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The Development of Lubricating Greases for Wind Turbine Applications

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Abstract

With the continued growth of wind turbines (WT) for renewable energy generation, a significant amount of work has been published looking at improved gearbox fluids. However, there has been little focus on the greases and open gear lubricants used in wind turbine systems and components.

The grease lubricated components are main bearings to support the rotor assembly, pitch and yaw bearing greases. Depending on the pitch and yaw control mechanisms employed, they may also include open gear lubricants for gear mechanisms and can also include electric motors with grease lubricated bearings. In non-direct drive applications, there are shaft bearings on the generators.

In addition to standard tests for bearing greases, there are additional primary requirements that make the formulating of such greases a significant challenge. Micropitting, fretting and corrosive wear are the key issues. Unlike the gear oils specifications, there is no current dedicated test for micropitting test for greases and so the FE8 is utilized. To screen for corrosion the Emcor is used and there is a choice of two ASTM standardized tests for fretting wear. For the combination of false brinelling and corrosion under quasi-static loading, a new test was developed. The Riffel (Ripple) test utilizes a large angular contact bearing, under a high oscillatory thrust loading with no rotation and salt solution pumped through. At the end of test the amount of wear is measured and the visible corrosion is rated.

This paper will discuss issues with developing greases to meet the WT specification requirements of friction, low wear, fretting, and corrosion. It will also report on learnings to enable lubricating greases to pass the standard bearing grease test requirements and the Riffel test.

Introduction

Renewable energy has been used as a source of energy for millennia. Sailing boats utilizing wind power sailed the River Nile at the time of the Great Pyramids. Wind power has been used as a source of energy to pump water, grind grain and other things for centuries.

With a desire to reduce greenhouse gas (carbon dioxide) emissions, countries have been developing renewable energy to supplant the burning of hydrocarbon fuels. Hydroelectric, solar, wind, biomass and wave powers are all being harnessed to generate electricity. According to US Government figures, the amount of energy consumed in the USA in 2017 was 97.7 quadrillion BTUs (103 exaJoules). Of this amount, approximately 11% was generated from renewable sources, with 2.3% of the total (2.4 exaJoules) was from wind turbines. This is projected to grow at a compounded annual growth rate (CAGR) of 7% up to 2030 (1).

In December 1952 (2) the Indian Council of Scientific and Industrial Research (CSIR) sponsored a research project to explore the possibilities of harnessing wind power in India. From this beginning, wind surveys were carried out and regions identified with potential for installing wind turbines (WTs). Sites identified included ones in what is now Gujarat State with winds from the Arabian Sea and from the Western Ghats mountains of Tamil Nadu State (3). Experimental turbines were set up in these areas and used for localized generation of electricity. The first large scale wind farms were built in 1986 (4) under the patronage of the Ministry of New and

Renewable Energy (MNRE) in coastal regions in Maharashtra (Ratnagiri), Gujarat (Okha) and Tamil Nadu (Tirunelveli). The wind turbines installed there were rated at 55 kW and with 30 m (100 ft) towers that had blades 7.5 m (24 ft) long. This is very small compared to today's 12 MW offshore giants with tower heights of 260 m (850 ft) and blades 110 m (360 ft) long.

According to the Indian Wind Turbine Manufactures Association (IWTMA), the installed capacity, as of December 2018, was almost 35,000 MW (5), which is 10% of the generating capacity of India and the fourth largest of any country in the world. The latest Government of India figures (4), this installed capacity produced 52,666 GWh of electricity which accounts for 3% of the electricity needs, but 48% of the total volume of renewable energy. The MNRE has set a target of 60,000 MW of installed capacity by 2022 and has identified the total potential for more than 300 TW. The CAGR of capacity is above 5% per annum. So far, all the installed capacity in India is onshore, but a 30 MW an offshore wind farm is being planned for Arichamunai, Tamil Nadu (6). According to the published information (5), the most common wind turbines installed in India today are in the 350 kW to 2.1 MW range. Looking at the 350 kW model, the tower height is between 50 m (164 ft) and 70 m (229 ft) and the blade length is approximately 17 m (55 ft). No weight information could be identified for this model. A 1.5 MW WT would have a tower height of above 80 m (250 ft) and blade lengths of 35 m (116 ft). Looking at the approximate weight of an installation this size, the nacelle with a conventional gearbox and generator assembly would weigh about 56 metric tons (MT), the blade assembly another 36 MT and the tower over 70 MT. A 2.1 MW WT has 44m (144 ft) long blades and sits atop of a tower 80 m (262 ft) high with a total weight approaching 350 MT (7). Typical rotational speeds are in the range of 6 r/min to 20 r/min, again depending on size with blade tip speeds of between 67 m/s to 90 m/s (240 km/h to 320 km/h). Most WTs need wind speeds between 3.5 m/s (12.6 km/h) and 25 m/s (90 km/h)

Based on the CAGR for India, lubricant demand for wind turbine applications has grown to a significant level to attract the interest of major lubricant suppliers. However, the actual demand for lubricants for factory fill installations is unclear. Gearboxes, where used, are usually supplied without oil, which is added on installation, and is typically as specified by the original equipment manufacturer (OEM). The multiple bearings typically come pre-greased from the manufacturing location. The main reason for this is to prevent Brinelling that can occur between the rolling elements when the bearings are transported to the assembly location and then onto the final installation. On a normal maintenance cycle, the bearings would be given their final application of grease at this point and then switched to a standard routine of re-lubrication every six months. Normally, the bearing OEM dictates the re-lubrication grease to be used under warranty, which may last 10 to 20 years. Typically, after the warranty period has expired, a local lubricating grease that the purchasing arm of the windfarm operator has procured will be used. The key for potential grease suppliers is to get their products approved by the OEM or by the operating company. The OEM approvals are based on technology and passing rigorous specification testing, whereas price is a major factor in post warranty procurement. One desire of wind turbine operators is to have only one grease for all applications, but looking at the lubrication needs of the applications, this is not practical without potentially compromising performance of one or more components. This is discussed in more detail later.

Lubricated Contacts

Apart from the gearbox, which is not covered by this paper, the other grease lubricated contacts are as follows:

- Main bearings to support the load of the rotor
- Yaw bearings to support the load of the rotor and the nacelle
- Pitch bearings which allow the blades to get optimum power from the prevailing winds
- Bearings on the anemometer mounting and wind speed-measuring rotor
- On wind turbines that have a gearbox and generator installed (indirect drive), there are high speed deep groove ball bearings on the generator.

The main Bearings need to support the weight of the blade assembly, which may be up to 60 MT. In addition, wind blowing against the blades causes significant axial thrust on the main bearings. The magnitude of this thrust load has not been well quantified and as such is a major unknown. The force typically varies with the height of the tower and the length of the blade, as well as the position of the blades with respect to the nacelle. The main bearings need to counter this thrust and so in some WT designs, spherical roller bearings (SRB) are used and in others tapered roller bearings (TRB). The lubrication requirements of SRB and TRB are different and two different greases should be needed, but only one per tower. The blade pitch rotor bearings need to support the weight of the blade weighing up to 20 MT each. The Yaw bearings need to support both the weight of the nacelle, that can be upwards of 60 MT, and the blade assembly. Typical bearings used for the yaw applications are vertical angular contact ball bearings (ACB) with diameters of 1.5 m (5 ft) on the smaller tower diameters to > 4 m (14 ft) on the very large towers. Pitch bearings also use the same type of bearings as the yaw application but are significantly smaller in diameter and have much less applied load. The mechanisms are typically re- greased with the same product. One option to reduce the number of greases is to design a grease that could be used to lubricate either the main bearing types but also the pitch and yaw bearings.

The bearings on the anemometer mounting and wind speed-measuring rotor now are typically sealed for life and require no maintenance unless they fail or get accidentally damaged in service.

In addition, there are open gear lubricants of the ring gears of the pitch and yaw mechanisms that may be grease lubricated but are more commonly treated with extremely viscous fluids. There are also electric motors to adjust the yaw of the nacelle to optimize wind capture and in some WT designs, the pitch adjusters are driven by electric motors. In both of these applications, typical electric motor bearing greases are used. It is anticipated that these electric motors would use a similar grease to that in the generator bearings.

Focusing on the main bearings, the critical application elements of the WT applications are as follows:

- Low rotational speed
- High radial loads
- High transient axial loads
- Humid atmospheres
- Fretting conditions (when stationary)
- Long life without contact fatigue

For pitch and yaw bearings, the critical application elements of the WT applications are as follows:

- Oscillatory rotary motion
- High oscillating axial loads

- Humid atmospheres
- Fretting conditions
- Radial bending moments
- Long life without contact fatigue

Comparing these critical application elements there is the clearly the potential for a common grease, for main pitch and yaw bearings but that needs to be tempered with the need to use a different grease for SRB And TRB applications. Unlike ACB and TRBs, there are no published public specification tests for SRBs and so it makes the development much more difficult. The FAG FE8 test method (DIN 51819-2) (8) is used to test the wear properties of ACB and TRB lubricating greases under a variety of test conditions This paper will cover the requirements for these greased lubricated bearings. Prior to 2000, there were no public test methods for determination of both fretting wear or false Brinelling and corrosion. The Riffel (or Ripple) test was developed to screen for both of these properties (9). This paper will now look at the requirements of the various tests and show how learning their appetite helped to developed new grease technology for pitch and yaw bearing greases.

Grease Testing Requirements

Several OEM specifications and some WT industry standard grease specifications were reviewed along with product data sheets of existing approved greases and most of them had several common elements. Typical properties were identified which were defined by standard tests such as dropping point and penetration. Other properties defined by standard test equipment but used under non-standard conditions were also reviewed.

Non-standard and special grease property test requirements such as the Riffel test were analyzed. The most difficult one was the Riffel test, as no industry standardized test had anyway near the contact conditions employed.

