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## Conference Preview

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# Abstract

Thread compounds play an important role in the sealing ability of casing connections in the oil and gas industry. Next to their lubricating role during assembly, most of these thread compounds make use of nonbiodegradable or persistent particle additives to aid in the sealing ability. Soon, these additives need to be replaced by benign alternatives as agreed in the proceedings of the Oslo-Paris Commission. This is, however, a challenge in high temperature (>150◦C) well environments. This paper presents an investigation of the high temperature failure mechanisms of thread compounds with the aim to develop biodegradable high temperature resistant thread compounds. To this end, the performance of commercially available, environmentally acceptable thread compounds was investigated with thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), high temperature rheometry and high temperature pin-on-disc experiments. The compounds are assessed on their stability, consistency, lubricity, and the resulting wear at high temperature. The results indicated that, without exception the commercially available thread compounds investigated in this study fail by adhesive and/or abrasive wear at around 150 degrees Celsius because of thermally induced degradation. To remedy this and to validate the mechanisms, a prototype thread compound was developed which exhibits strong film forming. The conclusion is that a successful high temperature resistant environmentally acceptable thread compound can likely be developed. The key property of this thread compound should be the ability to form a tribofilm during make-up which protects the surface at a later stage when the lubricant has lost its consistency and the base oil is fully evaporated.

# 1 Introduction

The assembly of (casing) connections is performed with grease; also called thread compound. The base greases are typically made with a mineral base oil, and metal soaps or metal complex soaps. Additives are subsequently added in the form of metallic, mineral or metallic oxide based particles. Thread compounds are thus relatively simple grease formulations. What is special about them is the high solids content of up to 50wt% to 60wt% compared to regular greases [1]. The function of the grease and the added particles is threefold; it provides a repeatable friction factor for a predictable assembly torque response [2], provides surface protection [3–6], and aids in the seal ability of the system by blocking or bridging potential leak channels [7–11].

After assembly the casing is lowered into the well bore for the purpose of fortifying the drilled hole. During its lifetime the casing will experience several stress states. For instance, when the well is flowed it will heat-up and the casing experiences a transition from tension to being loaded in compression because of thermal expansion; this leads to small movements in the metal-to-metal seal in the axial direction, which is defined as micro sliding. The micro sliding is typically in the order of 0.5 mm and operates at extremely low velocities i.e. $0.01\mathrm{mms}^{-1}$, and thus fully in the boundary lubrication regime [12]. As typical contact widths are >1.0mm, this can also be characterized as fretting [7].

The casing or tubing string and connections are thus subjected to substantial loads under high subsurface temperature conditions (up to 240°C, which is the limitation of current test frames and covers the majority of all HPHT wells). The seal ability of the system needs to be guaranteed under the micro sliding conditions described previously; this means that lubricity needs to be guaranteed to avoid cumulative damage leading to seal failure. Therefore, the long term thermal stability of the grease and related tribofilms is of great importance for the metal-to-metal seal tribosystem. This is the reason why the *de facto* standard thread compound, API modified [1], still uses metallic lead in its formulation.

Initiatives are under way to ban the use of heavy metals in thread compounds (which can currently only be used in Europe with special permission from the legislator) and to push the industry to formulate fully biodegradable alternatives. These initiatives are led by the Norwegian and British regulatory bodies: the Norwegian Environment Agency (NEA) and the Centre for Environment Fisheries and Aquaculture Science (CEFAS) respectively. They execute the outcomes of the Oslo-Paris Commission for the protection of the Marine Environment of the North-East Atlantic (OSPAR) by implementing the Harmonised Offshore Chemicals Notification Format (HOCNF) [13]. HOCNF is a scheme to harmonize the regulation of chemicals used in the offshore industry in the North Sea and the North-East Atlantic. The aim is to minimize the risk of serious spills and damage to the local marine environment. The regulators define an environmental friendliness scale to categorize the chemicals for use offshore. The scale runs from readily biodegradable and non-bioaccumulative, designated as E or Green, to nonbiodegradable and bioaccumulative, designated as A or Black, by CEFAS and NEA respectively. API modified belongs in the A or black category. The goal of CEFAS and NEA is to push developments in the direction of E, or green category, thread compounds. In between are the yellow and red category, with yellow being more environmentally friendly than red. Environmentally acceptable products are in the yellow (and green) category. To qualify as a yellow compound, the compound should have a biodegradability of at least 60 wt% over 28 days in sea water and have no components that bioaccumulate.

To be able to replace API modified, the lubrication and sealing mechanisms of thread compounds first need to be understood. At this stage, limited information is available about high temperature degradation of thread compounds and the mechanisms that ultimately lead to the failure of the metal-to-metal seal.

As discussed, the standard thread compound is API modified [1]. The compound was formulated over 70 years ago [14]. It contains a base grease made with a heavy mineral oil and a metal soap thickener, combined with graphite, lead, zinc and copper. Several explanations for its success in protecting the surface during assembly and sealing ability are given. The work by Ertas et al. [6] attributes this mainly to the lead particles that form a protective film. Zinc and copper are said to be added to control the friction coefficient. In addition, the copper particles are the largest and probably aid in thread sealing [9,14]. Finally, the graphite is not of lubrication grade and therefore acts mainly as a filler [6]. This, together with the broad particle size distributions of the metallic additives [14], helps in the sealing ability [6].

In a study by Murtagian et al. [11] it was shown that the presence of a thread compound has a strong influence on gas sealing ability performance of the metal-to-metal seal. The onset of leakage was at a lower seal contact intensity, and instantaneous, compared to experiments without a thread compound. There is, however, a large difference in the sealing performance between the different commercial thread compounds, as shown by [10]. This was mainly attributed to differences in formulation of each compound and the resulting temperature stability. Still, API modified holds up well against recently developed environmentally acceptable thread compounds, particularly under high temperature conditions.

Inose et al. [8] showed that thermal degradation of the thread compounds plays a significant role in the reduction of the sealing performance of metal-to-metal seals. The researchers exposed API modified and an environmentally acceptable thread compound containing inorganic particles to temperatures of 180°C and evaluated the sealing ability. It was concluded that API modified performed better compared to the environmentally acceptable thread compound. This was attributed to the mineral oil which performed better under elevated temperature conditions, and its soft metallic particles closed potential leak paths and thus improved sealing ability. They thus show that a connection can be successfully made-up but fail during load cycling because of thermal degradation of the lubricant. This exposed the surface directly to the hard inorganic particles contained in the environmentally acceptable thread compound. The particles subsequently abraded the surface leading to formation of scratches and/or galling in the seal area; reducing its sealing performance.

