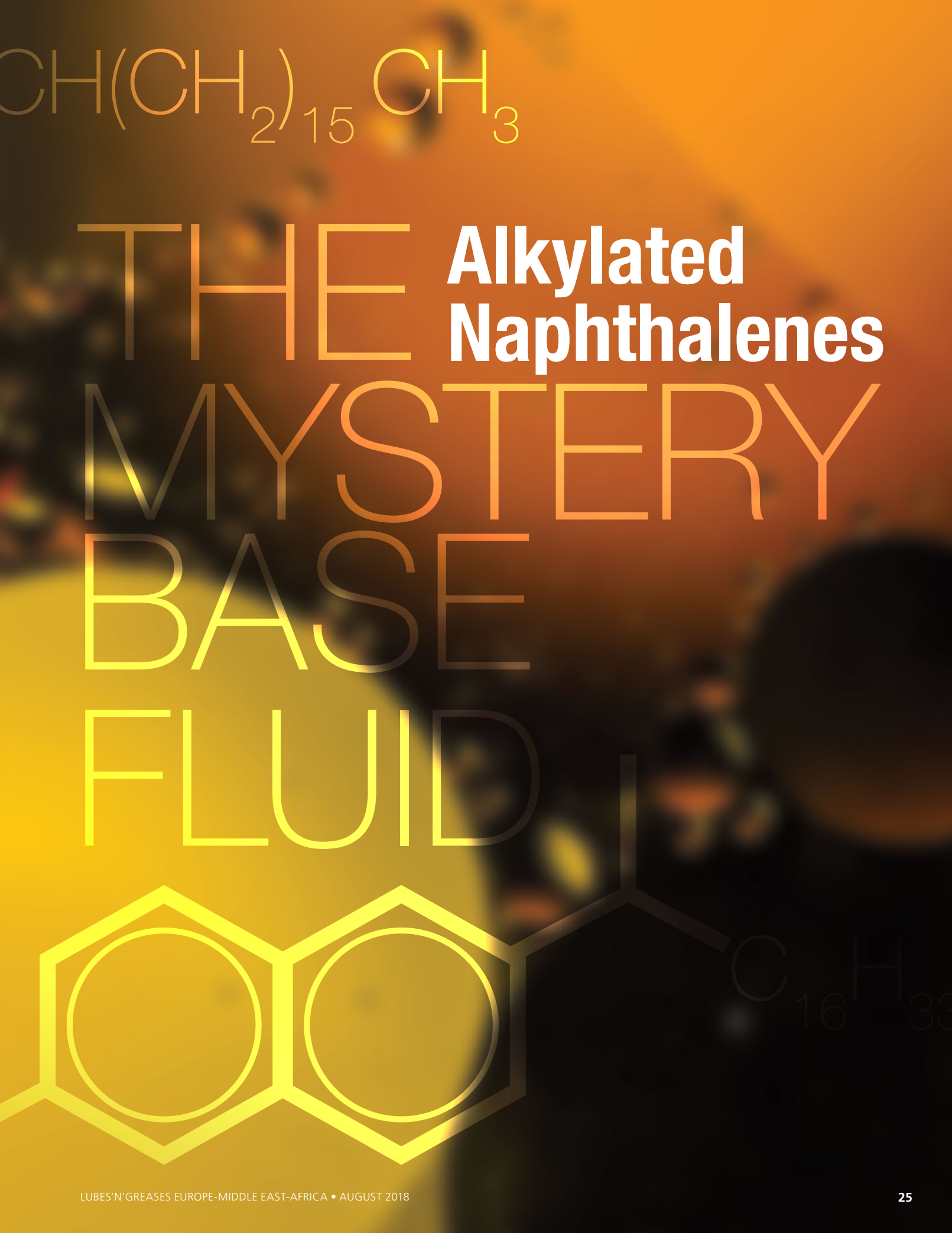
THE MYSTERY BASE FLUID

Alkylated Naphthalenes



The demands placed on lubricants have been increasing for many years, driving formulators away from API Group I base oils to Group II, Group III or newer fluids such as metallocene polyalphaolefins. All of these fluids have lower polarity, which many formulators compensate for by using Group V esters.

There is, however, another solution in the form of alkylated naphthalenes. These substances have been commercially available for more than 20 years but are largely a niche product and have only recently warranted significant mention in the additive industry reference literature. Only three companies manufacture ANs and market them as lubricant additives.

Solubility and Stability

ANs were first developed by the United States during World War II as synthetic fluids in engine oils because of the scarcity of mineral oil. But mass production did not get off the ground until long after the war. Fast forward five decades to the 1990s when ExxonMobil first introduced ANs into the lubricants market, citing significant performance benefits and advantages in combination with polyalphaolefins.

PAOs' low-temperature performance, viscosity index and resistance to oxidation were advantages. But PAOs were so low in polarity compared with commonly used base fluids that many formulators had to compensate for reduced additive solubility and seal shrinking.

Generally, they turned to esters, but they found that PAO-ester formulations could suffer from oxidative and hydrolytic degradation, which was mainly due to the ester. ANs could address the shortcomings of ester-based formulations and more.

