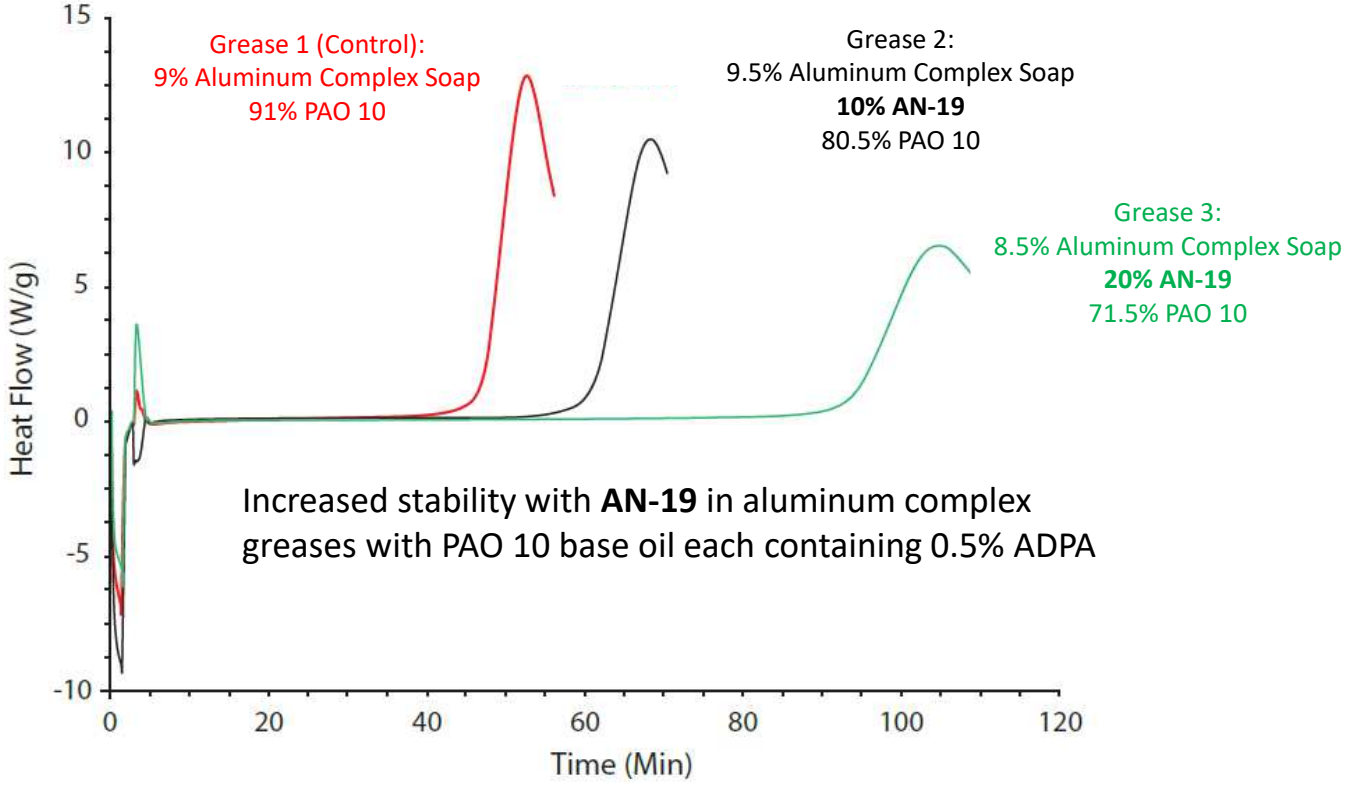
PDSC (ASTM D5483) 210°C, 500 psi oxygen



*Additive Package contains:
- Synergistic rust inhibitor blend
- Alkylated diphenylamine
- Sulfurized fatty acid ester
- Ashless dithiocarbamate
- Tolyltriazole derivative

Performance of AN Modified Al Complex Grease

PDSC (ASTM D5483) 180°C, 500 psi oxygen



Increased stability with **AN-19** in aluminum complex greases with PAO 10 base oil each containing 0.5% ADPA

ADPA = alkylated diphenylamine antioxidant

Greases courtesy of FedChem, LLC

Presentation Outline

- Alkylated Naphthalene Background
- Physical/Chemical Properties
- Performance Evaluations
- 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

King Industries Offers

- Alkylated Naphthalenes
- Blends/Packages
- Friction Modifiers
- Antiwear Additives
- Antioxidants
- Extreme Pressure Additives
- Corrosion Inhibitors
- Rust Inhibitors
- Rust Preventives
- Technical Product Support

For more information, contact:

Sachin Kumbhar
Environ Speciality Chemicals Pvt. Ltd.
Mumbai, India
Mob: +91-9075313595
Email: sachin@environchem.com