The surface topography and its orientation was shown to play an important role in metal to metal seals by Ernens et al. [7]. This was further confirmed using a stochastic sealing ability model by Pérez-Ràfols et al. [15]. Damage of the surface because of scratching can bypass the seal contact, leading to diminished sealing performance.

These studies suggest that the choice for base oil, thickener and additives needs to be balanced to get an acceptable interplay between tribology and sealing ability. How to design a high temperature, stable and environmentally friendly thread compound was however not part of these studies.

Lubrication and sealing mechanisms of metal-to-metal seals are investigated and described in this paper. In addition, current thread compound qualification and test procedures [1] are not pushing manufacturers enough to bridge the gap from black to green dope. Therefore, a proposal for a new test method which incorporates the high temperature degradation is provided in this paper. Then, the mechanisms are validated using the new test method and a newly developed prototype thread compound. This compound is designed to remedy thermal degradation issues existing in current commercially available environmentally acceptable thread compounds.

# 2 Methodology

Thermal stability was assessed with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). This was followed by rheometer experiments at increasing temperatures to investigate the changes in consistency as a consequence of the thermal degradation. The rheometer experiments were performed by imposing a shear stress sweep to also investigate yielding behaviour. The outcomes of TGA/DSC and rheometer experiments were subsequently used to explain the high temperature pin-on-disc experiments. The pin-on-disc experiments are designed to investigate make-up sliding and micro-sliding in a single experiment, and are the same as [7], except for the addition of elevated temperatures. The used test set-up is open to atmosphere, so components in the grease can evaporate or react with oxygen. This is not, or to a lesser extent, the case in a real connection. Therefore, the test is accelerating degradation and is a worst-case scenario for the thread compound. The experiments are summarized in Table 1 and will be described in more detail hereafter.

*Table 1 Summary and overview of the used test protocol for the various screening methods.*

| Test type | Measurement geometry | Protocol | Atmosphere |
|---:|---|---|---|
| TGA and DSC | 100µL Al open cup, 60µL Au closed cup | Dynamic 30°C to 250°C at 10°Cmin$^{-1}$, iso hold 30min at 250°C, dynamic 250°C to 30°C at -10°Cmin$^{-1}$ | Open cup 80mLmin$^{-1}$ air or $N_2$ |
| Rheometer 1 | Coaxial cylinder (PZ38) 50mL | Perform shear stress sweep 1.5Pa to 800Pa at 20-50-100-150-200 °C with 30min temperature hold per step | Half-open pressure vessel $N_2$ |
| Rheometer 2 | coaxial cylinder (Z10) | Perform shear rate sweep 1.0s$^{-1}$ to 100s$^{-1}$ at 20-40-70-100-140-180-200°C with 30min temperature hold per step, hold for 3 hours, perform another sweep at 180°C | Open cup air |
| Pin-on-disc | 10mm AISI52100 ball on AISI4130 disc | Perform 250 reciprocating cycles at 1GPa with stroke 500µm at 30-70-100-150-200-250°C | Half-open drive air |

## 2.1 Lubricants

The screened lubricants consist of “off-the-shelf” environmentally acceptable thread compounds that were compared to the reference compound API modified. The lubricants are listed in Table 2. Because of trade secrets most commercial compounds have undisclosed compositions, except for ingredients that need to be stated in the material safety data sheet (MSDS) or that are stated with a general description on the technical data sheet (TDS). The dropping points listed in table 2 indicate the upper temperature limit at which a grease retains its structure [16]. This depends on the type of thickener used. In addition, a clay based base grease was mixed in the laboratory with various additives to explore the feasibility of formulating a high temperature, environmentally acceptable thread compound based on the film forming hypothesis that will be developed in this paper. The final formulation was also mixed in a production facility, as indicated in Table 2.

*Table 2 Overview of the commercial thread compounds that were screened and the subsequent prototype compounds that were designed using the methods described in this paper. The data is obtained from the TDS and MSDS.*

| Short hand | Base oil | Thickener | Additives based on MSDS (particles) | Dropping point °C |
|---|---|---|---|---|
| | | Commercial thread compounds | | |
| API mod [1] | Mineral oil | Undisclosed | Lead, copper, zinc, graphite | >204 |
| YD A | Synthetic PAO and Ester | Undisclosed | Calcium fluoride, calcium sulphate, calcium carbonate, etc. | >288 |
| YD B | Synthetic oil | Calcium complex | Calcium fluoride, titanium dioxide, calcium carbonate, etc. | >288 |
| YD C | Synthetic ester | Undisclosed | Mineral fillers | >200 |
| | | Prototype thread compounds | | |
| SA | Mineral oil | Clay | Melamine cyanurate | >288 |
| SB | Mineral oil | Clay | Lubrication grade graphite | >288 |
| SG | Mineral oil | Clay | Calcium phosphate | >288 |
| SJ | Mineral oil | Clay | SA + SB | >288 |
| SK | Mineral oil | Clay | SB + SG | >288 |
| SL | Mineral oil | Clay | SB + SG diff. ratio | >288 |
| SM | Mineral oil | Clay | SA + SB + SG | >288 |
| SN | Mineral oil | Clay | SA + SB + SG mixed in grease plant | >288 |

## 2.2 TGA/DSC

The thermal stability test entails a temperature sweep using a Mettler Toledo TGA/DSC 1 from ambient temperature (25°C) to 250°C, at a temperature increase rate of 10°C $\text{min}^{-1}$, followed by a hold period of 30 minutes at 250°C. At the end of the hold period, a cooling rate of 10°C $\text{min}^{-1}$ was imposed to reduce the temperature from 250°C back to room temperature. For the thread compounds the resistance to oxidation and their general thermal behaviour was investigated using:

1. Open cup vs. closed cup experiments
2. Air vs. nitrogen atmosphere
3. Open cup and mixing the thread compound with approximately 2 mg iron oxide (hematite) to simulate wear particles

The open cups were all loaded with 62.5±0.5 mg of product, the closed cups were all loaded with 61.5±0.5 mg of product.