"When added to Group II oils, Group III oils and PAOs, ANs enhance the thermal and thermo-oxidative stability, solvency, dispersancy, additive response, varnish control, seal swell, volatility and hydrolytic stability to extend the lifetime of these high-performance lubricants," Maureen Hunter, technical service manager for U.S.-based King Industries Inc., told *Lubes'n'Greases*. King Industries entered the AN market in the early 2000s.

When ExxonMobil Chemical launched ANs as unique base fluids for use in engine oils, it rapidly settled on its trade marked Synesstic products, one low and one high viscosity grade, which it continues to sell. Meanwhile, King Industries' portfolio is based on decades of experience producing naphthalene sulfonates. ANs are intermediates in the manufacture of its sulfonates. This let the company easily transition into the market and gave it the ability to supply products of different molecular weights and structures

Industry Calendar

AUGUST

1-2. AMEA BLW
The Leela, Mumbai, India
- **info@baseoilreport.com**
- **www.amea-conferences.com/baseoil**

SEPTEMBER

10-11. BFPA International Conference
University of Bath, U.K.
- **www.bfpa.co.uk/events**

17-20. SAE International Powertrains, Fuels & Lubricants Meeting
Heidelberg Convention Center, Heidelberg, Germany
- **kimberly.inniger@sae.org**
- **www.pfl18.org**

OCTOBER

9-12. Global Lubricant Week
Radisson Royal Hotel, Moscow, Russia
- **Konstantinova.Elena@rpi-inc.ru**
- **www.rpi-conferences.com/en/lubricants-week**

15-17. ICIS Middle Eastern Base Oils & Lubricants Conference
Intercontinental Dubai Festival City, Dubai, UAE
- **www.icis.com/conferences/base-oils-lubricants**

24-26. UEIL Annual Congress & General Meeting
Hilton, Budapest, Hungary
- **www.ueil.org/events**

30-1 November. ICIS African Base Oils & Lubricants Conference
Century Conference Center, Cape Town, South Africa
- **www.icis.com/conferences/base-oils-lubricants**

NOVEMBER

28-29. ACI Annual European Base Oils and Lubricants Interactive Summit
Florence, Italy
- **www.wplgroup.com/aci/event/base-oils-lubricants-summit**
- **sajawin@acieu.net**

JANUARY

29-31. OilDoc Conference and Exhibition
Kultur und Kongresszentrum, Rosenheim, Germany
- **www.conference.oildoc.com/en/home**

FEBRUARY

TBA. ICIS World Base Oils & Lubricants Conference
London, UK

APRIL

2-3. UNITI UMFT 2019
Stuttgard, Germany
- **www.umft.de**

Additive Response Comparison of Ester and Alkylated Naphthalene

ISO VG 220	Ester Blend	AN Blend
40 cSt PAO	78%	78%
Adipate Ester	20%	---
5 cSt AN	---	20%
Additives	2%	2%
4-Ball Wear Test	Wear Scar (mm)	
1,800 rpm, 93˚C for 30 minutes		
60 kg load	0.822	0.739
80 kg load	2.094	0.822

Source: ExxonMobil Chemical

on demand. King Industries currently offers nine AN products with a viscosity range between 4 and 20 centistokes at 100 degrees Celsius.

Alkylated naphthalenes can be mono- or poly-alkylated with either linear or branched alkyl chains, leading to a wide variety of properties. "We are able to make products of different viscosities with the desired inherent thermo-oxidative stabilities, volatilities, pour points, aniline points and other properties," Hunter said.

Hot and Sweaty

Some formulations use ANs at a treat rate of 10 percent or less, but there are some applications that lend themselves to ANs' intrinsic oxidative and hydrolytic stability, plus their low volatility. In these cases, they are used at greater than 10 percent of the base fluid.

ExxonMobil uses the ASTM D943 turbine oil stability test to measure the lifetime of compressor fluids based on ANs, relative to similar fluids based on esters. King Industries, meanwhile, uses the ASTM D6186 PDSC test to show improvement in the thermo-oxidative stability of a 6 cSt PAO when modified by 10 percent with its own NA-LUBE KR-008. Oxidative stability improved due to a synergy between the AN and an aminic antioxidant.

"The excellent thermo-oxidative stability imparted by the alkylated naphthalene is the result of the electron-rich naphthalene ring, which can absorb energy, resonate and disperse energy much like antioxidants do," said Hunter.

King Industries has promoted another property of ANs – that of reducing the volatility of the overall blend. "High-temperature chain lubrication is a prime example of how alkylated naphthalenes can extend the lifetime of a high-temperature lubricant. Replacing 20 percent of a polyisobutylene-containing polyol ester formulation with alkylated naphthalene synergistically reduced the evaporation loss from 94 percent to 71 percent when held in an oven at 260 C for 8 hours. The theoretical loss was 84 percent. The addition of the alkylated naphthalene also imparted thermal and thermo-oxidative stability to inhibit viscosity increase and varnish formation," said Hunter.

