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Impact of oxidation on grease life in rolling bearings

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ABSTRACT

In this paper the lubrication mechanism of lithium grease lubricated ball bearings in the bleed phase is described. Oxidation plays an important role and therefore grease life “in air” and grease life “in nitrogen” is studied in real bearings. It is shown that grease life is strongly dominated by oxidation but that this is by far not deterministic. Oxidation starts up at a certain time, the induction time, which is the point at which the anti-oxidants have been consumed. This induction time is a function of the bearing operational conditions and the oxygen concentration. Oxidation leads to loss of base oil and loss of lubricity, partly repaired by replenishment and oil release from the grease reservoirs (bleed).

1. Introduction

The life of grease lubricated rolling bearings is usually limited by the life of the grease [1,2]. Grease life is determined by the point in time where the grease can no longer provide the ball-ring contacts with sufficient lubricant and/or by the time where the grease has lost its ‘lubricity’. Both are strongly affected by oxidation. Oxidation is a process where low molecular weight products are formed that easily evaporate and therefore contribute to a loss of base oil from the bearing. It also produces high molecular weight products, such as lacquer and/or varnish that do not have lubricating properties. The free radical mechanisms with various phases have been described intensively in the literature. The basics of oxidation modeling has been done by Klaus and co-workers in the 1980’s [3–6]. A review on the mechanisms of anti-oxidants is written by Reyes [7].

In order to delay the oxidation process in lubricating greases for rolling bearings anti-oxidants are used as additives (usually amines). Oxidation does not take place until a so-called ‘induction time’ has passed [8]. This induction time can be measured in standardized tests such as ASTM D942 [9], Pressure Difference Scanning Calorimetry (ASTM D5482 [10]). A quicker method, based on the same principles, was developed for fuels, called the ‘Rapid Small Scale Oxidation Test (RSSOT) [11] where a fluid is aged in pure oxygen and high temperature and pressure, applied to grease by Dodos [12] and Matzke et al. [13]. Osara et al. [14] developed a model that makes it possible to translate the results of this accelerated test back to atmospheric conditions and any temperature. Bearing tests in pure oxygen have been performed by Mahncke and Boes [15]. We recently published a method using Thermo Gravimetric Analysis (TGA) [16], where the temperature is stepwise increased. The concept of oxidation induction time and consumption of anti-oxidants in rolling bearings was proven by Ito et al. [17] who measured both the anti-oxidant concentration and total acid number of grease samples taken from bearings, showing that oxidation is absent in the presence of anti-oxidants but happens at a high reaction rate once these have been consumed.

Measuring the anti-oxidants concentration can also be used to measure the remaining grease life in bearings. V.d. Kommer and Ameye [18] reported that anti-oxidants are consumed after 50% of grease life.

Both base oil and thickener may degrade by oxidation. Actually, there can be interactions. The metals in the thickener act as catalysts to oxidation. A simple urea grease with mineral oil and no additives has a better oxidation stability than a simple lithium complex and mineral oil grease (Reyes-Gavilan [19]). The oxidation of grease also has an impact on the interaction between oil and thickener. As an example, oxidation may prohibit further bleeding of a grease (Komatsuzaki and Uematsu [20]).

As illustrated above, most oxidation studies are done on oxidation tests in the laboratory. Not much is known about the exact impact of oxidation on grease life in bearings. Lubricating grease in a bearing is not only degraded by oxidation but also by mechanical degradation. In addition, in a rotating bearing, flow/mixing happens, where continuous “fresh surface” is generated, which is clearly different from aging in the above mentioned laboratory instruments where grease is stationary and oxidation may be limited by diffusion. In addition, the “thermal

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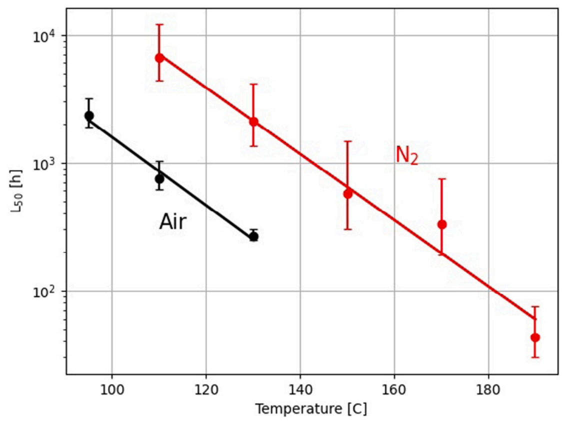

Fig. 1. Grease life. For both Nitrogen and air tests: Arrhenius temperature $T_A = 11$ °C.

load” on the grease will vary throughout the bearing. Komatsuzaki and Uematsu [21] measured acid numbers of the extracted base oil showed that the acid number (related to the degree of oxidation) increases more inside than outside the bearing (and is affected by bearing load).