## 2.3 Rheometry

The rheology characterization was performed with a Haake Mars III rheometer. Two protocols were used; for protocol rheometer 1, the measurement geometry was a coaxial cylinder (PZ38) allowing measurements in a half-open (evaporation still happens) environment under $N_2$ conditions. The rheology measurements were carried out on a sample volume of 50±1 mL.Temperature was controlled using the Peltier module (TM-PE-C) up to a maximum temperature of 200˚C. The temperature was step-wise increased: 20-50-100-150-200˚C. At each of those set-points a 30 min hold period was followed by a stress-controlled test over the range from 1.5 Pa to 800 Pa. Protocol rheometer 2 used an open coaxial cylinder (Z10) performing a shear rate sweep 1.0 $s^{-1}$ to 100 $s^{-1}$ at 20-40-70-100-140-180-200˚C with 30 min temperature hold per step. This was followed by a 180˚C hold for 3 hours and another sweep at 180˚C to further investigate the degradation effects.

## 2.4 High Temperature Pin-on-Disc

The tribological screening experiments were performed with a Bruker UMT-3 equipped with the 350˚C drive module (S35HE-350). In addition to room temperature experiments, elevated temperature experiments were performed. The temperature set points were 30–70–100–150–200–250˚C. Once the temperature set point was reached a 15 minute hold period followed to ensure the disc surface temperature also reached the set-point. Then 250 reciprocating cycles were made with a stroke of 500 µm. Hence a total of 1500 cycles are made for an equivalent sliding length of 1.5 m. The location on the disc, ball and lubricant were not changed or replaced during the temperature steps. However, the ball was taken out of contact by 1 mm during the hold periods to avoid an offset on the load measurement by thermal influences on the load cell.

## 2.5 Performance Assessment

Based on the known correlations between sealing and surface quality and the role of the thread compound [8,15,17], the results of the experiments were assessed according to the following criteria:

1. High temperature stability (e.g. dropping point)
2. High temperature consistency (e.g. shear/temperature thinning behavior)
3. High temperature lubricity (coefficient of friction (COF))
4. Surface damage (wear)

The assessment was done by combining observations on the change in consistency, appearance and surface texture after the experiments. In addition, the resulting wear scars were investigated with a digital light microscope and a scanning electron microscope.

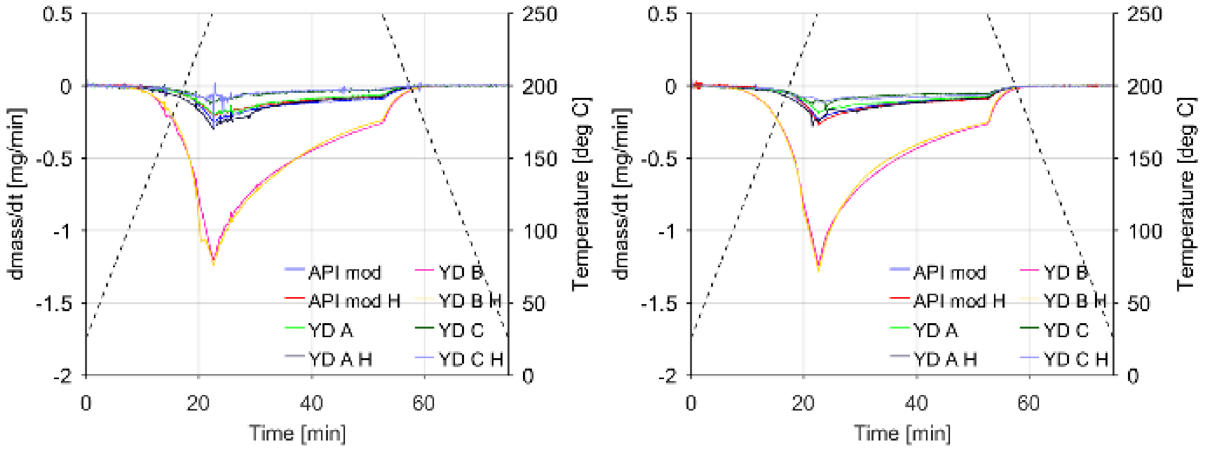
## 2.6 Anvil-on-Strip

The anvil-on-strip experiments on the prototype compound were performed with a Quiri tribometer and compared to the results of our previous paper [7]. In this case, unidirectional sliding experiments were performed. The strip was mounted in a tensile tester. On each side of the strip an anvil was pressed at a prescribed load. The strip was then moved up at a prescribed velocity while measuring the resultant friction force. The sliding experiments were performed at a maximum Hertzian contact stress of 1.4 GPa by applying a 20 kN normal load on the anvils. For the experiments with as machined surfaces (no coating), a linear load ramp was applied over the first 5 strokes. The contact spot was elliptical and approximately 5.7 mm x 1.1 mm. The sliding velocity is 24 mm $s^{-1}$. Up to 50 strokes were made with a sliding length of 31 mm which sums up to 1550 mm of cumulative sliding length for the anvil.

# 3 Results

## 3.1 TGA/DSC

The results of the TGA screening experiments are given in Figure 1 by the rate of mass loss as a function of time. The results with a nitrogen atmosphere and an air atmosphere are shown in Figure 1a and Figure 1b respectively. The results for nitrogen and air show similar amounts of mass loss for the various compounds, and their onsets of mass loss are all around 150°C. There is one clear outlier in the set, YD B has a substantially higher mass loss compared to the other products. The others display similar mass loss with YD C having the lowest value. No significant differences were observed coming from the presence of hematite.