More from Less

The lower polarity of ANs relative to esters can lead to formulations requiring less anti-wear additive. "Alkylated naphthalenes are less polar [than esters]. But the polarity of esters is so strong that instead of just solubilizing additives, they end up competing with the additives for the surface you are trying to protect," Michel Hourani, vice president of King Industries, told *Lubes'n'Greases* back in 2010.

The pitch was that formulators could potentially gain the same anti-wear or friction-reducing effects with less additive if they replaced some base fluid with alkylated naphthalenes.

Indeed, ExxonMobil claims enhanced performance, including improved anti-wear for industrial gear formulations. The company demonstrated this using the ASTM D4172 four-ball test, albeit at higher rotation speeds, temperature and loads and over a shorter time than the usual test parameters of 1,200 revolutions per minute at 75 C with a 40 kilogram force load for 60 minutes.

"Some lubricant bench tests do not show the advantages observed with alkylated naphthalenes in the field unless the test conditions are stressed, such as running the four ball wear test at higher temperatures and loads than typical conditions," Hunter explained. She also observed that ANs like to be on the move. "In dynamic systems, it's that continual motion that enables them to inhibit the formation of deposits and varnish. Static bench test conditions don't always show this advantage."

Solubility plays a significant part in the "more from less" selling point for grease formulators. ANs can disperse grease thickeners better, so less thickener is required for a specific NLGI grade, leading to the grease having better low-temperature flow.

This may become increasingly important for those formulating lithium or lithium complex greases, as prices continue to rise and supply becomes less predictable.

Champing at the Bit

King Industries was the first of the two Western suppliers to acquire NSF H-1 and HX-1 food grade certification for products in its range. ExxonMobil followed in 2009 for both of Synesstic products. NSF H-1 registration allows a fluid to be used as a lubricant in applications where they have potential for incidental food contact, while NSF HX-1 registration is for the ingredients of such lubricants.

It is the area of incidental food contact that caused a recent concern in the otherwise positive story of ANs. Chemically, ANs are considered mineral oil aromatic hydrocarbons, as they have 16 or more carbon atoms and the naphthalene aromatic ring. The European Union has taken steps to restrict MOAH contamination in food and drinks, but the definitions of MOAH do not align with any petroleum products on the market. One source of MOAH in food is from ink found in recycled card and paper used as food packaging.

Speaking at the ICIS and ELGI Industrial Lubricants Conference in June in Amsterdam, Juan-Carlos Carrillo, toxicologist for Shell and Concawe, the research division of the European Petroleum Refiners Association, indicated he was confident that ANs would not be affected by MOAH definitions. The German Federal Institute for Risk Assessment (known in German as BfR) issued an opinion in February 2018 that accepted Concawe's position on a toxicological detail that would remove the MOAH restrictions from all lubricants and therefore from ANs.

Have We Been Here Before?

The introduction of metallocene PAOs has opened new possibilities for the marketers of ANs, where their intrinsic properties and those they enhance in the formulation bring benefits in highly demanding applications.

MPAOs bring another step-change in low-temperature properties and V.I. relative to base fluids currently on the market. This echoes the step-change from the introduction of PAOs in the 1990s, relative then to mineral oils, except this time the change is relative to conventional PAOs. However, the performance boost offered by ANs is different this time. Applications where mPAOs really shine, such as wind turbine gear boxes, require high additive treat rates that benefit from the addition of a solubilizer.

As Hunter explained, wind turbines are exposed to some of the harshest lubrication conditions, including vibration, extreme temperatures and debris. ANs can help extend oil-drain intervals, and some synthetic wind turbine oils are now warrantied for up to seven years. This also results in less frequent human-equipment interaction and improved safety. "It's costly to hire a technician to climb up great heights to service a high-powered turbine," she said.

One of the first things that a formulator sees on technical data sheets is the low viscosity index of certain products. The lower the kinematic viscosity (at 40 C or 100 C), the lower the V.I. Is this a big issue? Not really, says Hunter.

"You can make alkylated naphthalenes with no appreciable V.I., but our higher viscosity alkylated naphthalenes have [viscosity indices] greater than 115."

ExxonMobil staff also point out that ANs do not radically affect the overall V.I. of a formulation.

Both companies are quick to highlight the performance benefits of fluids formulated with ANs, looking beyond their customers to the end users. ExxonMobil makes the "synergies" between ANs and mPAOs a large part of its sales and technical pitch, emphasizing the benefits that result from the use of both. King Industries, meanwhile, focuses much more on the ANs that it manufactures.

Bright Future

Shanghai Naco Lubrication Co. introduced Chinese-manufactured ANs into the market in 2014 and currently offers one product called SynNaph AN23. In keeping with the varied properties of these materials, SynNaph AN23 has a much higher viscosity than products from ExxonMobil and has similarities to King Industries' highest viscosity product, NA-LUBE KR-023. Like ExxonMobil, Naco emphasizes the synergies between ANs and the PAOs that it also manufactures. King Industries, meanwhile, plans additional capacity at its second site in Waterbury, Connecticut.

All of which indicates that this research project from the 1940s might have reached its moment after almost 25 years on the market. □

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