In this paper we will quantify the significance of oxidation on grease life by the analysis of grease samples collected from bearings that have been run to “the end of grease life” in air and in a nitrogen environment where hardly any oxidation takes place. Running in the absence of oxidation will give a much longer grease life. To investigate the mechanisms behind this we have evaluated the condition of grease over time by taking grease samples from bearings that have been run at different times. We will show how oxidation evolves over time and how this impacts consistency, oil content and bleed. We will identify the mechanisms that lead to end of grease life/bearing failure. We will also show that the distribution of failures is essentially different from what is commonly used for bearing life.

2. Impact of temperature on mechanical properties and degradation

It is apparent that the main grease properties such as base oil viscosity and yield stress follow more-or-less the same Arrhenius behavior with approximately the same activation energies. Also the way they degrade, i.e., mechanical and thermal degradation, follow an Arrhenius behavior and therefore also grease life. Not much work has been done on pure thermo-mechanical degradation of grease in the absence of oxidation. The standard test for this is using the grease worker (ASTM [22]) where the consistency is measured before and after working the grease. Unfortunately, these tests are done at fixed (room) temperature, so do not give information on the effect of temperature on grease degradation. Zhou et al. [23] measured the change of yield stress (a measure for the consistency of the grease) as a function of imposed energy density corrected by an Arrhenius coefficient:

$$E_m = C_T \frac{W}{V_a} \tag{1}$$

with an engineering approach to the Arrhenius equation [24]:

$$C_T = 2^{\frac{T-T_0}{T_A}} \tag{2}$$

where W is the work imposed on the grease and V_a the grease volume. T_0 is a reference temperature. They used a modified grease worker and a Couette aging machine and found $T_A = 10$ °C. Very recently, Akchurin et al. [25] measured the change in oil separation (grease bleed) for grease in rolling bearings as a function of energy density for bearings running at different temperatures but such that no oxidation took place and also found an Arrhenius temperature of $T_A = 10$ °C. Other work on thermo-mechanical degradation was done by Kuhn [26], Khonsari and co-workers [27,28] and Osara and Bryant [29]. However, the experiments in these papers were mainly focused on mechanical degradation where the temperatures were very low and not varying much.

Applying the same Eq. (2) to viscosity gives

$$\eta(T) = \eta(40)\left(\frac{1}{2}\right)^{\frac{T-40}{T_A}}, \tag{3}$$

for the base oil in the grease that is used in this paper and for which the grease life test results shown in Fig. 1, $T_A = 18$ °C. So the T_A found for the base oil viscosity is in the same order of magnitude as that for grease life ($T_A = 11$ °C, as will be shown later in this report). For the yield stress Froishteter et al. [30] found values of $T_A = 25$ °C and Cyriac et al. [31] found Arrhenius temperatures for the yield stress of $25 < T_A < 70$ °C (with different grease). So apparently, also these mechanical properties of lubricating greases follow an Arrhenius behavior. The yield stress (consistency) of the grease is less dependent of temperature than the base oil viscosity. It can therefore be expected that grease life would follow an Arrhenius behavior. In this report we will address mechanical degradation by means of testing in N_2.

3. Impact of temperature on oxidation

The oxidation process is complex where oxidation is assumed to occur via a free radical chain reaction. Anti-oxidants are added to the grease to prevent oxidation for very long times. Some of these act as radical scavengers terminating the free radical chain reactions, others may decompose radicals. These additives are (slowly) consumed as a function of time and temperature, where oxidation at higher temperatures occurs at a high rate after the point in time where these are totally consumed [17]. This time is called the ‘induction time’, Rhee [10]. This induction time is believed to correspond well to grease life at very high temperatures (where oxidation is the dominating degradation process). Rhee [8] developed a simple equation to predict induction times:

$$t_i = \frac{4.6}{k_0} \exp\left(\frac{E}{RT}\right) \tag{4}$$

with E an activation energy, k_0 a rate constant. R the universal gas constant and T the temperature. He compared oxidation time with grease life as measured on ASTM D3527 (wheel bearing, high temperature high load test) [32] and found

$$L = 65 \times t_i^{0.32} \tag{5}$$

This induction time was measured using the Pressure Differential Scanning Calometry method ASTM D5483 under high pressure and in pure oxygen. As mentioned above, this is different from what we have in a bearing [14]. Moreover, the ASTM test is done at a fixed load and speed. It is also important to notice that the ASTM bearing tests are all done at a very high temperature (180 °C, [8]) where oxidation obviously dominates grease life. Nevertheless, Rhee tested a very large number (10) of greases, with very different chemistry, which illustrates that oxidation is a very important cause of failure.