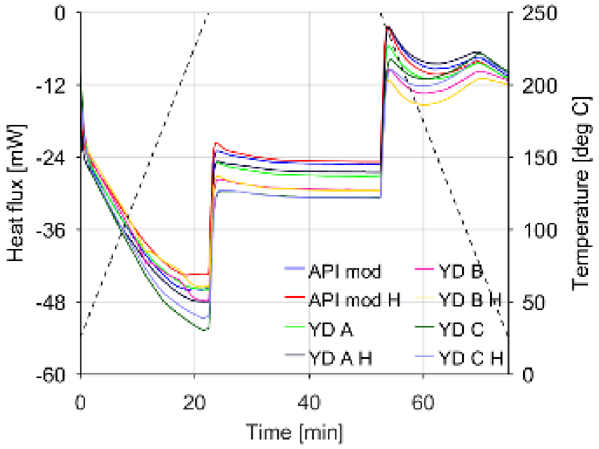


(a) nitrogen

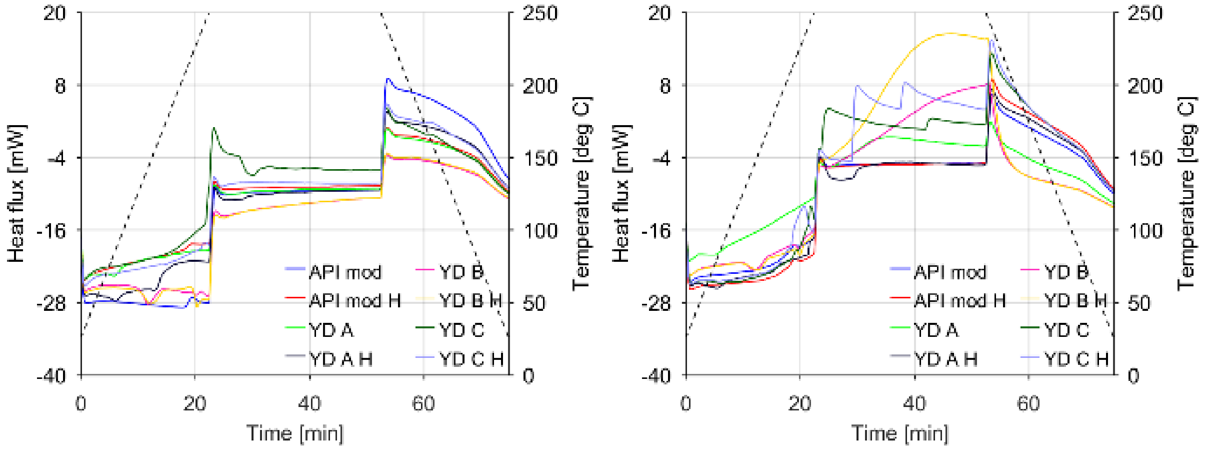
(b) air

*Figure 1 Overview of TGA experiments for open cup in nitrogen atmosphere in Figure 1a and open cup in ambient air atmosphere in Figure 1b. The mass loss was differentiated versus time for each experiment to obtain a mass loss rate. The dashed line belongs to the secondary y-axis displaying the heating and cooling program. H in the legend represents dope with 2% hematite mixed into it.*

The DSC results are shown in Figure 2 for closed cup, open cup in $N_2$ and open cup in air. In the closed cup experiments in Figure 2a, only YD B is undergoing permanent (phase) transitions with endothermic peaks around 150°C and 200°C. The first peak coincides with the onset of the high rate of mass loss in Figure 1. No measurable effect of hematite was observed. When performing the experiments in an open cup under both a nitrogen (Figure 2b) and an air (Figure 2c) atmosphere, evaporation and/or oxidation effects were found. In both cases all thread compounds show endothermic peaks at relatively low temperatures probably corresponding to lighter fractions evaporating. The endothermic peaks for YD B are more pronounced. In air indications of oxidation are present during the hold period with strong exothermic peaks for YD B and YD C which get more pronounced when hematite is added. API modified shows the highest thermal stability with no indications of a phase transition or reaction.



(a) closed cup



(b) nitrogen (c) air

*Figure 2 Overview of the DSC experiments belonging to the TGA results in Figure 1 for closed cup in Figure 2a, open cup in nitrogen atmosphere in Figure 2b and open cup in air atmosphere in Figure 2c. The dashed line belongs to the secondary y-axis displaying the heating and cooling program. H in the legend represents dope with 2% hematite mixed into it.*

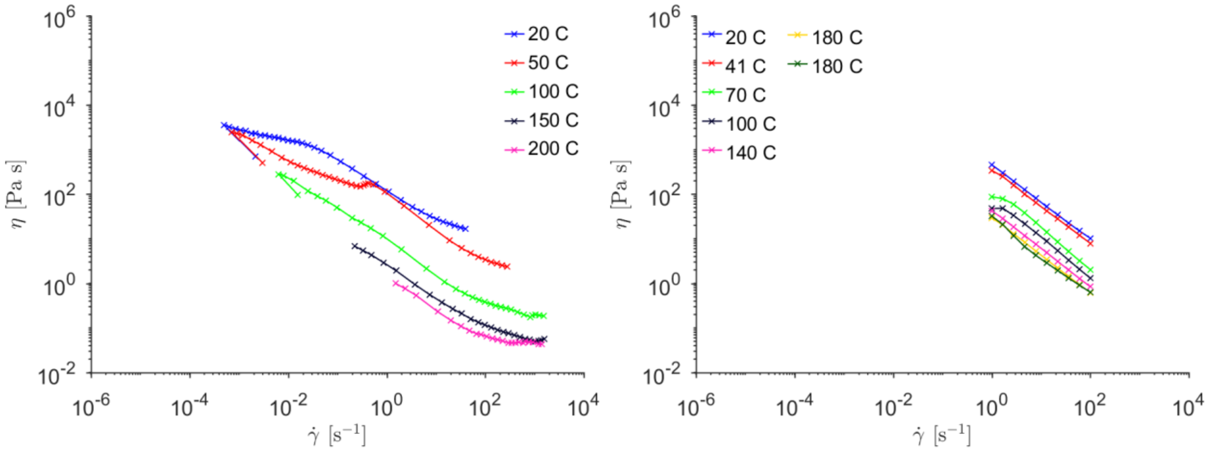
## 3.2 Rheometry

The rheological characterization as a function of temperature is shown in Figure 3 for the dynamic viscosity. API modified in Figure 3a shows shear thinning behaviour as the viscosity drops monotonically with increasing shear rates. At high shear rates ($>10^2 s^{-1}$) a plateau is reached which typically coincides with the base oil viscosity [16]. This happens only for the 100, 150, and 200C curve because of temperature thinning of the compound. When observing the rheological experiment in an open version of the coaxial set-up, indications of shear banding could clearly be seen [18,19]. Shear banding means that only part of the fluid in the gap is entrained by the rotating cylinder and part of the fluid is stationary. Only above a certain threshold shear rate will the complete gap have uniform flow. Indications of this effect are observed in the flow curves of 20°C and 50°C. Where the 20°C curve shows a relatively extended region, the 50°C curve shows a shorter region because of the added temperature thinning of the lubricant. This is because next to a thickener, this thread compound contains 60% solids. At higher temperatures the effect is not observed as the elevated temperature has reduced the viscosity enough to develop a uniform flow immediately. Part of this could be attributed to gravimetric segregation of the metal particles which was observed after the experiment shown in Figure 4a.