Standardized property tests, run under standardized conditions:

- Lubricating grease consistency (cone penetration)
- Dropping point (aluminum heating block)
- Shear stability (change in penetration after prolonged working for 1k, 10k, 100k double strokes)
- 4-Ball EP weld point and load wear index (ASTM Conditions)

Standardized property tests run under non-standard conditions:

- Roll stability, 50 hours 80 °C
- Water spray off at 60 °C
- Water washout at 60 °C
- Four ball wear at 60 °C
- High temperature oil bleed at 60 °C
- Emcor test with 1% NaCl solution
- SRV load carrying (step load) at 60 °C
- SRV Friction and wear at 60 °C
- Pressure vessel oxidation duration is 500 hours with a report at 100 hours

Bearing tests

- Fafnir friction oxidation test (FFOT) for fretting wear

- FE8 Type B (ACB, metal cage)
- FE8 Type C (TRB)
- Riffel test
- FAG FE9 grease life test at 120 °C (optional)

The bearing test conditions employed are shown in table 1

Characteristic	Test Method	Requirements
Fafnir friction oxidation test (FFOT) weight loss determination	ASTM D4170	Weight loss (mg) ≤ 2.0 (run in duplicate)
FE8 Type B (AC) 60 °C 7.5 r/min 80 kN 500 hours	DIN 51819-2	Weight loss (mg) Rolling elements (balls) ≤ 35 Inner and outer raceway ≤ 35 Cage ≤ 100
FE8 Type C (TRB) Ambient (room)temperature 75 r/min 50 kN 500 hours	DIN 51819-2	Weight loss (mg) Rolling elements (rollers) ≤ 35 Inner and outer raceways ≤ 35 Cage ≤ 100
Riffel (Ripple) Test QJ212 four-point contact bearing 70 kN alternating load at 9 Hz ± 1 Hz 1 million cycles 1% NaCl solution at 6 mL / min	Institute of Machine Elements (IME) In-house procedure	Maximum wear depth, RD_{max} <10.0 µm
		Average wear depth, RD_{ave} < 3.0 µm
		Corrosion rating ≤ 2

Table 1 Bearing lubricating grease test conditions

The basic specified formulation is for a lithium complex thickened ISO VG 460 fully synthetic oils Reviewing the basic property and testing requirements, they are for the most part relatable to the application. There are however several things that do not make technical sense in view of the known requirements for the application. All requirements for basic property and testing are reviewed below. The grease is designed to work from -40 °C to +120 °C. The dropping point for the grease has a specified value of above 300 °C which requires a lithium complex grease with a ratio of complexing acid to thickening acid of 2:1. At this ratio and in a PAO base fluid, the thickener content has to be 15 wt% to 18wt% when made with lithium hydroxide monohydrate and a 2-step manufacturing process. For the application, thickener does not need to be lithium complex, but a conventional lithium 12- hydroxystearate soap could be used, lowering the thickener content and saving significantly on production time and costs. The target range for consistency was a 60 stroke worked penetration between a soft NLGI grade #2 and firmer NLGI #1 (290 – 320). This was to strike a balance between how easily the grease would re-flow back into the contact after the rolling element had passed by and prevented channeling and being too soft so that the grease would readily leak out from the bearing.

Running and reporting prolonged work penetration after 1k, and 10k, and 100k double strokes does not offer any additional information and would it be better if only the Δ100k was used. Fully synthetic PAO based grease can also be difficult to homogenize and care must be taken to ensure that the higher thickener content is fully dispersed. An easier way of ensuring good structure and homogeneity is to allow only a small change between unworked and worked 60 penetrations.

For a couple of specifications, fretting testing by both FFOT and by the SRV fretting wear test (ASTM D7594) were defined. With others either only FFOT or the ASTM D7594 were defined. The FFOT is known to have repeatability and reproducibility (r+R) issues (10) and it would be better moving forward with just the SRV fretting wear test.

Grease Formulation

The Long-life requirement and the ASTM D942 pressure vessel oxidation test requirements indicate that an oxidation inhibitor is needed in the formulation. The grease should have moderate load carrying capacity with no significant extreme pressure(EP) requirements as defined in terms of the 4-Ball EP test with a weld point of ≥ 250 kg and a load wear index (LWI) of ≥ 30 kg. The SRV step load requirement is also moderate at ≥ 600N. In terms of wear other than fretting, the SRV wear scar is a reportable value and the 4-ball wear scar diameter of ≤ 0.60 mm is also understood. To pass the 1% NaCl solution Emcor corrosion test needs a good salt water rust inhibitor. Whether measured by FFOT or by SRV, the fretting wear test requirement needs the presence of anti-fretting additives. The Riffel test has 1% NaCl solution flowing through an ACB under oscillatory road and suggests some polymer additive is necessary, but what sort polymer and how much to add is uncertain as there is only limited water resistance data in PAO based greases.

Some experimental formulations were made up comprising of the additives described above in a large batch of lithium complex grease. Initial screening showed that the appetite for the Riffel test was unclear. One formulation with a higher amount of salt water rust inhibitor failed the fretting wear test. A second formulation with much lower amount of the same salt water rust inhibitor failed the Emcor test. When a lower amount of an anti-wear and anti-fretting additives was used, the grease failed the fretting test, but when higher amounts were used, the grease failed both the Emcor and Riffel test. A lubricity aid was tested and was found to boost the Riffel and Emcor tests. Treat levels of the main components were optimized and a package and lubricity aid developed. A water resistance polymer need to be incorporated into the grease to stop the grease being washed out of the area where the water is introduced in to the test bearing. From this work two passes on the Riffel and Emcor tests were obtained and the formulation fixed. A bigger batch of grease was made but it failed the Emcor. By first pre-dissolving the polymer in a PAO fluid with a low kinematic viscosity at 100 °C (6 cSt or 8 cSt) or into an alkylated naphthalene, and then adding this pre-saponification to the batch, good passes were obtained in the Riffel test and some of the other key properties looked at.

The polymer, package and lubricity aid were incorporated into larger batches of greases and tested against the complete requirements. The final two grease formulations are in table 2

Grease Formulation		A	B
Base grease		#1	#2
Base oil grade	ISO VG	460	460
Base oil type	Report	100% PAO	PAO + AN
Additive package	wt%	5.0	5.0
Lubricity aid	wt%	2.0	2.0
Water resistant polymer	wt%	0.2	0.2
Thickener type	Report	Lithium complex	Lithium complex
Characteristic	-	Result	Result
Appearance	Smooth	Tan	Tan
NLGI grade	1.5	1.5	1.5

Table 2 – Final grease formulations

Test Results

The basic grease property tests are in table 3, the wear and SRV tests in table 4, and other reportable basic test data in table 5.

Characteristic	ASTM test	Specified Value	A	B
Dropping Point (°C)	D2265	Report	> 300	>300
Unworked penetration	D217		295	299
Worked 60 penetration	D217	290-320	309	303
Worked stability, Δ10k (% change)	D217	Report (≤ 10.0)	+7 (2.3%)	←
Worked stability, Δ100k (% change)	D217	Report (≤ 10.0)	+26 (8.4%)	←
Roll stability, 50 hours 80 °C, (% change)	D1831 Modified	Report Report	80 (25.7%)	100 (33.0%)
HT oil separation @ 60 °C (Weight%)	D6184	Report	0.7	←

Table 3 – Basic properties ← = test was not carried out because Grease A easily passed the requirements

Characteristic	ASTM test	Specified Value	A	B
4-Ball EP tester weld point (kg)	D2596	≥ 250	250	←
4-Ball EP tester LWI (kg)	D2596	≥ 30	63	←
4-Ball wear at 60 °C scar diameter (mm)	D2266	≤ 0.60	0.42	←
Fretting wear, mg loss	D4170	Report	2.6	4.6
SRV step load EP test 120 s step, 50 Hz, 60 °C, 1 mm stroke	D5706	≥ 600	1300	←
SRV friction and wear, 200 N, 80 °C 1.0 mm stroke, 50 Hz, 2 hours Wear scar width (mm) Coefficient of friction @ 2 hours	D5707	≤ 0.60 ≤ 0.120	0.45 0.115	0.54 0.111
SRV fretting wear, 100 N, 50 °C, 0.3 mm stroke, 50 Hz, 4 hours Wear scar width (mm) Coefficient of friction	D7594	Report	0.443 0.120	0.440 0.117

Table 4 Tribology tests ← = test was not carried out because Grease A easily passed the requirements

Characteristic	ASTM test	Specified Value	A	B
Water resistance rating 3 hours at RT	DIN 51807t1	1 max	1	←
Water spray off at 60 °C (%wt)	ASTM D4049	Report	71.0	87.8
Water washout at 60 °C (%wt)	ASTM D1264	2.0 max	2.4	2.8
Emcor test rating (1% NaCl solution)	ASTM D6138	1/1 max	0/0	0/1
Copper corrosion 100 °C, 24 hours	ASTM D4048	1b max	1b	←
Low Temperature Torque, 0 °C Starting mNm (g.cm) 0 °C Running mNm (g.cm)	ASTM D1478	Report	12.3 (125) 4.30 (0.42)	←
Low Temperature Torque, -40 °C Starting mNm (g.cm) -40 °C Running mNm (g.cm)	ASTM D1478	Report	499.1 (5089) 29.1 (296)	←
Flow pressure at -40 °C (hPa)	DIN 51805	Report	695	←
Oxidation pressure loss 500 hours 100 hours (kPa (psi)) 500 hours (kPa (psi))	ASTM D942	Report	17.2 (2.5) 51.0 (7.4)	←

Table 5 Other reportable test data ← = test was not carried out because Grease A easily passed the requirements

Having demonstrated good performance in all the tests to date, it was decided to schedule the remaining higher cost FE8 and Riffel tests. The data for in Grease A FE8 testing with DIN51819-2 type B ACB under test conditions of 80 kN load, 7.5 r/min, 60 °C, 500 hours (high torque very low speed) are in table 6, type C with TRB Grease A FE8 testing with DIN51819-2 – Type C TRB with 50 kN load, 75 rpm, monitored ambient temperature, 500 hours (high torque low speed) are in table 7. In table 8 the Riffel test results are shown for both greases.

Rolling Elements (Balls) Weight Loss (mg)			Cage Weight Loss (mg)		
Actual	Predicted	Requirements	Actual	Predicted	Requirements
30	$F_{w50} = 33.4$	$F_{w50} \leq 35$	67	$F_{k50} = 67.6$	$F_{k50} \leq 100$
36			68		
Inner Raceway Weight Loss (mg)			**Outer Raceway Weight Loss (mg)**		
Actual	Predicted	Requirements	Actual	Predicted	Requirements
7	$F_{IR50} = 7.0$	$F_{IR50} \leq 35$	34	$F_{OR50} = 30.0$	$F_{OR50} \leq 35$
7			25		

Table 6 FE8 ACB High torque low speed test results

Rolling Elements (Balls) Weight Loss (mg)			Cage Weight Loss (mg)		
Actual	Predicted	Requirements	Actual	Predicted	Requirements
4	$F_{w50} = 3.6$	$F_{w50} \leq 35$	43	$F_{k50} = 48.1$	$F_{k50} \leq 100$
3			52		
Inner Raceway Weight Loss (mg)			**Outer Raceway Weight Loss (mg)**		
Actual	Predicted	Requirements	Actual	Predicted	Requirements
10	$F_{IR50} = 11.1$	$F_{IR50} \leq 35$	8	$F_{OR50} = 9.7$	$F_{OR50} \leq 35$
12			11		

Table 7 FE8 TRB High torque load speed test results

IME Riffel Test	Specification	A	B
QJ212 four point contact bearing 70 kN alternating load at 9±1 Hz 1 million cycles 1% NaCl solution at 6 mL / min	Maximum wear depth, RD_{max} <10.0 µm	1.3	1.8
	Average wear depth, RD_{ave} < 3.0 µm	0.29	0.45
	Corrosion rating ≤ 2	1.0	1.0

Table 8 Riffel test results for greases A and B

Both Greases A and B passed the requirements for use in WT pitch and yaw bearings Summary and Conclusions Grease technologies have been combined to created fully synthetic lithium complex greases which pass all the basic requirements of pitch and yaw bearings A field trial is underway to test the grease under actual service conditions

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Preliminary Discussion on a Dynamic Grease Oxidation Test Based on Modified RPVOT

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Abstract:
Antioxidation capability of lubricating grease is one of several most important performance properties of the lubricant. Greases are generally fortified with suitable antioxidant or antioxidant combinations to extend the useful life of these lubricants in demanding applications, especially in very oxidative environment, such as in high temperature and high speed applications. While there are several existing test methods used in evaluating grease antioxidation feature and performance of antioxidant used, none seems to be ideal in getting a clear picture close to the reality in terms of grease oxidation in application, especially when information about grease dynamic and bulk oxidation is needed. The current paper will provide a preliminary discussion on a new grease oxidation test method. Instead of just measuring static and surface oxidation of the grease, this new test method will be based on a piece of existing test equipment used in the field; therefore the test equipment will be easily available. And it will also be able to measure dynamic and bulk oxidation of the grease tested. As it is first introduced to the grease field, the advantages and disadvantages of this test method will be discussed.