Komatsuzaki et al. [21] measured oxidation, in larger Cylindrical Roller Bearings, from samples taken inside the bearing and from the bearing covers. They saw the same trend in oxidation where oxidation of grease on the cover was delayed compared to that inside the bearing. This must be caused by a difference in temperature possibly in combination with the catalytic effect from iron containing wear particles in the tracks.

4. Experimental approach

4.1. ROF+ test

The tests that are described in this paper have all been done on ROF+ test rigs, which are specially designed to evaluate grease life [33,34]. In this paper we ran all tests under pure axial load,

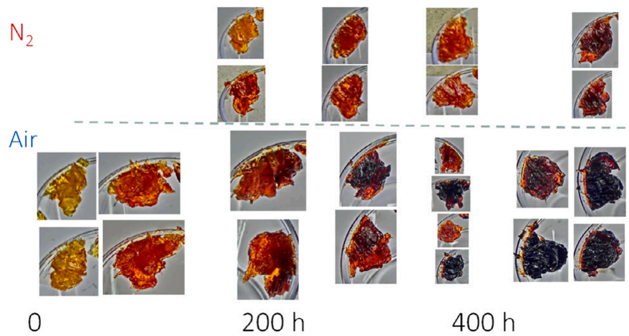

Fig. 2. Visual impression of the appearance of grease samples taken from the bearing tests.

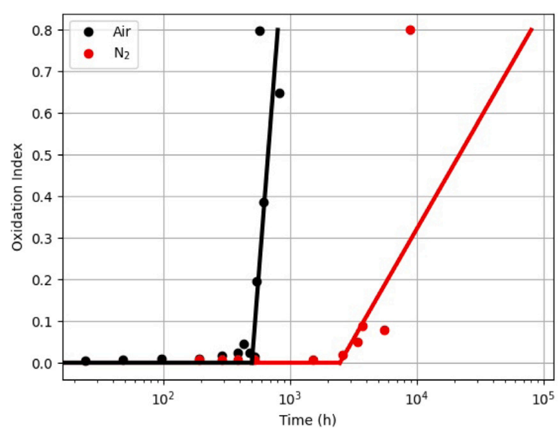

Fig. 3. Oxidation versus time in the 110 °C test.

which means that we do not need support bearings. So in these tests, we have 2 identical bearings (6204/C3-2Z) on a shaft, running at a given axial load (F_a = 470 N) and speed (n = 10 000 rpm) until grease failure (in one of the two bearings) or until the test is manually stopped. Prior to controlling the temperature to the 'test-temperature', the grease/bearings were run-in under self-induced temperature for 12 h. Each bearing was filled with 1.4 g grease: a standard lithium-hydroxy stearate thickened grease with mineral base oil with viscosity 101 cSt at 40 °C and 10 cSt at 100 °C and consistency NLGI 3. Some tests were run with a nitrogen gas flow rate of 5 l/min through the bearings. The oxygen concentration in the flow out from the bearing was measured and was less than 0.5%. To run under exactly the same conditions the same flow rate was also used for normal (air) running, since an N_2 flow will not only prevent oxidation but may also accelerate evaporation and therefore reduce grease life. This was done despite the fact that a reference test without any air flow through the bearings did not give a significant different grease life.

4.2. Grease life

Grease life has been tested in air at 95, 110 and 130 °C and at 110, 130, 150, 170 and 190 °C with nitrogen. Fig. 1 shows the result of the grease life tests, where L_{50} is the median for a 50% probability of failure. The figure also shows the 90% confidence intervals.

Grease life as a function of temperature follows Van 't Hoff or Arrhenius behavior, conveniently written to what is commonly used in engineering grease life models, as [24,35]:

$$L_{50} = L_{50,r} \left(\frac{1}{2}\right)^{\frac{T-T_r}{T_A}}, \tag{6}$$

where $L_{50,r}$ is L_{50} at temperature $T = T_r$ and T_A the Arrhenius temperature. T_A is typically $10 < T_A < 15$ °C, which means that grease life is reduced by a factor 2 with every T_A temperature increase. The temperature dependence depends on the grease chemistry, as shown by Ito et al. [36] for 10 greases.