As discussed, the results for YD A were obtained with a different measurement geometry and protocol (rheometer 2, section 2.3). Consequently, limited information is available on the rheological behaviour. YD A exhibits clear shear thinning behaviour with a monotonical decreasing viscosity with increasing shear rate as shown in Figure 3b. Even though the measurement window is limited, the behaviour of YD A appears similar to YD C. The compound consistency is not negatively affected by temperature as the viscosity at 180°C was measured twice at a 3 hour interval in this protocol which gave a repeatable result (compare yellow and green curve). This was also observed after the pin-on-disc experiment as shown in Figure 4b.

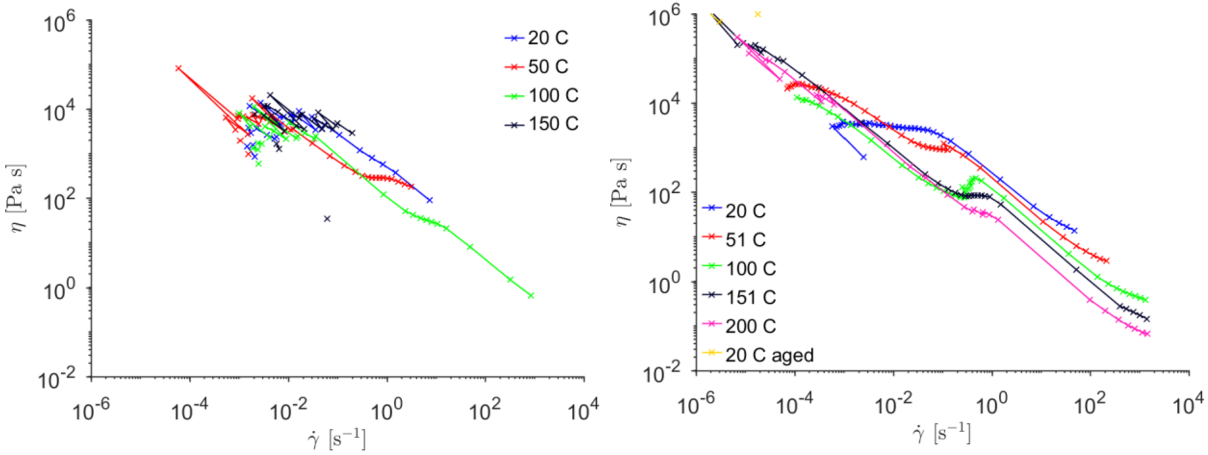
YD B has a higher resistance to flow, as shown in Figure 3c. The compound shows indications of a distinct yield point compared to the other thread compounds even though there is always flow according to [20]. Indications of shear banding were found up to 100°C because of the higher initial viscosity. At 150°C the temperature trend reversed compared to the other thread compounds, very little flow was observed. Therefore, the experiment was stopped at this temperature step, and the pressure chamber disassembled to investigate why this happened. It was found that the thread compound was completely dry explaining this behaviour. This agrees with the TGA/DSC observations in Figure 1 and Figure 2.

Figure 3d shows the behaviour of YD C. At 20°C a constant viscosity can be observed at low shear rates ($<10^{-1}s^{-1}$) which has similarities with a Newtonian plateau region as observed by Cyriac et al. [21]. However, this typically happens at much lower shear rates, therefore here it is seen as part of the shear banding region. YD C has a high initial viscosity and is least affected by temperature thinning effects. Therefore, the effects of shear banding were observed up to the highest applied temperature. After the set-up cooled down to room temperature it was observed that the cylinder would not rotate any more, even though the last experiment (at 200°C) showed fully developed flow. It was therefore decided to run an additional experiment at 20°C on the aged product, which revealed similar behaviour as the 150°C experiment of YD B (all data collapsed on the single data point). In Figure 4d shows the compound, which thickened into a clay-like substance.



(a) API modified

(b) YD A



(c) YD B

(d) YD C

*Figure 3 Dynamic viscosity as function of the measured shear rate for three commercial thread compounds. Figure 3a shows API modified, Figure 3b shows YD A, Figure 3c shows YD B, and Figure 3d YD C.*

(a) API modified

(b) YD A

(c) YD B

(d) YD C

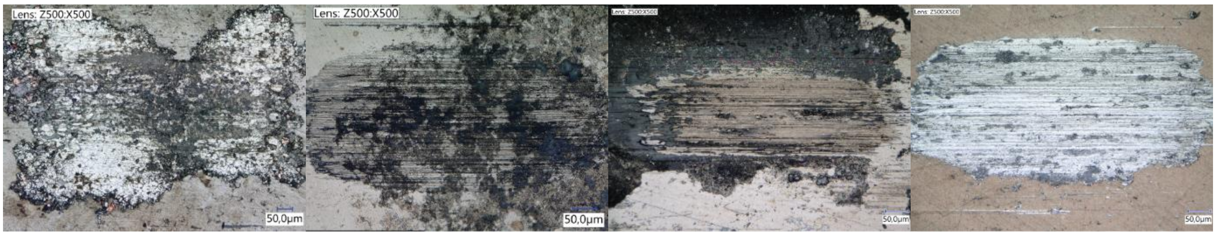
*Figure 4 Observations after the high temperature rheology or pin-on-disc experiments. Figure 4a shows the gravimetric segregation of particles observed in API mod. Figure 4b shows the still greasy consistency of YD A indicated by the arrow. Figure 4c shows the completely dried out YD B. Figure 4d the observed thickening of YD C.*