Introduction
Grease formulation is more of an art than an exact science. This is not to say there is no scientific guidance in formulating greases, rather it is to say the best practice might not necessary be using the most advanced materials available technologically. In other words, formulating grease is normally a balancing act. There are many factors to be considered in order to have a high performance grease which will be superb for the particular application intended while it can still be suitable for some of the other possible applications. Traditionally, such balancing will need to put grease performance, cost and safety and environmental concerns into consideration.
While cost, safety and environment concerns will continue to be major factors in grease formulation, the continued technological development in modern machinery, the demand on grease is more shifted towards higher performance, longer life and lower energy consumption. If we call performance, cost and environment concerns as an old balancing act, the modern grease formation will be a balancing act of higher performance, longer life and higher energy efficiency.
Either for developing greases with longer life capability in general or for formulating a grease targeted for a particular application in a severely oxidative environment, selection of a suitable combination of grease thickener, base oil and performance additives will be the key. Though longer life in grease normally will need newer oxidatively stable base oil derived from either synthetic fluid or mineral base oil from deep hydrogenation and isomerization, such as Group II+ and Group III base oils, suitable antioxidant which will match for these modern base oils is equally important. Therefore, during the process of developing and formulating a grease, there exists a need to measure grease's resistance to oxidation properly. As a consequence, numerous grease oxidation bench test techniques have been developed over the years. These grease

oxidation bench test techniques have helped grease formulator greatly not only in gaining a understanding of grease oxidation mechanism, but also in ways on how to further improve grease performance in resistance to oxidation both during development and in real life service.

Nevertheless, just like the task to find an ideal grease which will fit all potential applications universally is a mission impossible, none of the existing grease oxidation bench tests is perfect in providing full understanding or whole picture of grease oxidation. The deficiency in grease oxidation measurement is especially severe in terms of measuring dynamic oxidation and grease bulk oxidation instead of grease surface oxidation, due to the intrinsic property for grease as a semi solid ant its resistant to flow. The present paper will propose and discuss a new grease oxidation test method which will be able to measure dynamic and bulk grease oxidation, and it is based on a standard ASTM test method but with modification on test procedures, and also special preparation for the grease sample to be tested.

Discussion on Existing Grease Oxidation Tests

Several grease oxidation tests are wildly used in the measuring and evaluating grease oxidation resistance. These can be listed as follows.

"OPVOT" test: ASTM D942-15 Test Method for Oxidation Stability of Lubricating Greases by the Oxygen Pressure Vessel Method [1].

"PDSC" test: ASTM D5483-05(2015) Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry [2].

"Ruler" test: ASTM D7527-10 Test Method for Measurement of Antioxidant Content in Lubricating Greases by Linear Sweep Voltammetry [3].

"RSSOT" test: ASTM D8206-18 Test Method for Oxidation Stability of Lubricating Greases—Rapid Small- Scale Oxidation Test (RSSOT) [4]. (note: This test designed for fuels is ASTM D7545. For greases, it is a newly approved ASTM test method and it is not in the 2018 ASTM Standards Annual Book yet, but will be published in the 2019 Edition).

ASTM D942 and D8206 both are based on the principle of pressure vessel oxidation under oxygen pressure and measure grease surface oxidation under static conditions. The test results can be used as an indication for grease shelf live under storage. It has little relevance to grease oxidation in actual application which in most cases will involve grease dynamic and bulk oxidation.

ASTM 5483 measures how long antioxidant can last before auto-catalyzed severe oxidation will kick in, which is manifested by oxidation Induction time. It is a wonderful tool in comparing antioxidant performance at a specific temperature, but then again, it only measures static oxidation and surface oxidation since the grease sample is only presented as a thin film during the test.

ASTM D7527 will be able to measure the concentration or remaining concentration of couple type of typical antioxidants in the grease. But by the nature of this test, it is an analytical test for antioxidant concentrations instead of as an oxidation test by itself, though we normally can consider this test as related to grease oxidation, and this is true under the understanding that grease oxidation resistance can be improved with a suitable antioxidant. The other deficiency of this test is that it will not be able to differentiate the performance difference for members of the same family of antioxidant, either aminic or phenolic.

From above mentioned grease oxidation tests, it is easy to see that none of the existing test methods will be able to provide a measurement of grease oxidation in a dynamic setting or grease oxidation resulted in its bulk property changes, in other word, grease dynamic oxidation and grease bulk oxidation, these are probably more relevant to grease oxidation in actual applications.

On the other hand, varies grease lubricated bearing life tests can be considered as some sort of grease dynamic and bulk oxidation tests in a sense. But the test result of bearing life is a reflection of many factors. Grease oxidation, grease soap structure shearing down and decomposition, load condition, and subtle difference in mechanical and physical deviation of each bearing, to just a few, all will have an influence on the test result of bearing life measurement. This is to say, that bearing life can be affected by oxidation of grease inside the bearing, but grease oxidation is not the only factor to determine bearing life. Therefore, most bearing life tests, cannot be considered as a pure grease dynamic oxidation and grease bulk oxidation test.

Modified RPVOT test for measurement of grease oxidation

Modified rotary pressure vessel oxidation test "RVPOT" for grease was first introduced by ELGI Railroad Grease working group in 2012 [5]. It is based on standard test method of ASTM D2272 Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel[6] with modification on grease sample preparation to make it suitable for the test. A grease sample (20g) is diluted with silicone oil (30g) to make the grease into a liquid pourable mixture which would be suitable for testing. The main concerns in this modified RPVOT test for grease are sample manipulation with dilution and silicone oil impact. Silicone oil though considered as relatively stable in oxidation compared to a typical grease, it has its own issues. Silicone oil is not only a slip hazard if spilled, but it is intrinsically insoluble in most greases with petroleum oil or other synthetic fluid as base oils. Therefore, mechanically how to mix the grease into silicone oil might have heavy influence on how grease is distributed in the silicone oil. One might speculate that different morphology of grease dispersion in the silicone oil might lead to different test result, since the total grease surface area might be different in a different grease dispersion.

Nevertheless, the principle of this previous modified RPVOT test for grease pointed to a possibility of using this modified RPVOT test method as a test method for dynamic and bulk grease oxidation.

Based on this previous trials in using modified RPVOT for grease oxidation stability testing, the present new modified RPVOT test for grease will make couple changes. Firstly, in order to avoid the issues come with the silicone oil, a low viscosity PAO, such as PAO 4 or PAO 6, will be used instead. PAO base oil is generally more stable in oxidation compared to a base grease. In a situation when there is a small amount of antioxidant present, PAO will be far more stable compared to base grease or the finished grease containing antioxidant. In other word, grease and its base oil contained probably will be oxidized much easily compared to PAO, therefore PAO's contribution to oxygen consumption probably is minimal. PAO will be compatible with most greases except probably silicone greases and PTFE greases. When a typical NLGI grade 2 grease is mixed with PAO at 50: 50, a pourable liquid mixture will be available. This liquid mixture will be uniform, and it will just look like a liquid grease about the consistence of a NLGI grade 00 grease.

Secondly, water will be removed from the test. The standard RPVOT test is originally designed for measuring steam turbine oil oxidation, the presence of water in the steam turbine oil is probably inevitable. For grease lubrication, the presence of large amount of water is less likely. Also water will have more strong interaction with grease thickener system, which will make the oxidation mechanism in grease more complicated than necessary, since the intension is to measure grease oxidation not the water resistance of the grease.
In summary, the new modified RPVOT test for grease will use a low viscosity PAO to dilute the grease at 50:50 ratio to turn it into a liquid pourable mixture. Then use the standard RPVOT test machine and test conditions to run the test. But considering the uniqueness of grease, water will be removed from the test but with copper coil still present as oxidation catalyst.

Test Results

This new modified RPVOT test were used to evaluate several different antioxidants for their effectiveness in improving grease oxidation resistance. The base grease used is a NLGI grade 2 lithium complex base grease with paraffinic base oil. The PAO diluent oil used is a 6 cSt. The grease and PAO ratio is 50:50. The modified RPVOT test results are listed in following table. The AO treat rate listed is referred to AO concentration in the diluted liquid mixture.

AO Treat Rate (wt %)	0.25	0.5	0.75	1
Mod. RPVOT with AO 1 (min)	42	78		160
Mod. RPVOT with AO 2(min)	82	116		116
Mod. RPVOT with AO 3 (min)			113	149
Mod. RPVOT with AO 4 (min)	41.8	104		104
Mod. RPVOT with AO 5 (min)			114	144

Table: Modified RPOVT test for grease oxidation with various antioxidants The same test data were also plotted. See figure below.

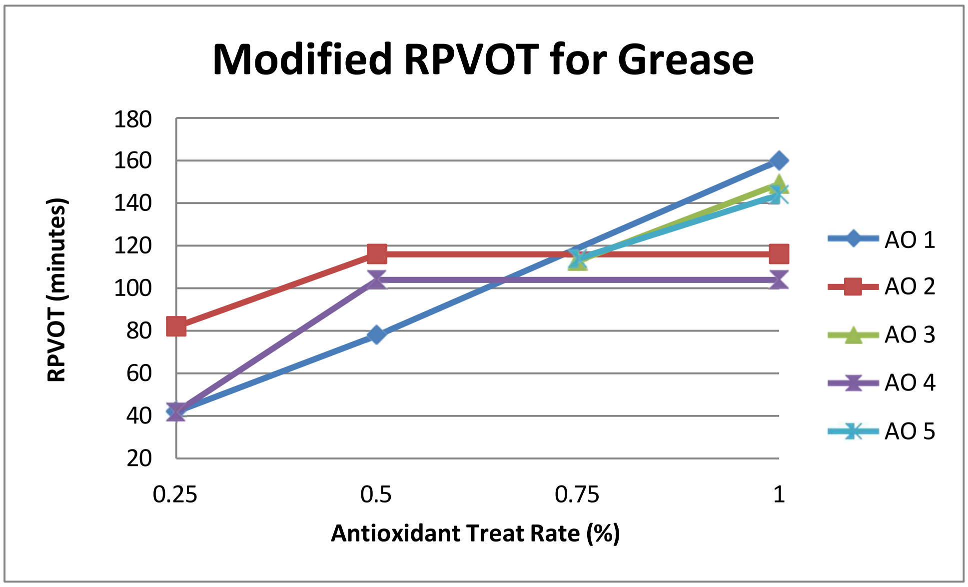

Figure: Modified RPOVT test for grease oxidation with various antioxidants

Discussion and Conclusion

This new test method is still at early stage of development. We only have limited test data to report. But it is obvious that the test method can differentiate varies AO performance in the same base grease. Of course, it can also tell the performance difference when same AO is used at different treat level.