As shown in Fig. 1, the Arrhenius temperature for grease life for this grease, both in air and nitrogen reads T_A = 11 °C. The fact that the same Arrhenius temperature in air and in nitrogen was found is remarkable. Earlier tests from Kleinlein [37] suggested that the Arrhenius temperature would decrease with decreasing temperature, so smaller values of T_A, meaning that grease life is even more strongly dependent on temperature at lower temperatures. He suggests that this would decrease from T_A = 15 °C at T = 100 °C to T_A = 6 °C at T = 70 °C. This is not due to an absence of oxidation at lower temperature. An explanation will be given later in this paper.

5. Grease post test analysis

In order to investigate the lubrication mechanisms we have done grease analysis from R0F+ bearing tests using the same speed and load conditions as in the grease life tests, described in Section 4.2, but at a fixed temperature of T = 110 °C. A complete analysis was not possible for all the samples due to the lack, for some samples, of a sufficient amount of grease. Next we have done some additional tests at a lower temperature of T = 95 °C. In order to have a sufficient amount of grease for the various tests, the grease samples from the 2 bearings where merged. The test times are listed in Table 1. Fig. 2 gives an impression of the grease appearance from samples that have been running for various times in these tests. The figure clearly shows that the grease changes color already in an early stage in the tests but gets black, indicating oxidation, after 300 h in the test with air, where this does not happen in the N_2 test.

5.1. Oxidation

The change in appearance is consistent with the oxidation measurements, shown in Fig. 3. Fig. 3 shows the 'oxidation index', measured using Fourier Transform Infrared Spectroscopy (FTIR). This index is defined as the absorbance ratio of the oxidation band in the 1710 cm^{-1} region vs. a reference peak at 1465 cm^{-1}, [18]:

$$R_{ox} = \frac{A_{ox}}{A_{ref}} \tag{7}$$

If the grease is severely oxidized, the samples lose transparency, which reduces the accuracy of the measurements. This explains the scatter of the results at higher values. Fig. 3 shows that some oxidation was detected after about 300 h in air, where-after a rapid increase of oxidation is seen after about 500 h. Grease life under the same conditions in air (Fig. 1 shows the L_{50} result, which is L_{50} = 745 h), gave a 90% confidence interval of $249 < L_{10} < 636$ h ($L_{10,50}$ = 493 h). This approximates the time that oxidation really started. This indicates that the increase in probability of failure starts at the time that oxidation starts. In the case of the test with pure nitrogen, oxidation started much later, after about 2500 h. Apparently even small traces of oxygen are enough to cause oxidation. However, now after very long times where again this induction time corresponded to $L_{10,50}$ = 2472 h life (note that with a 90% confidence interval $702 < L_{10} < 4307$ h, $L_{50,50}$ = 6600 h at this temperature). Blackening was already visible much earlier, which suggests that this color change is not the result of oxidation only.

5.2. Anti-oxidants

The Ruler©method was used to measure reduction of anti-oxidants versus time in the bearing tests. This uses cyclic voltammetric techniques. Here a voltage ramp is applied over electrodes in the grease samples diluted in a solvent containing a dissolved electrolyte. The voltage induces oxidation of the anti-oxidant, releasing electrons, which

Table 1
Bearing running times (h) for the various grease samples where numbers denoted by an asterix refer to failed sets of bearings where samples were taken from the suspended bearing. T = 110 °C test.

Hours	24	48	96	192	288	384	432	480	528	548*	574*	615*	820*	1524	2612*	3397*	3710*	5571*	8787*
Air	X	X	X	X	X	X	X	X	X	X	X	X	X						
N_2				X	X	X			X					X	X	X	X	X	X

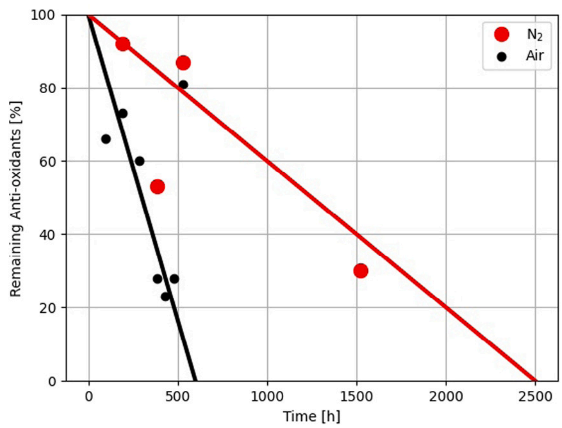

Fig. 4. Anti-oxidants versus time for the tests in air and in nitrogen. T = 110 °C.