### 3.3 Pin-on-disc

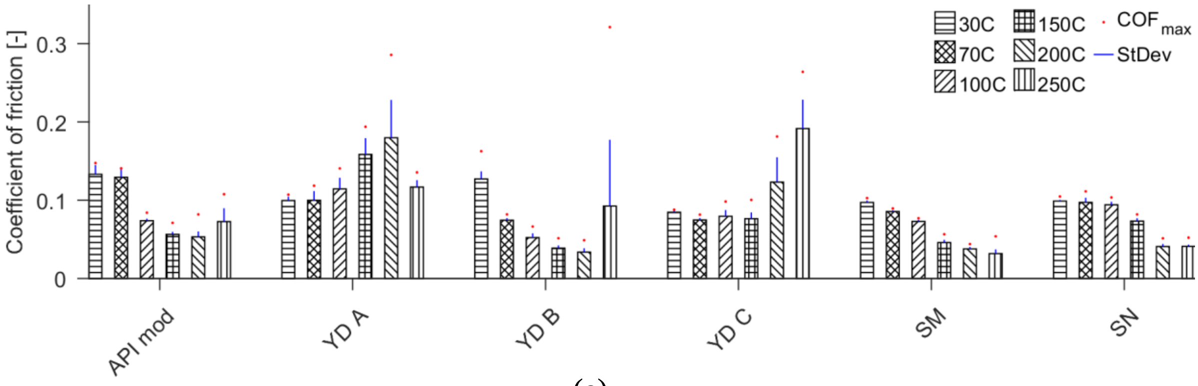
The screening results of the pin-on-disc experiments are summarized for each temperature step comprising of 250 reciprocating cycles by their mean COF (bars), standard deviation (vertical lines) and maximum COF (dots) as shown in Figure 5e. The COF was found to be a good indicator of thread compound failure. Based on the experiments performed a monotonically decreasing or constant COF with temperature typically indicated a well performing compound. If this trend showed an increasing COF this indicated a poor performing compound which failed because of adhesive and/or abrasive wear which was the case for the environmentally acceptable thread compounds tested, as observed in Figure 5.

The observations after the experiments are shown by the wear scars in Figure 5a-d. API modified retained most of its consistency until the end of the experiment with some segregation of the base oil from the grease structure, as shown in Figure 4a, which could indicate that the dropping point was reached. The microscopy of the wear scar in Figure 5a revealed many particles in the contact, forming a protective film. This also explains the relatively constant COF as this is dictated by the interfacial shear strength of the metallic film.

The environmentally acceptable thread compounds (YD A-C) all showed degradation of their lubrication performance on or shortly after the 150°C step. This can be observed in Figure 5e from the increase in mean COF, its standard deviation and the maximum COF. The reason is different for each compound, however, for all it resulted in failure of the tribosystem, leading to scratched surfaces. YD A shows the earliest indications of imminent failure at 100°C, followed by YD C at 150°C, and then YD B at 250°C.



(a) API modified (b) YD A (c) YD B (d) YD C



(e)

*Figure 5 Wear scars after the pin-on-disc experiments. All three environmentally acceptable thread compounds failed because of adhesive and/or abrasive wear as evidenced by the wear scars in Figure 4b, Figure 4c and Figure 4d. The results of the PoD are shown in Figure 4e. Each experiment is summarized by mean COF (bars), standard deviation (vertical lines) and maximum COF (dots).*

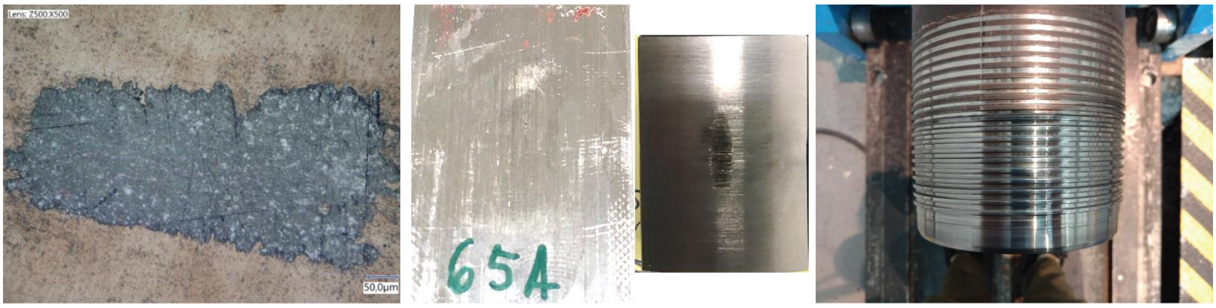
# 4 Prototype thread compound based on strong film formation

Based on the presented findings a lubricant was designed with a strong film forming tendency. The idea was to form a tribofilm during make-up, and thus before the base oil has evaporated. The design was made using the high temperature pin-on-disc approach as an evaluation tool for intermediate lubricant compositions.

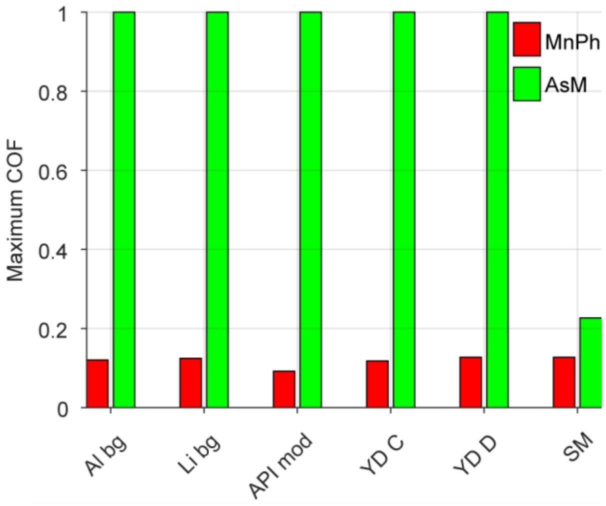
For this a thermally stable mineral oil was selected designated "S" in Figure 7a, which was combined with a clay thickener to yield a base grease with a high dropping point [22] and stable rheological behaviour as shown in Figure 7c. Additives (as per Table 2) were subsequently added to the base grease with the same wt% across all specimens and tested using the room temperature and elevated temperature pin-on-disc method. The final selection of the components resulting in compound SM (Table 2) was based on the swelling of melamine cyanurate at elevated temperatures to aid in seal ability and the film forming of graphite and calcium phosphate. In addition, graphite and calcium phosphate are considered to Pose Little

Or No Risk (PLONOR) to the environment by OSPAR [23]. The result with this compound after the pin-on-disc experiment is shown in Figure 6a.

The performance of compound SM was subsequently confirmed at ambient conditions in an As Machined (AsM) versus As Machined (no coatings) P110 tribosystem using the anvil-on-strip set-up and compared to previous results with the commercial thread compounds in [7]. This was the first thread compound of the ones tested that did not show galling in the AsM-AsM experiment as shown in Figure 6b. The COF comparison with the results of our earlier work [7] are shown in Figure 6d. The prototype mixture was subsequently manufactured professionally in a manufacturing plant, designated compound SN, which was used for assembly experiments. Before the assembly experiments, the performance was confirmed in pin-on-disc experiments which yielded equivalent results as compound SM (Figure 5e). The assembly test entailed three make-ups and break-outs of a 5.5" 23# L8013Cr VAM TOP HT connection. This is a chromium material (13 wt%) which is more susceptible to galling, and therefore considered challenging for thread compounds. The connection box side is copper plated, and the pin side is AsM. Assembly was performed with a bucking unit, which means that assembly is performed at a low velocity (<1 RPM) and discontinuous because of the limited stroke length of the hydraulic arm. No galling was observed after 3x make-ups/break-outs as shown in Figure 6c.