The advantages of the test is that it can measure grease oxidation in a dynamic mode, and since the diluted grease mixture is constantly churning inside the pressure vessel, the oxidation process will not be just limited to surface oxidation. Therefore, it is believe that at present, this is the only grease oxidation test method that will be able to measure both dynamic and bulk oxidations, two very important features characteristic to grease oxidation in real applications.

The disadvantages of this test are that it involves grease sample manipulation and dilution. How to make sure that each dilution with PAO will be made efficiently and repeatable is still a subject for further discussion (maybe propose a standard mixing procedure like mix the grease with PAO in a Hobart mixer for 30 minutes?). Also if the grease is very stable in oxidation, the slow drop of oxygen pressure in the rotating vessel might make the test repeatability poor.

Further work related to this new modified RPVOT test for grease is definitely needed. Correlation of test results of this test method with other existing grease oxidation test methods will help to further understand its uniqueness and advantages. Hopefully, the next paper on this new modified RPVOT test can provide more insight into grease oxidation, especially when dynamic and bulk grease oxidation is of concern.

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Application Research Of Cpu-A Premade Thickener

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ABSTRACT

Based on isocyanate, organic amine, carboxylate soap and in a medium of selected solvent, novel thickener CPU-A was prepared. Physical and chemical properties of greases made from various bases tock thickened by it were tested, and application of it in grease-making process was also studied. It concludes that good temperature tolerance, well mechanical stability and colloidal stability, fair water resistance and lubricity are obtained by greases made from CPU-A thickener. Versus generic lithium grease, the greases are equivalent in physical and chemical properties, and with better lubricity. Manufacturing greases by CPU-A also benefits with lower cooking temperature, less processing facilities ,and less manufacturing cost.

Keyword: premade, thickener, grease

Introduction

Lithium-based grease is the most produced grease globally, based on statistics by NLGI, total global output of grease reached 1,173,500 ton, wherein lithium based grease amounted to 630,110 ton, accounting for 53.7% of total grease output. And total output of grease in India and Indian peninsula area in 2017 was 81,588 ton, wherein lithium based grease was 61,422 ton, accounting for 75.28% of total grease output. That shows the significance of lithium based grease in grease industry.

It deserves concern that recent years, rapid development in new-energy auto industry results to price of lithium hydroxide rising sharply, which brings producers and customers more cost burden, and limits its distribution and application also. To cope with such situation, some producers are eagerly looking for alternatives for lithium based grease. For this reason, here we prepared a novel thickener: premadethickener CPU-A, short as CPU-A.

Making grease from premade thickener characterizes with many benefits: compatibility with base stock, short processing period, high manufacturing efficiency, no sophisticated facilities needed, getting rid of producing waste of water oil mixture, avoiding handling dangerous chemical substance such as hydroxide and isocyanate. Hence making grease by premade thickener is attracting more and more concerns from grease manufacturers.

In this article ,a novel premade thickener CPU-A is presented, which is made of isocyanate, organic amine and soap of fatty acid, reacting and complexing in selectedsolvent. The flow chart in figure 1.

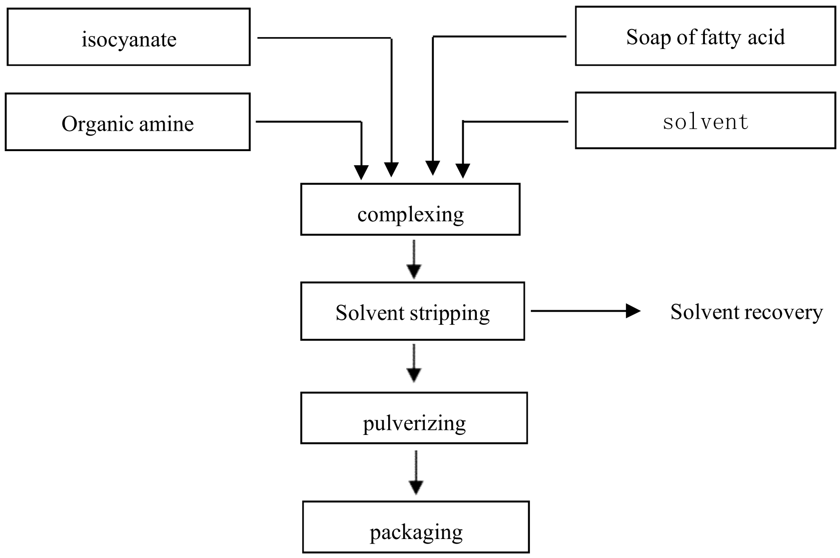


Figure 1 flow chart of preparation of premade thickener CPU-A

This article focuses on testing properties of greases with several types of basestock thickened by CPU-A and comparing them with that of lithium grease.

Experiment

CPU-A and lithium based thickener are used to thicken several types of base stock to prepare greases, thickener content is set to 11%(wt), then their physical and chemical properties are tested to evaluate and compare thickening ability, temperature resistance, mechanical stability, colloidal stability, water resistance andlubricity.

1.1 experimental materials

1.1.1 thickener

(1) some main properties of CPU-A premade thickener listed in table 1.

Table 1.Main physical and chemical properties of CPU-A

ITEM	TYPICAL DATA	TEST METHOD
Appearance	White powder	visual
Odor	No offensive smell	Olfactory
Apparent Density，Kg/m3	0.27	ASTM D1298
Granularity, um median diameter(D50)	8.21	ISO 13320:2009
median diameter(D90)	22.63	
median diameter(D100)	53.12	

(2) Raw materials for lithium based grease are 12-hydroxystearic acid, lithium hydroxide monohydrate, water.

1.1.2 Base stock

For further evaluate CPU-A's performance in application, generally used base stock types are selected including paraffin base, naphthenic base, and PAO, their properties are listed in table 2.

Table 2 Typical properties of selected base stock

Item			Base stock			Test method
	500N	KN4010	150BS	PA010	PA040	
KV，@100℃，mm^2/s	10.42	9.927	32.09	10.29	40.26	ASTM D445
KV，@40℃，mm^2/s	90.64	132.7	553.3	62.49	405.8	ASTM D445
VI	96	21	87	153	149	ASTM D2270
Flash point(COC),℃	255	220	281	259	289	ASTM D92
Pour point,℃	-25	-25	-20	-48	-45	ASTM D97

1.2 Grease making process

Grease making process utilizing CPU-A listed in figure 2, that of lithium basedgrease listed in figure 3.

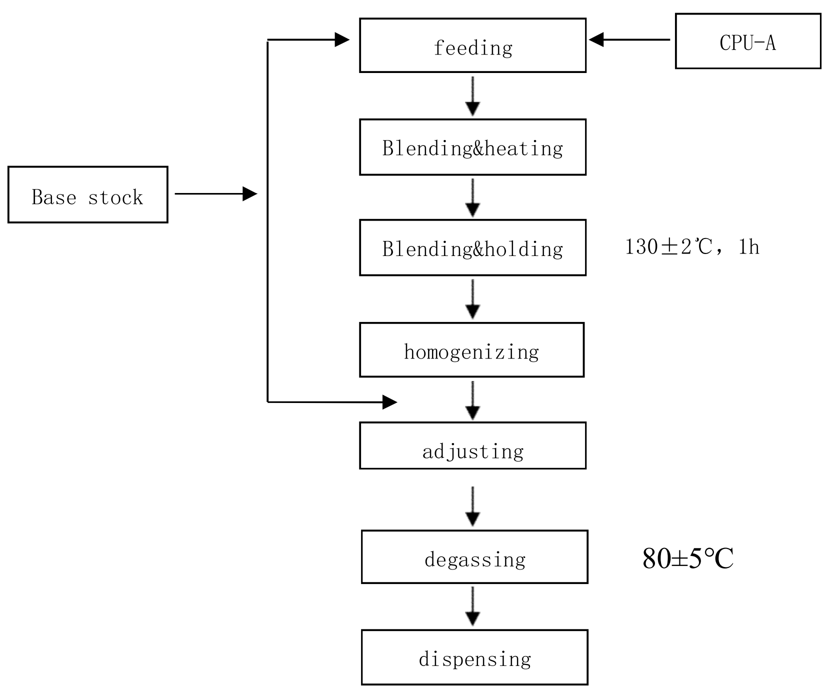


Figure 2. Grease making process flow chart utilizing CPU-A

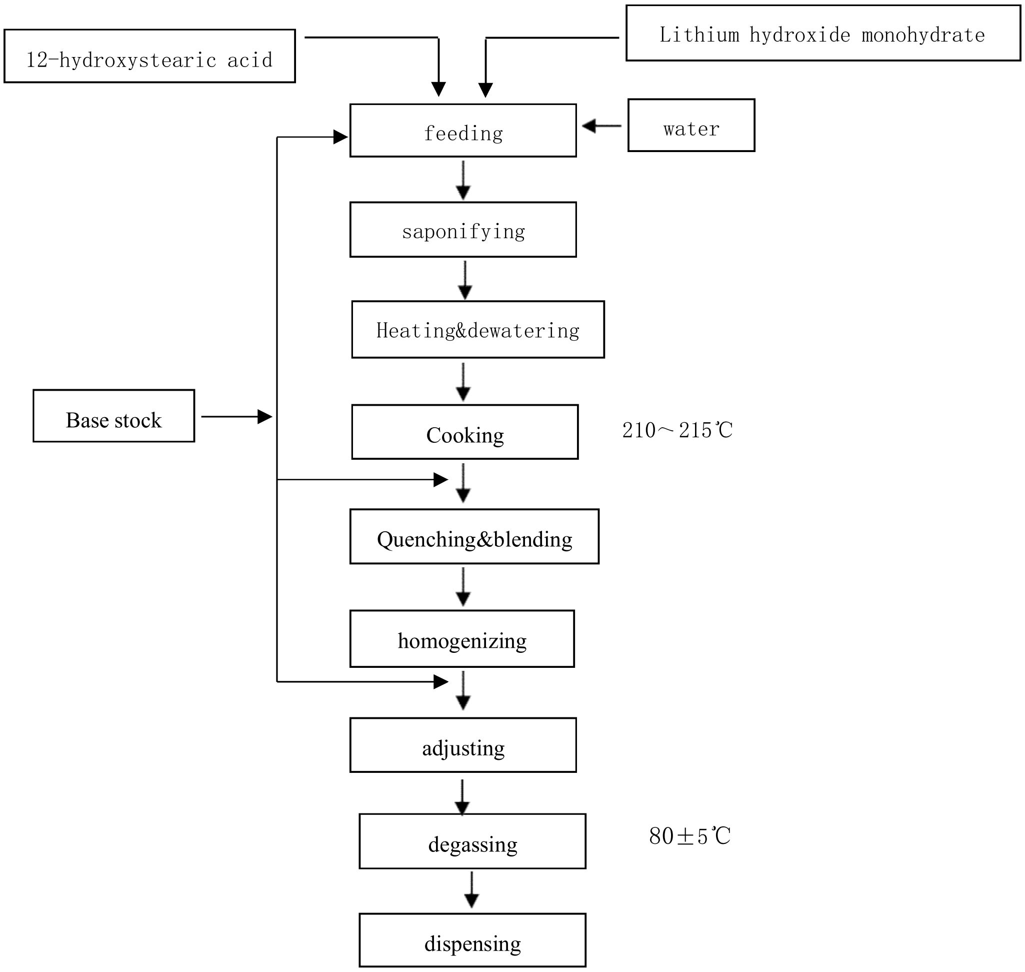


Figure 3. Process flow chart of lithium based grease

1.3 test method

1.3.1 appearance

Appearance: visual.