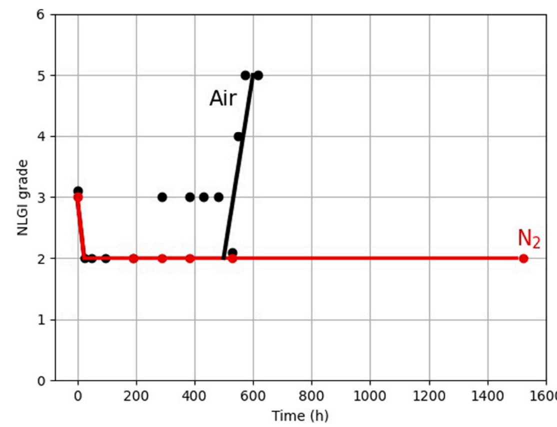

Fig. 5. Evolution of the consistency of grease in tests in air and in nitrogen. T = 110 °C.

again generates a current, which is linearly related to the additive concentration. This current is measured and gives an indication of the concentration of the anti-oxidant. The accuracy is about 15%, which means that it cannot be used to measure the exact anti-oxidant concentration but gives a fair indication of its concentration, Van Leeuwen [38]. The accuracy is reduced by the fact that the sample size was very small (approximately 2 g, 1 g from each bearing) and from the fact that each point represents an average of 2 bearings. Nevertheless, clear trends can be observed. Fig. 4 shows that the concentration of anti-oxidants reduces very clearly in the test in air where the anti-oxidants were depleted after about 500 h, so similar to the oxidation induction time mentioned above. This confirms that oxidation starts quickly after the depletion of the anti-oxidants. The tests in nitrogen also show some decline in anti-oxidants concentration. However, the decline in nitrogen is much slower. This confirms the results from Fig. 3: the N_2 atmosphere was not totally inert, there were traces of oxygen present that caused oxidation. However, the reduction in anti-oxidant concentration is so small that oxidation will start only after very long times (2500 h).

5.3. Rheology

Fig. 5 shows the evolution of the consistency of the grease in the tests in air and in nitrogen. For a definition of the NLGI grade, the reader is referred to [2,39]. The ASTM standards D217 [40] and D1403 [41] require a sample size of 290 ml or 3.8 ml [42]. This is too large and we therefore used the SKF Grease Test Kit TKGT [43] where only 0.5 g is needed (so approximately 0.5 ml).

Initially this grease had an NLGI grade 3. Very quickly after starting up the bearings the consistency dropped to NLGI2 (the grease became softer). This is the result of thermo-mechanical degradation in the churning phase [44]. After 300 h the grease stiffened again to its original grade. However, after 500 h, the time at which oxidation started (see Fig. 3), further stiffening occurred. For the bearings running in nitrogen, we initially see the same behavior as in air: the consistency drops after starting up the bearings. However, other than in the air tests the consistency did not increase after 300 h. It continued staying low, even up to 1500 h. The stiffening of the grease prior to oxidation in the case of running in air must be related to the presence of oxygen and may be caused by the consumption of anti-oxidants. This needs to be investigated further in the future. However, the increase of consistency by 2 more points after the oxidation induction time is clearly the results of oxidation, an effect that does not occur in the case of an absence of oxygen.

The grease that is used in this paper hardens. This must be grease-type dependent. Sometimes softening (and therefore loss retaining ability) is caused by oxidation [20].

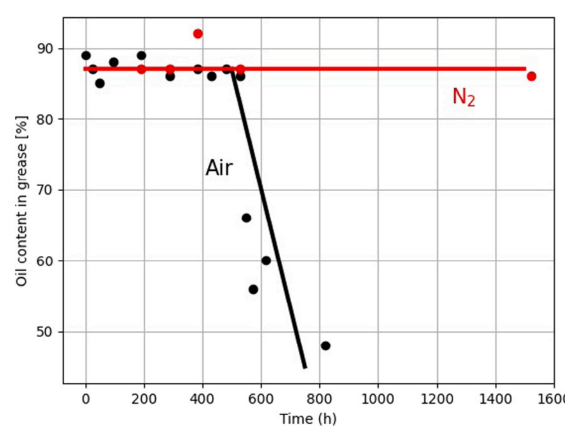

Fig. 6. Oil content in grease versus time for the tests in air (black line) and in nitrogen (red line).