(a) SM and SN (b) SM (c) SN



(d)

*Figure 6 Prototype compound combining SA, SB and SG. Figure 6a shows pin-on-disc results after 250 reciprocating cycles per temperature step, for a total of 1500 at 1GPa with a 10mm AISI52100 ball on a AISI4130 flat. Strong film forming was observed, providing successful surface protection. The performance in the anvil-on-strip experiments was equally good with no galling observed in an AsM-AsM P110 tribosytem in Figure 6b. Finally, the performance was confirmed by assembly tests of a 5.5" 23# L8013Cr VAM TOP HT connection which showed no galling after multiple make-up and break-outs as shown in Figure 6c. Figure 6d shows the summarized results for the anvil-on-strip experiments of [7] with the result of SM added. Note that a COF of 1 indicates galling. Results are shown for the anvil-on-strip experiments with as machined (indicated AsM) strips and anvils, and manganese phosphated (indicated MP) strips and AsM strips. Reproduced from [7].*

# 5 Discussion

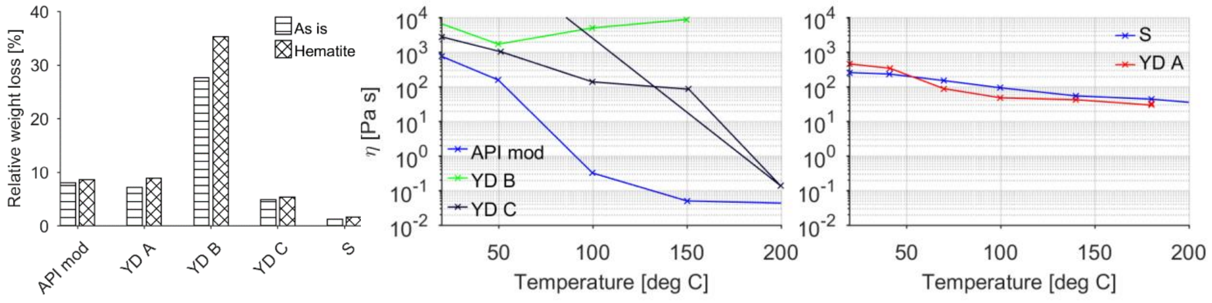
In the investigation of commercially available thread compounds, none of the tested environmentally acceptable compounds meet the specifications needed for high temperature, high pressure oil and gas wells. Each of these compounds failed for different reasons in the tribological experiments. An overview of the TGA/DSC and rheology experiments is given in Figure 7.

API modified showed the most stable elevated temperature behaviour (Figure 5e) with minimal weight loss in the TGA (Figure 7a) and no indications of reactions or phase transitions in the DSC (Figure 2). It also provided stable rheological behaviour over the duration of the rheology experiment (Figure 7b) with gravimetric segregation of its particles at the end of the experiment (Figure 4a). However, this should not pose a problem in a metal-to-metal seal as only a thin film is applied in a narrow gap. In addition, at the end of the rheological experiments (Figure 4a) and tribological experiments, it was observed that the base oil bled from the thread compound indicating that the dropping point was reached.

YD A failed earliest in the pin-on-disc experiments (Figure 5e) even though TGA/DSC (Figure 7a, Figure 1 and Figure 2) and rheology (Figure 7c) showed stable behaviour for this compound. It still had its original consistency as observed after the pin-on-disc experiment (Figure 4b). Therefore, it is possible that a film is formed initially, which is rubbed off over the course of the experiment and not replenished leading to failure.

YD B failed because of evaporation of the base oil. The onset of accelerated evaporation is around 150°C, as found in the TGA/DSC and the rheology experiments in Figure 6a and Figure 6b respectively. In addition, the DSC (Figure 2) revealed oxidation of the compound in air. This resulted in a dry compound (Figure 4c) which allowed no replenishment of the lubricant in the contact area, leading to starved conditions. In addition, as the base oil has evaporated, this leaves hard inorganic particles in the contact area, leading to abrasion. From this point onwards, the contact relies on the tribofilm formed in the earlier steps of which remnants can still be observed in Figure 5c. Therefore, failure is only observed at 250°C. These observations are similar to the ones by [8].

YD C showed the best performance in the TGA experiments (Figure 7a) with the lowest weight loss of all compounds. In the DSC phase transitions were observed under a nitrogen and air atmosphere (Figure 2). These can probably be related to the thickening observed after the rheology experiments (Figure 4d) and oxidation, as observed in the TGA/DSC experiment (Figure 1 and Figure 2). The compound reduced to a clay-like consistency after exposure to high temperatures for an extended period. In the tribological experiments this led to removal of the compound from the contact by mechanical action of the ball. No protective tribofilms were formed as failure followed relatively quickly and catastrophically, as observed from the wear scar in Figure 5d.



(a) TGA (b) Rheology 1 (c) Rheology 2

*Figure 7 Summary of TGA and rheology experiments. Figure 7a shows the relative weight loss for all tested compounds in a nitrogen atmosphere. Figure 7b shows the effect of temperature on the viscosity at* $\tau = 50$ *Pa, and, because of the different test protocol, Figure 7c shows the effect of temperature on viscosity at* $\dot{\gamma} = 1\ s^{-1}$.

In summary, the thermal degradation starts with evaporation, resulting in drying out of the compound. This is further exacerbated by oxidation, and in some cases thickening or bleeding of base oil (dropping point). The resulting increase in consistency leads to removal of lubricant from the contact by pushing the dry residue out. Subsequently, this leads to failure because of adhesive wear and, finally, galling at the subsequent temperature steps. In some cases, the failure was accelerated by the presence of the (hard) inorganic particles that became abrasive once the consistency increased. It is clear though that even if the physical and chemical characteristics indicate stable behavior, the tribological outcome is not necessarily the same.