1.3.2 thickening ability

Penetration: per ASTM D217.

1.3.3 heat stability

Dropping point: per ASTM D566.

1.3.4 colloidal stability

Mesh bleeding: per ASTM D6184.

1.3.5 mechanical stability

Prolonged worked penetration change ratio: per ASTM D217.Roll shear change ratio: per ASTM D1831.

1.3.6 water reistance

Water washout: per ASTM D1264.

1.3.7 lubricity

PB value: per ASTM D2596.

Wear scar diameter: per ASTM D2266.

2 Results and discussions

Utilizing lithium base thickener and CPU-A thickener respectively to thicken above 5 base stock in table 2 , 10 grease samples are prepared. Physical and chemical properties are listed in table 3.

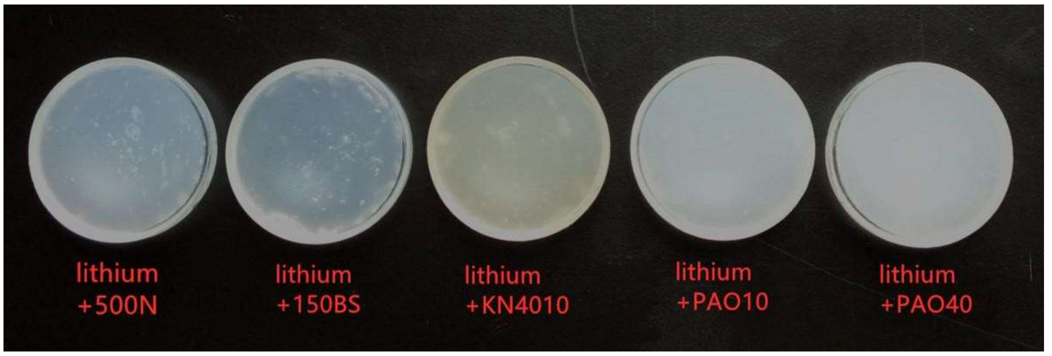
Table 3 Test results of the grease samples

Base stock	500N		150BS		KN4010		PAO10		PAO40	
Thickener type	lithium	CPU-A	lithium	CPU-A	lithium	CPU-A	lithium	CPU-A	lithium	CPU-A
Appearance	Off-white	Off-white	Off-white	Off-white	yellowish	yellowish	Off-white	Off-white	Off-white	Off-white
Drop point,℃	201	194	203	194	202	198	198	189	199	190
Worked penetration,0.1mm	262	274	228	267	227	232	295	298	290	286
Prolonged worked penetration(10^5 strokes)change,%	10	11	13	13	12	11	11	13	10	12
Roll shear change,%	9	12	11	11	10	12	9	11	7	9
Mesh bleeding(100℃，24h),%	3.9	1.4	1.5	1.3	1.8	1	4.6	2.4	4.2	1.8
Water washout(38℃，1h),%	0.75	0.50	0.50	0.50	1.75	1.50	2.25	2.0	1.50	1.50
EP(4-balls),P_B/N	461	530	530	618	392	490	431	618	667	667
4-balls,wear scar diameter，mm	0.659	0.485	0.589	0.479	0.623	0.441	0.603	0.442	0.704	0.586
Corrosion protect(T_2 copper strip,100℃,24h)	No green or black stain									

Followed are comparisons and discussions on test results of grease samples in table 3.

2.1 Appearance

Appearances of 10 prepared grease samples are shown in figure 4. It shows that the appearances of greases made of 2 type of thickeners are almost the same, without substantial difference.



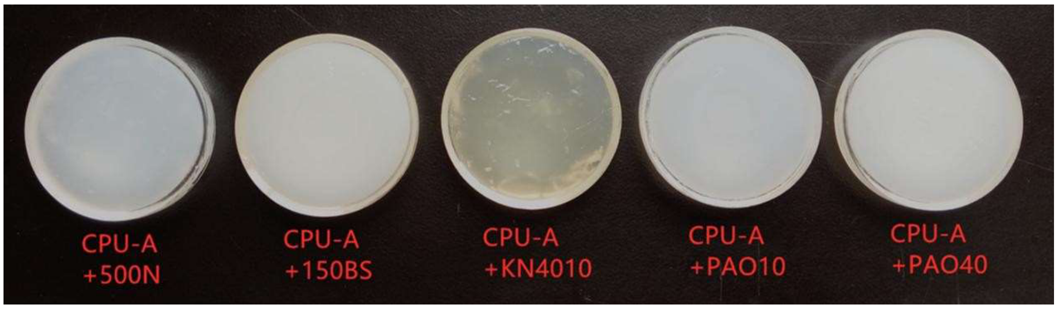


Figure 4. Appearance and texture comparison

2.2 Thickening ability

Comparison of worked penetration of greases made of 2 type of thickeners ischarted in figure 5. The figure shows except 150BS which somehow responds differently, the 2 thickeners exhibit similar thickening ability to left 4 base stocks.

Figure 5. Comparison of worked penetration

2.3 Heat resistance

Comparison of dropping point is charted in figure 6. The figure shows lithium based greases have higher dropping point than that of CPU-A, but the margins are notsignificant, generally below 10℃. The dropping points of greases made of CPU-A approaching 190℃ or even higher exhibits good heat resistance.

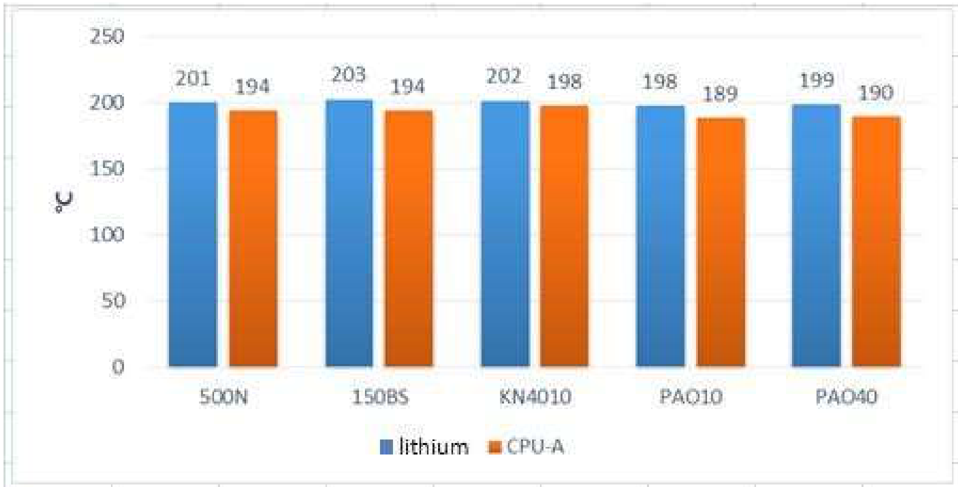


Figure 6. Comparison of dropping point

2.4 Colloidal stability

Comparison of mesh bleeding test data are shown in figure 7. The figure shows greases made of CPU-A exhibits much less bleeding than that of lithium based greases, generally below 2.5%, which shows good colloidal stability.

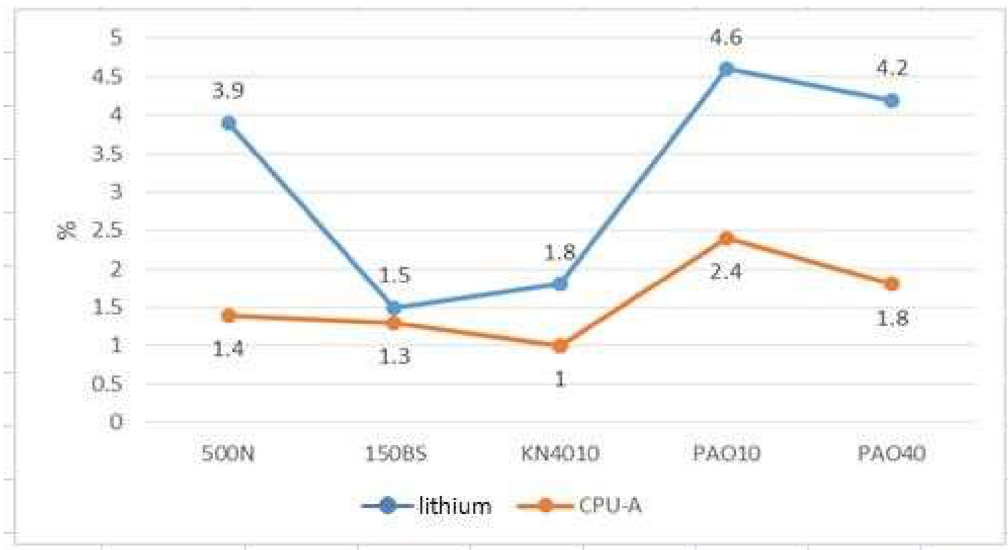


Figure 7. Comparison of mesh bleeding

2.5 Mechanical stability

Shear test data are charted in figure 8. The figure shows when thickening the 5 base stocks ,greases made of lithium base thickener and CPU-A thickener perform well prolonged worked penetration test and roll shear test, test results are all around 10%. No obvious differences are noticed, which means good mechanical stability.

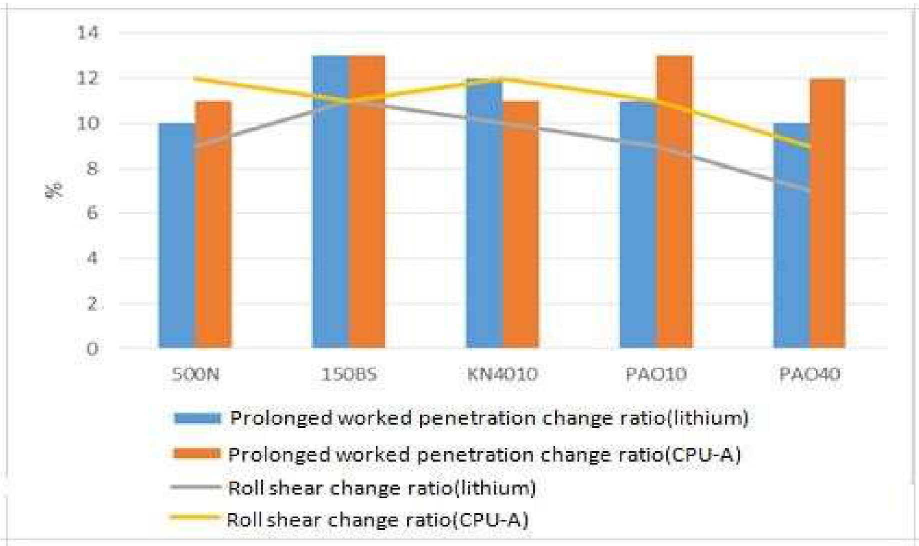


Figure 8. Comparison of shear stability

2.6 Water resistance

Water resistance test data are charted in figure 9. The figure shows utilizing whether lithium base thickener or CPU-A to thicken the 5 base stocks, the washout data of the greases are quite close, generally below 2.5%, which indicates good waterresistance.