5.4. Oil content

Fig. 6 shows the oil content of the grease taken from the bearings that were running at 110 °C. The oil content is constant (equal to that of fresh grease) until oxidation starts in the case of "Air". For the tests in a nitrogen environment this does not change. A similar result was shown by the best performing grease of the two greases that were tested by Komoriya et al. [45].

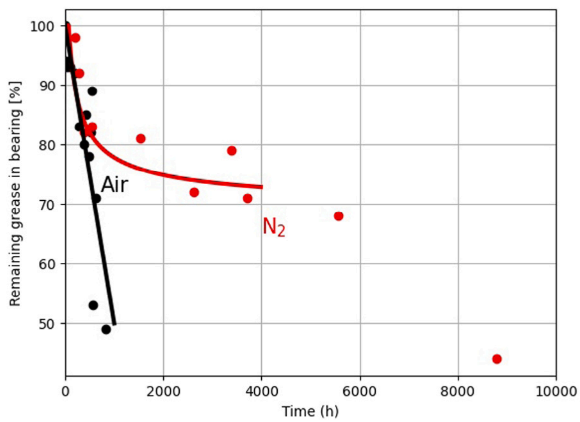

Fig. 7. Grease leakage for the test in air and in nitrogen.

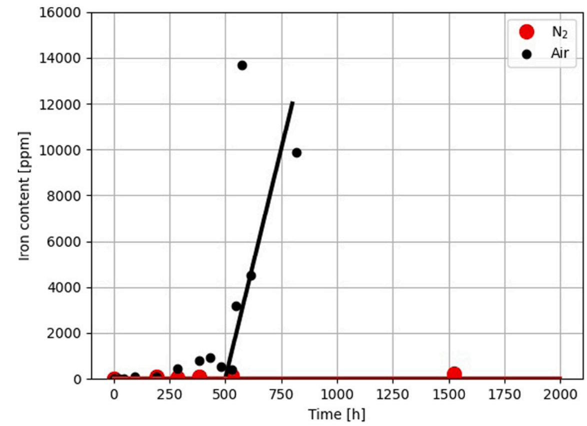

Fig. 8. Iron content in grease versus running-time for the tests in air and in nitrogen. T = 110 °C test.

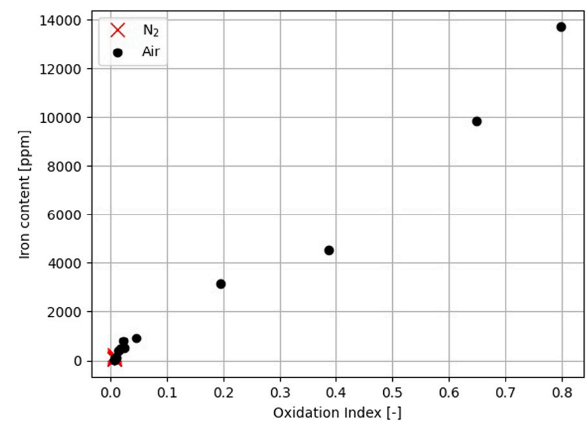

Fig. 9. Iron content in grease versus level of oxidation for the test in air and in nitrogen. T = 110 °C test.

5.5. Leakage versus mass loss

Fig. 7 shows the remaining mass fraction of grease in the bearings as a function of time and defined as:

$$\text{Remaining grease} = 1 - \frac{(\text{weight before} - \text{weight after})}{\text{grease fill}}. \tag{8}$$

Both the tests with air and those with nitrogen show similar behavior until about 500 h. This corresponds to the oxidation induction time that was shown in Fig. 3. Initially the mass loss rate is very high due to churning (which lasts only a few hours), followed by a smaller loss rate, Chatra et al. [44]. The reduction of grease in the bearing is not linear with time. The rate (reduction per unit time) decreases and approaches zero after long times where all access of grease has left the bearing.

Since the oil content in the grease in our tests does not change significantly before the induction time (see Fig. 6) this reduction of mass loss must be due to leakage of grease. This “leakage” continues after the grease oxidation induction time of about 500 h as shown in Fig. 7. However, now this reduction in mass continues due to the formation of volatiles, generated by oxidation [5,6]. Note that the oil content in the grease also starts changing after this point, see Fig. 6. It should be noted that in these tests non-contacting seals were used. So there is a gap between seal and inner ring. This gap will cause some leakage and also makes it possible for volatiles to leave the bearing. The formation of volatiles is expected to not only cause a continuous loss oil but also a change in loss rate. This could not be detected with the relatively large uncertainty in the measurement results.