Based on the experiments using commercially available compounds, the following challenges were identified:

1. The required biodegradability, leading to the use of lighter oils (e.g. esters) which compromises the high temperature stability and, with that, lubricity.
2. Use of inorganic (mineral) particles to replace soft metal particles leads to (sealing) surface damage, which was also observed by [8].
3. TGA/DSC or elevated temperature rheology experiments do not reveal the high temperature performance of a thread compound. High temperature tribological experiments, however, do reveal this and are in line with earlier work by [8].

To validate the understanding of the mechanisms leading to failure and the high temperature pin-on-disc method, a prototype lubricant was designed that successfully mitigates the observed failure modes by film formation prior to degradation. The compound outperformed all the tested commercially available thread compounds.

# 6 Conclusion

A simple high temperature tribological test method was developed and validated using cross testing with TGA/DSC, high temperature rheometry, anvil-on-strip, pin-on-disk, and full-scale make-up/break-out experiments. The method was developed by using it to investigate the high temperature failure mechanisms of commercially available thread compounds. The method and mechanisms were successfully validated by designing a prototype thread compound. The results indicate the following:

- Relying on just TGA/DSC, or rheometry, or even a combination thereof, is not sufficient for the development of thread compounds for high temperature (>150°C) applications.
- The commercial environmentally acceptable thread compounds fail at elevated temperatures because of evaporation of the base oil combined with oxidation of the thread compound. This increases consistency, which leads to starved lubrication conditions. The remaining tribofilm is worn until the system fails because of adhesive wear. This is

sometimes further enhanced by abrasive action because of the inorganic particle additives.

- The identified mechanisms were solved with a prototype thread compound developed using the methodology described. This was achieved by increasing the film forming tendency of the lubricant before the base oil is evaporated. This film is then able to protect the surface long after the lubricant has lost its consistency.
- The performance of the thread compound was successfully validated against earlier anvil-on-strip experiments using P110 material and full-scale make-up and break-out test using L80 13Cr material.

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## References

[1] API. Recommended Practice on Thread Compounds for Casing, Tubing, and Line Pipe. Washington: 2015.

[2] Carper HJ, Ertas A, Issa J, Cuvalci O. Effect of Some Material, Manufacturing, and Operating Variables on the Friction Coefficient in OCTG Connections. J Tribol 1992;114:698. doi:10.1115/1.2920938.

[3] Ekwaro-Osire S, Karpat F. Experimental Studies on Galling Onset in OCTG Connections: A Review. J Energy Resour Technol 2008;130:014502. doi:10.1115/1.2835616.

[4] Cuvalci O, Sofuoglu H, Ertas A. Effect of surface coating and tin plating on friction characteristics of P-110 tubing for different thread compounds. Tribol Int 2003;36:757–64. doi:10.1016/S0301-679X(03)00057-4.

[5] Carper HJ, Ertas A, Cuvalci O. Rating Thread Compounds for Galling Resistance. J Tribol 1995;117:639. doi:10.1115/1.2831529.

[6] Ertas A. Experimental Investigation of Galling Resistance in OCTG Connections. J Manuf Sci Eng 1992;114:100. doi:10.1115/1.2899745.

[7] Ernens D, van Riet EJ, de Rooij MB, Pasaribu HR, van Haaften WM, Schipper DJ. The Role of Phosphate Conversion Coatings in Make-up and Seal Ability of Casing Connections. SPE Drill Complet 2018. doi:10.2118/184690-PA.

[8] Inose K, Sugino M, Goto K. Influence of Grease on High-Pressure Gas Tightness by Metal-to-Metal Seals of Premium Threaded Connections. Tribol Online 2016;11:227–34. doi:10.2474/trol.11.227.

[9] Teodoriu C, Badicioiu M. Sealing Capacity of API Connections--Theoretical and Experimental Results. SPE Drill Complet 2009;24:96–103. doi:10.2118/106849-PA.

[10] Hoenig S, Oberndorfer M. Tightness Testing of Environmentally Friendly Thread Compounds. SPE Eur. Annu. Conf. Exhib., vol. 1, Society of Petroleum Engineers; 2006, p. 473–80. doi:10.2118/100220-MS.

[11] Murtagian GR, Fanelli V, Villasante JA, Johnson DH, Ernst HA. Sealability of Stationary Metal-to-Metal Seals. J Tribol 2004;126:591. doi:10.1115/1.1715103.

[12] Stachowiak G, Batchelor AW. Engineering Tribology. Butterworth-Heinemann; 2013.

[13] OSPAR. Guidelines for Completing the Harmonised Offshore Chemical Notification Format (HOCNF). 2015.

[14] API. WI 2317 : Tech Report on LTC / BTC Performance Properties and Leak Resistance. 2006.

[15] Pérez-Ràfols F, Larsson R, Almqvist A. Modelling of leakage on metal-to-metal seals. Tribol Int 2016;94:421–7. doi:10.1016/j.triboint.2015.10.003.

[16] Lugt PM. Grease Lubrication in Rolling Bearings. Oxford, UK: John Wiley & Sons Ltd;

2012. doi:10.1002/9781118483961.
[17] Pérez-Ràfols F, Larsson R, Lundström S, Wall P, Almqvist A. A stochastic two-scale model for pressure-driven flow between rough surfaces. Proc R Soc A Math Phys Eng Sci 2016;472. doi:10.1098/rspa.2016.0069.
[18] Delgado MA, Valencia C, Sánchez MC, Franco JM, Gallegos C. Thermorheological behaviour of a lithium lubricating grease. Tribol Lett 2006;23:47–54. doi:10.1007/s11249-006-9109-5.
[19] Britton MM, Callaghan PT. Nuclear magnetic resonance visualization of anomalous flow in cone-and-plate rheometry. J Rheol (N Y N Y) 1997;41:1365–86. doi:10.1122/1.550846.
[20] Barnes HA, Walters K. The yield stress myth? Rheol Acta 1985;24:323–6. doi:10.1007/BF01333960.
[21] Cyriac F, Lugt PM, Bosman R. Impact of Water on the Rheology of Lubricating Greases. Tribol Trans 2016;59:679–89. doi:10.1080/10402004.2015.1107929.
[22] Lugt PM. Modern advancements in lubricating grease technology. Tribol Int 2016;97:467–77. doi:10.1016/j.triboint.2016.01.045.
[23] Comission O. Ospar list of substances used and discharges offshore which are considered to pose little or no risk to te environment (PLONOR). 2013.