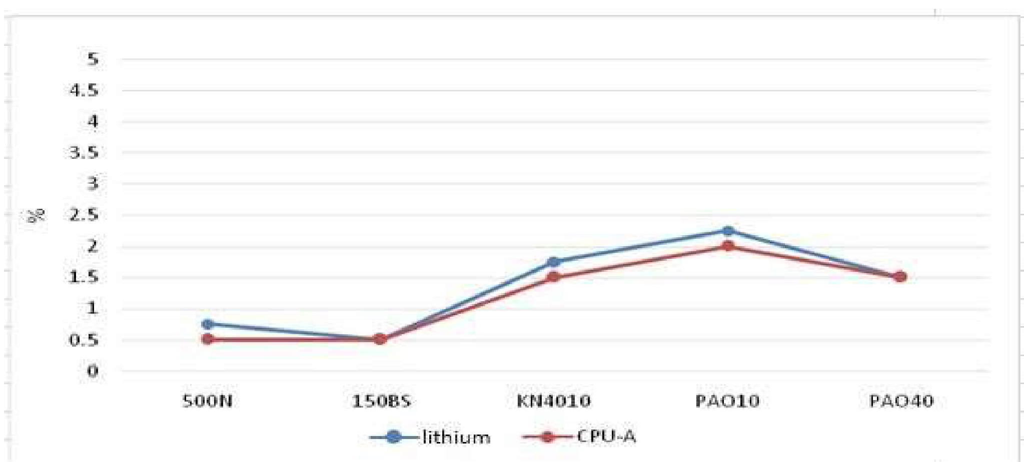


Figure 9.Comparison of water resistance

2.7 Lubricity

PB and wear scar diameter data tested by 4-ball tester of greases made of 5 basestock thickened by lithium base thickener or CPU-A are shown in figure 10 and 11.

The charts shows greases made of CPU-A demonstrate higher PB and smaller wear scar diameter than that of lithium based greases. And their wear scar diameters are within 0.6mm which indicates better lubricity.

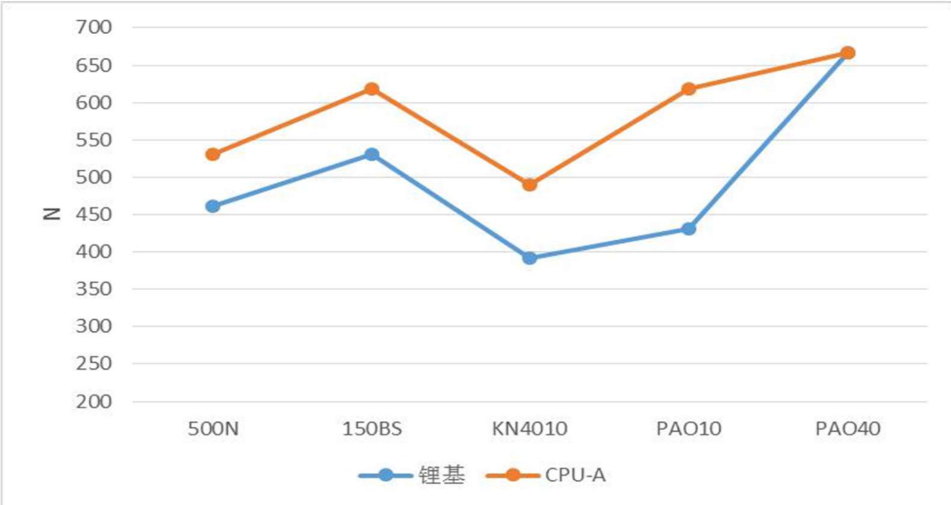


Figure 10. comparison of PB

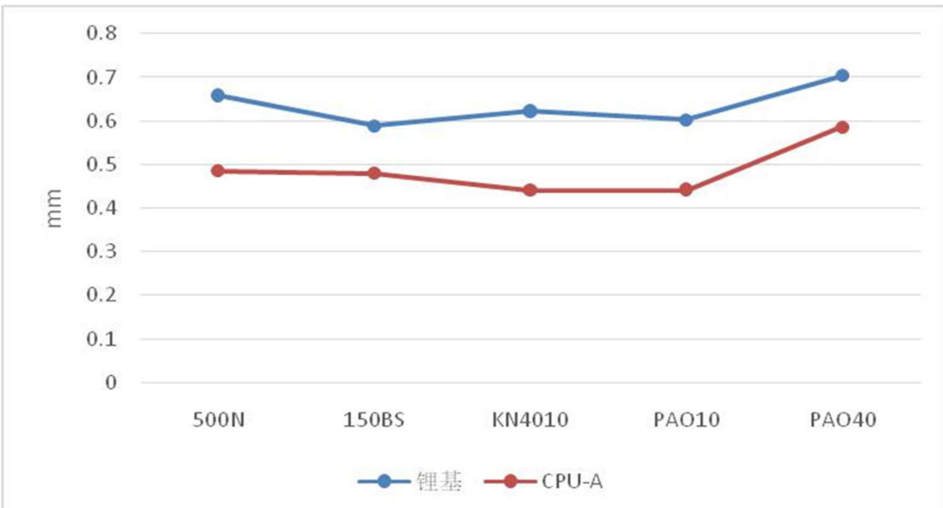


Figure 11. comparison of wear scar diameter

3. Conclusion

(1) Cooking temperature is only 130 when utilizing CPU-A premade thickener to make grease, furthermore there are no oil mist or water vapor emission, and no dangerous chemicals contact, so it facilitates grease-making with safety and environment-friendship.

(2) CPU-A can be utilized to thicken generally used bae stock such as paraffin base, naphthenic base and PAO efficiently.

(3) Grease made of CPU-A demonstrates comparable performance to that of lithium base grease in heat resistance, mechanical stability, water resistance and colloidal stability and better lubricity.

(4) It suggests that greases made of CPU-A are able to work where generic lithium applied.

Alkylated Naphthalenes for High Temperature Applications

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Abstract

Alkylated naphthalenes are multifunctional, high performance co-basestocks available in a diverse ISO viscosity range from 22-193 cSt. They are typically incorporated into oil and grease formulations replacing a portion of a Group II, Group III or PAO base oil. Most alkylated naphthalenes also have approvals for incidental food contact.

This paper highlights some selected results for high temperature applications, including chain lubrication, plywood manufacturing, and grease, showing how alkylated naphthalenes extend the lifetime of high-performance lubricants by improving their thermal and thermo-oxidative stability, decreasing their volatility, and providing excellent dispersancy and varnish control for system cleanliness.

Introduction

Alkylated naphthalenes are classified by the American Petroleum Institute (API) as part of the Group V base oil category. However, alkylated naphthalenes are rarely use as the sole base fluid. They are typically incorporated into lubricant formulations replacing a portion of a Group II, Group III or PAO base oil. This is done to extend the lifetime of high-performance lubricants by:

- Improving the thermal and thermo-oxidative stability
- Enhancing the solubility and response of additives
- Imparting seal swell
- Decreasing volatility
- Providing varnish control for system cleanliness

Naphthalene Ring

As shown in Figure 1, alkylated naphthalenes consist of two fused six-membered rings with the alkyl groups attached. It is the electron-rich ring structure that imparts these performance enhancing properties, notably to non-polar fluids. It is the ability of the naphthalene ring to absorb energy, resonate, and then disperse that energy, much like antioxidants do, that gives alkylated naphthalenes their inherent excellent thermal and thermo-oxidative stability. The naphthalene ring also provides the right balance of polarity for imparting additive solubility, seal swell, and varnish retardation.

Alkyl Chain

It is the alkyl groups that control most of the physical characteristics of alkylated naphthalenes. In Figure 1, R_1 to R_8 are independently a linear or branched alkyl group or hydrogen. By carefully controlling the type of alkylating agent used and the degree of alkylation, the chemical and physical properties of alkylated naphthalenes can be significantly influenced.

Products

For flexibility in designing lubricants for a variety of applications, alkylated naphthalenes are available in a diverse viscosity range from about 22-193 cSt a 40°C and about 4-20 cSt at 100°C. As show in Table 1, in general, as the viscosity increases: viscosity index increases, aniline point increases (which means the polarity decreases), volatility decreases significantly, and the pour point and the flash point increase.

Applications

These products are used by lubricant formulators to meet demanding requirements in a wide variety of applications, including:

- 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 (Rust and Oxidation) Oils
- Screw Compressor Oils
- Heat Transfer Oils
- Windmill Oils
- Conveyer Belt Oils for Presses
- Automotive and Industrial Greases

High Temperature Chain Lubrication

High temperature chain lubrication is a prime example of how alkylated naphthalenes can extend the lifetime of a high temperature lubricant by reducing the volatility to retain the fluid longer and by imparting thermal and thermo-oxidative stability to inhibit viscosity increase and varnish formation.

Chain lubricants are used in many applications where the temperatures can range from less than 150°C to greater than 600°C, including:

- Transportation
- Agriculture
- Mining
- Bakeries, where approvals for incidental food contact are required
- Automotive coating plants
- Beverage can-coating plants
- Manufacturing of plywood, textiles, ceramics, and plastic films
- Kilns for making pottery, brick, and cement

Alkylated naphthalenes are typically used in applications where temperatures range up to 300°C.

Typical chain lubricant formulations contain a thickener, tackifier or adhesion improver, such as poly isobutylene (PIB), and a viscosity index improver. They may also include antioxidants, usually combinations of aminics and phenolics, various EP/AW additives, corrosion inhibitors to protect iron and copper, and a defoamer.

Testing was conducted to determine if the addition of alkylated naphthalene to various chain lubricant formulations would help with the high temperature performance. In a simple test, three grams of the test fluid were placed in an aluminum pan, and the sample was heated in an oven at 260°C for 8 hours. At the end of 8 hours, the evaporation loss and condition of the fluid were determined.

Table 2 shows how the addition of AN-19 alkylated naphthalene to a polyol ester (POE), which is recommended for high temperature chain lubricants, reduced the evaporation loss to retain the fluid longer. Both the polyol ester alone and the ester with 3% of a 50:50 antioxidant blend of alkylated diphenylamine and phenyl-alpha naphthylamine resulted in 94% evaporation loss. Replacing 20% of the polyol ester with the alkylated naphthalene significantly reduced the evaporation loss to 71%. The addition of the 3% antioxidant blend had essentially no effect on the evaporation.

Table 3 shows that the evaporation loss of AN-19 alone at these test conditions was only 43%, so for the polyol ester containing 20% of the AN-19, the theoretical evaporation loss is 84%. However, the observed evaporation loss was 71%, indicating that there is a synergy helping to reduce the evaporation loss and retain the fluid longer.

Another formulation was tested, as shown in Table 4, where 12% of the polyol ester was replaced with PIB thickener and where again 3% of the antioxidant blend was added. The addition of PIB had no effect on the evaporation loss, which was essentially the same as the polyol ester alone at 94% loss. Again, replacing 20% of the polyol ester with alkylated naphthalene significantly reduced the evaporation loss to 69%, and the 3% antioxidant blend had no effect. It was also observed that the addition of the PIB to the polyol ester with no alkylated naphthalene (Blends 5 and 6) resulted in hazy fluids, while the addition of the 20% alkylated naphthalene eliminated the haze, resulting in clear solutions.