This was expected to happen in the tests with N_2 too but again after the oxidation induction time, which was now 2500 h. One would expect a change in mass reduction rate at this time. Surprisingly this was not measured. This can be ascribed to the very low rate of oxidation in the case of N_2. After all, the oxidation reaction rate, after the induction time, is a function of the oxygen concentration, which is very low here, making a change in mass loss rate hardly measurable. More measurements would be required for this. This is the reason why the red line in Fig. 7 was not extended after 4000 h.

The mass loss caused by the loss of volatiles could have been accelerated by the air/N_2 flow though the bearing. After all, our earlier study on the impact of base oil evaporation on mass loss showed that this was very small [46]. To investigate this, the impact of this air flow on grease life, also a test without air flow was done and the result was identical. This confirms the extreme volatility of the oxidation products compared to that of the base oil.

5.6. Bleed

The fact that oil concentration does not change before the oxidation induction time suggests that the grease had not lost oil and therefore no bleed occurred in the first 500 h. The bleed ability does change though. This was not measured specifically here but is known from the work of Akchurin et al. [25] where the change in grease permeability was measured in polyurea lubricated bearings where no oxidation had taken place.

5.7. Iron content

Fig. 8 shows the Iron content in the grease as a function of the running time. This clearly follows the oxidation trend. Even after a very long running time in nitrogen (1500 h) the iron content was very low (≈200 ppm), whereas the iron concentration starts increasing at the point in time where also oxidation starts. Fig. 9 shows the oxidation index versus iron content. It is remarkable that there is a linear correlation. Oxidation causes an increase in acidity, leading to corrosion of the bearing metal surfaces and wear. However, no increase in chromium was found indicating that the iron particles must originate from the cage. This confirms the conclusions from the tests of Komoriya et al. [45] where the cage started wearing earlier then the raceways in their grease lubricated bearings. The iron particles act as catalysts for the oxidation reaction [47], creating again more iron

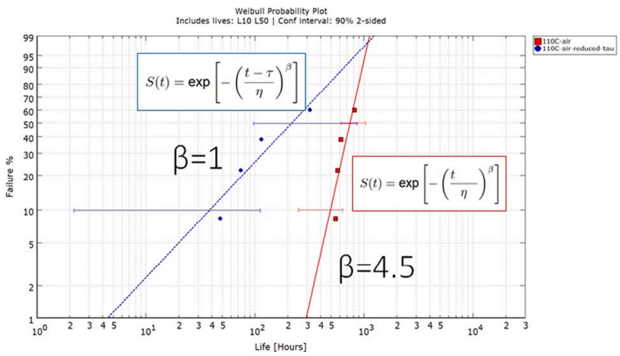

Fig. 10. Weibull distribution and the individual failures for the test in air at 110 °C for $\tau = 0$ and for τ is equal to the oxidation induction time. For the test methodology the reader is referred to [2,33,34].

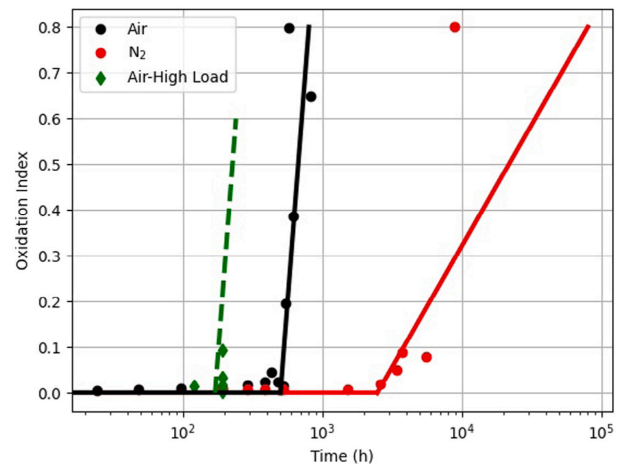

Fig. 11. Impact of load on oxidation. The green diamonds are measurements done at high load (T = 110 °C).

containing particles, accelerating oxidation again, etc.. This is nicely illustrated in this plot.