Before aging, the fluids all flowed easily. After aging at 260°C for 8 hours, all the samples that did not contain AN-19 resulted in a thin, hard varnish that was not self-healing when scratched. An example is shown in Figure 2. However, all the samples that did contain AN-19 resulted in less evaporation leaving thicker, and therefore darker, samples that remained fluid and functional. Figures 3 and 4, respectively, shows that the samples containing the AN-19 were self-healing when scratched and flowed after aging.

Chains were also dipped in the 100% polyol ester and the ester containing 20% AN-19 and then allowed to dry overnight. The chains were then pushed into an accordion shape, baked for 8 hours at 260°C, and then their post-bake hanging performance was observed. As shown in Figure 5, the chain on the left that was lubricated with 100% polyol ester was covered in solid varnish at the end of the test, and the chain remained frozen in place when hung. The chain on the right that was lubricated with the polyol ester containing 20% AN-19 alkylated naphthalene was covered in a viscous liquid at the end of the test that continued to lubricate, and the chain fully extended within 2 seconds when hung.

Plywood Manufacturing

A field example of a commercial conveyer belt oil containing AN-19 also resulted in excellent system cleanliness. When used for the first time in a press, the alkylated naphthalene dissolved the old deposit on drive roller friction liners that had formed from the oxidation products of the previously used oil.

In Figure 6, the pictures on the left show the friction liners with heavy deposit from the previously used oil. The pictures on the right that were taken 6 months after using the AN-19 containing oil show that the alkylated naphthalene removed the deposit, completely cleaning the friction liners. This caused the oil to darken. But when the darkened oil was exchanged for fresh oil, the formation of deposit and the darkening of the oil did not reoccur. It was also noted that this significantly reduced unwanted noise, vibration and wear of the equipment, and greatly reduced maintenance cost.

Greases

Three NLGI #2 greases made using lithium 12-hydroxystearate, lithium complex, and aluminum complex with 10 cSt PAO containing various amounts of alkylated naphthalene were evaluated.

<u>Lithium 12-hydroxystearate</u>

Lithium 12-hydroxystearate greases made with AN-15 and PAO of a similar viscosity were evaluated. The grease made with the alkylated naphthalene had several improved properties over the grease made with the PAO, as shown in Table 5. The grease made with AN-15 required less thickener – 7% compared to 12% for the PAO grease.

Less thickener can result in improved low temperature properties. The alkylated naphthalene grease was also more transparent than the PAO grease. This can be seen in Figure 7 and is probably because the alkylated naphthalene acts as a bridging solvent, reducing the opaqueness of the grease. The AN-15 grease was also a smoother grease than the PAO grease probably because the alkylated naphthalene acts as a highly effective dispersant. The AN-15 grease also resulted in superior thermal gravimetric analysis and PDSC (Pressurized Differential Scanning Calorimetry) performance, liberating very small amounts of heat.

PDSC (ASTM D5483) testing was also conducted using greases made with lithium 12-hydroxystearate thickener and PAO containing 10% and 50% AN-15. In this test, 2 mg of grease were placed in an aluminum test pan and the temperature was ramped at 100°C/min to the test temperature. Then the sample was allowed to equilibrate at the test temperature for 2 minutes. The oxygen valve was opened, and the system was pressurized to 500 psi within 2 minutes. When equilibrated, the oxygen was adjusted to a flowrate of 100 ml/min. The oxidation induction time is measured from the time when the oxygen valve is opened. Figure 8 shows the temperature ramp to the test temperature, the 2-minute equilibration, and the opening of the oxygen valve, which always causes a spike.

Figure 9 shows PDSC test results at 180°C. The temperature ramp, the 2-minute equilibration, the oxygen valve opening, and the spike can clearly be seen followed by whatever happens afterwards. The grease made with 100% PAO oxidized immediately and quickly. Adding 10% AN- 15 to the PAO imparted oxidation resistance to the grease. And adding 50% alkylated naphthalene to the PAO imparted significant oxidation resistance making the grease completely stable and equivalent to the grease made with 100% alkylated naphthalene.

Norma Hoffman (ASTM D942) oxidation testing was also conducted using the lithium 12-hydroxystearate greases. In this test, five glass dishes are filled with 4 grams of test grease and placed in a pressure vessel. The vessel is sealed and pressurized to 110 psi with oxygen and then placed in a bath held at 99°C. The pressure in the vessel is recorded at various times throughout the test.

As shown in Figure 10, the Norma Hoffman testing showed the same results as the PDSC testing. The grease made with 100% PAO was the least stable and oxidized immediately and quickly. Adding 10% AN-15 to the PAO imparted oxidation resistance to the grease. And adding 50% alkylated naphthalene to the PAO imparted significant oxidation resistance making the grease very stable.

Lithium Complex

A fully additized lithium complex grease made with 30% AN-19 had improved properties over the grease made with 100% PAO. The greases contained 3.35% of an additive package consisting of calcium sulfonate, alkylated diphenylamine antioxidant, sulfurized olefin / fatty oil, zinc dithiophosphate, and a tolyltriazole derivative. The grease made with the alkylated naphthalene showed superior PDSC performance at 200°C, resulting in an increased induction time and reduced heat flow, as shown in Figure 11. The grease containing the alkylated naphthalene also had no negative effects on other grease properties, including cone penetration, four ball weld and wear, copper corrosion, and water stability, as show in Table 6.

Aluminum Complex

PDSC testing was also conducted at 180°C comparing aluminum complex greases made with all PAO base fluid, 10% AN-19, and 20% AN-19, as showed in Figure 12. All the greases contained 0.5% alkylated diphenylamine antioxidant. The greases made with the AN-19 additions showed superior thermo-oxidative resistance, resulting in increased induction times and reduced heat flows.

Conclusions

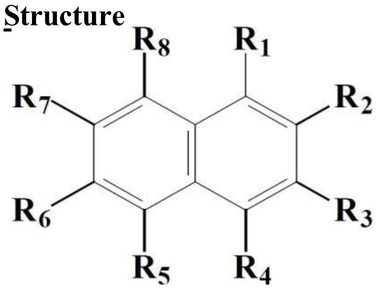
Alkylated naphthalenes are Group V fluids that are available in a diverse viscosity range for flexibility in designing high performance oils and greases for a variety of applications. They are typically incorporated into lubricant formulations replacing a portion of a Group II, Group III or PAO base oil to extend the lifetime and performance.

For the high temperature chain application, the addition of alkylated naphthalene resulted in less evaporation loss, sample clarity, and superior varnish control that allowed the fluids to remain liquid and continue to lubricate.

In the commercial plywood manufacturing application, the alkylated naphthalene containing oil removed heavy deposit that formed from a previously used oil and inhibited subsequent formation.

For the various greases made using different thickeners, adding alkylated naphthalene to the PAO base oil imparted several improvements, including superior thermo-oxidative stability, less required thickener, improved transparency, and a smoother texture.

Figure 1: Alkylated Naphthalene Structure



The core naphthalene system consists of two fused six-membered rings with an electron rich conjugated **π** system.

R_1 to R_8 are independently a linear or branched alkyl group or hydrogen.

Table 1: 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-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

Table 2: 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%.

* Priolube 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.

Table 3: 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%

Table 4: Reduction of Evaporation Loss to Retain Fluid

	88% POE 1963* 12% PIB 950	85% POE 1963 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%.

Figure 2: Varnished Blends Without Alkylated Naphthalene

The samples without AN-19 created a thin, hard varnish on the metal surface and were not self-healing when scratched.

Figure 3: Alkylated Naphthalene Blends After Aging

The samples that contain AN-19 showed an increase in viscosity after being heated but were still fluid and self-healing when scratched.

Figure 4: Alkylated Naphthalene Blends After Aging

The samples that contain AN-19 flowed after aging.

Figure 5: Extended Service Life of a POE Containing 20% AN-019

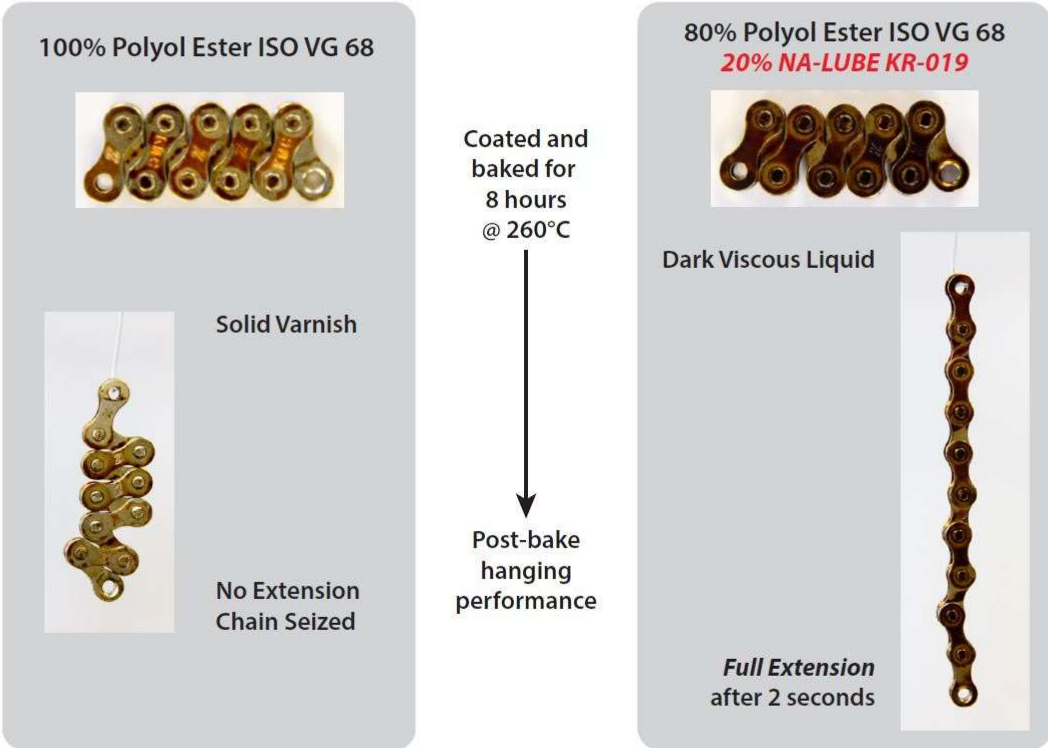


Figure 6: Removal of Deposits formed from a Previously Used Oil

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

Table 5: AN-15 vs. PAO 10 in Lithium 12-Hydroxystearate Grease

	PAO 10 (88%) Li 12-OH Stearate (12%)	AN-15 (93%) Li 12-OH Stearate (7%)
Color / Appearance	Tan / Opaque	Amber / Transparent
P (0) P (60) P (10K) P (100K)	275 273 309 350	285 288 335 366
Oil Separation	4.1%	2.8%
Dropping Point	202ºC	200ºC
Viscosity @ -40ºC	4.0 x 106 mPa.s	6.6 x 106 mPa.s
TGA	233ºC	304ºC
PDSC (500 psi O_2, 210ºC)	400 W/g after 3.7 minutes	5 W/g after 5 minutes

Figure 7: Grease Color / Appearance

Alkylated Naphthalene advantages:

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

Figure 8: PDSC ASTM D5483 Explanation

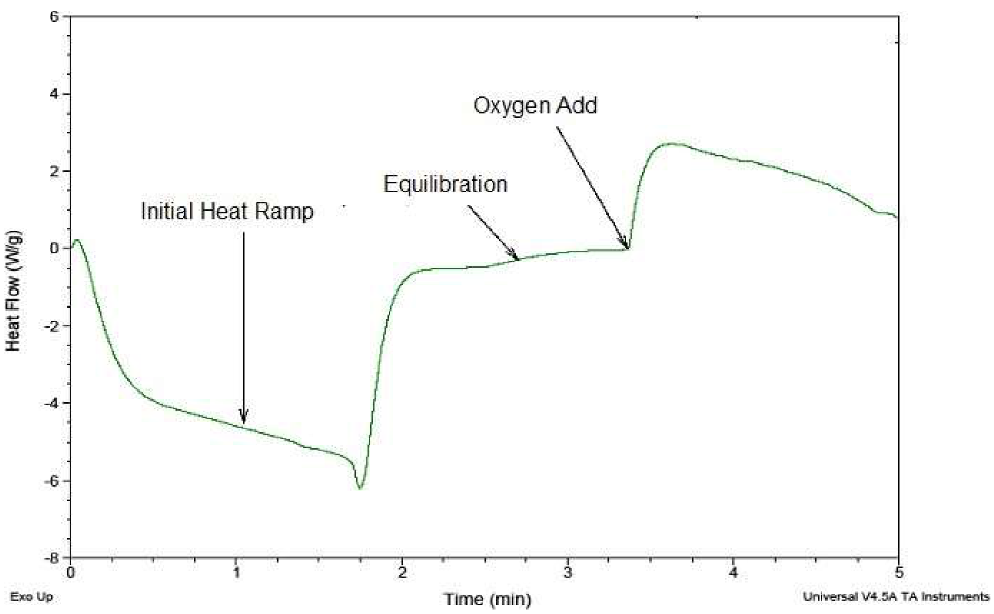


Figure 9: AN-15 in Lithium 12-Hydroxstearate / PAO 10 Grease

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

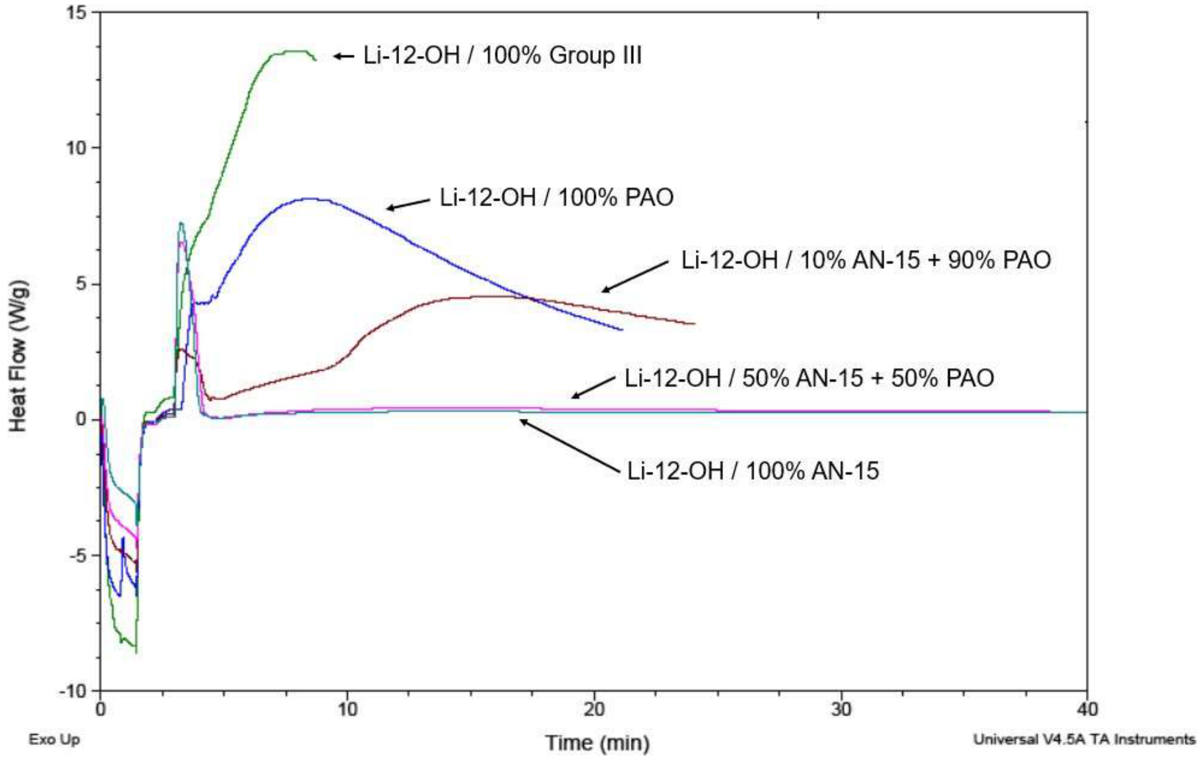


Figure 10: AN-15 in Lithium 12-Hydroxstearate / PAO 10 Grease

ASTM D942 – Norma Hoffman

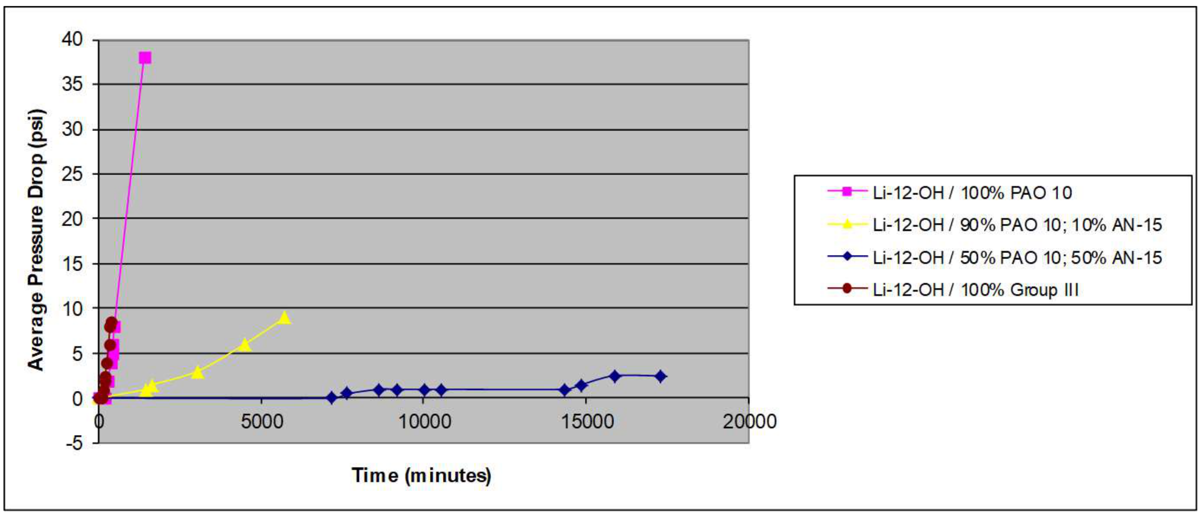


Figure 11: AN-19 in Lithium Complex / PAO 10 Grease

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

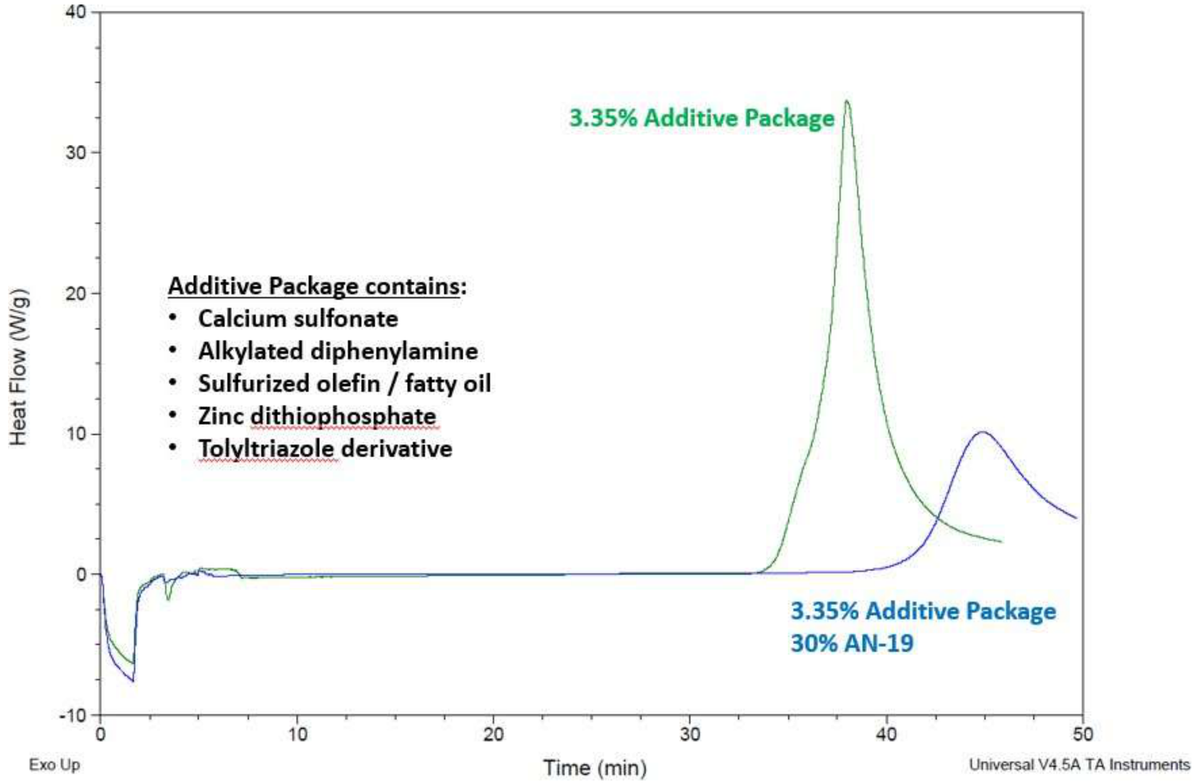


Table 6: AN-19 in Lithium Complex / PAO 10 Grease

	Base Grease Made with PAO	3.35 Additive Package in Grease Made with PAO	Base Grease Made with 30% AN-19	3.35 Additive Package in Grease Made with 30% AN-19
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
Norma Hoffman (ASTM D942) 100 h, pressure drop (psi)	86	2	0	0
Cone Penetration (ASTM D217)				
Unworked	298	300	281	284
60 Strokes	299	310	282	294
10,000 Strokes	303	317	292	309
Four Ball Weld (ASTM D2596) 10 seconds, 25ºC, 1800 rpm				
OK Load (kgf)	120	240	140	280
Weld Load (kgf)	140	260	160	300
Four Ball Wear (ASTM D2266) 1 hour, 75ºC, 40kgf, 1200 rpm, (mm)	0.53	0.45	0.43	0.41
Copper Corrosion (ASTM D4048) 24 hours, 100ºC	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.

Figure 12: AN-19 in Aluminum Complex / PAO 10 Grease

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