6. The impact of oxidation on the Weibull distribution

The probability $S(t)$ that a bearing, running under given conditions, survived after running at least time t can be described using the 3-parameter Weibull distribution and is given by

$$S(t) = \exp\left[-\left(\frac{t-\tau}{\eta}\right)^{\beta}\right] \tag{9}$$

Here β is the Weibull slope that determines the shape of the distribution of S, η is the scale parameter and τ the location parameter, which is generally assumed to be $\tau = 0$. This distribution for the 110 °C test in air is given in Fig. 10. The Weibull slope is $\beta = 4.5$ for this test. This is in line with what was mentioned in the introduction of this paper as consensus in the bearing and grease community: if oxidation dominates grease life, life is deterministic resulting in a very high Weibull slope. If we now subtract the induction time, i.e., using Eq. (9), but now with $\tau = 500$ h, and again fit the Weibull distribution, we get the blue line in Fig. 10 and a Weibull slope $\beta = 1$, meaning random failures (constant failure rate, i.e. number of failures per unit time is constant). As mentioned above, oxidation is a deterministic process and if the bearings would fail at the induction time, the Weibull slope β would be very large, even if the induction time is subtracted. It is expected that replenishment with 'fresh' oil from the grease reservoirs by bleed will retard the failure of a bearing. This bleed is not deterministic. There are several reasons that could be behind this.

- the reservoir is not perfectly uniform
- bleed is accelerated by an increase in temperature (reduction of viscosity, stationary grease: [48]; dynamic grease: [49]). Contact temperature is again determined by level of starvation which is again a function of bleed
- bleed is determined by grease again in the churning phase, which is not deterministic [44].

7. Film thickness

The film thicknesses, calculated assuming fully flooded conditions and using the base oil viscosity, at the inner ring contacts was h_i = 0.214 μm and for the outer ring h_o = 0.262 μm. The combined roughness R_q = 0.04 μm. Grease lubricated bearings are running under starved lubrication conditions. Cen and Lugt [50] performed film thickness measurements for an axially loaded deep groove ball bearing (6209-type) and established a relationship between level of starvation and the product of contact size, viscosity and speed (ηbu) where the film thickness was about 70% of the fully flooded film thickness during the start of the bleed phase (20 h, the film thickness had reached a 'steady state value'). Assuming similar values here gives film thickness that have values that are four times larger than the combined roughness of balls and rings. With the rule of thumb that full film conditions prevail when this is a factor 3, it can be assumed that the bearings are running in full film lubrication conditions, at least during the first part of the test.

8. Impact of load on grease life

The main conclusion of what was shown above is that grease life in ball bearings is strongly determined by oxidation. Komatsuzaki et al. [21] showed that oxidation close to the bearing running tracks happens earlier than oxidation of grease away from this. This explains the impact of bearing load on grease life [2]. The temperature of the running track increases with load, which makes oxidation and therefore grease life a function of load. To validate this hypothesis we did the same test as described above, at T = 110 °C, with increased load, F_a = 1.1 kN, in air. Out of the 5 pairs of bearings, 2 failed at 121 and 192 h, after which the test was stopped. This results in a shorter grease life: $L_{10,50}$ = 150 h, obviously with a large uncertainty because of the limited number of failed bearings. Fig. 11 gives the same plot as was shown earlier, Fig. 3, but now the oxidation index measured in the test with higher load is included. At higher load, oxidation clearly happens at an earlier stage, confirming that this is induced by the higher contact temperatures. Again, the onset of oxidation represents the L_{10} grease life. It should be noted that oxidation measured in an oxidation test can therefore not be used to predict grease life, as suggested by Rhee in Eq. (5). These tests can only be used to screen greases for their oxidative stability.

9. Discussion on grease bleed

The results in this paper lead to a new view on 'grease bleed' or 'grease oil-separation'. It is generally accepted that oil separation or bleed is a very important property of a lubricating grease and is always specified/measured for fresh grease. We have shown here that the grease in a running bearing does not loose oil until the point in time where oil is lost from the running tracks. In this paper this is caused by oxidation where volatiles are formed, but could also have other reasons such as leakage.

Grease bleed is driven by pressure. A grease that is put on a clean plate (even in an oven to accelerate possible bleed) does not show bleed. The oil in the grease is maintained in the thickener matrix due to an affinity between oil and thickener. Release of oil is driven by a pressure that should be higher than this affinity pressure (Zhang et al. [48]). A yet unproven hypothesis is that, for stationary grease, the driving pressure in a bearing may be induced by capillary pressure by the oil/air interface between ball and raceway (meniscus). It therefore only occurs in the case of starved lubrication, so in the case that the oil layers in the running tracks are very thin. If bleed would happen continuously, the tracks would also be fed with oil continuously, leading to oil churning, leading to very high temperatures and base oil leakage from the bearing. Moreover, the oil content of the grease would continuously reduce as a function of time. In this paper we show that this does not happen. 'Grease bleeds only when needed'. This is a favorable property of lubricating greases, making the grease lubrication process very efficient.

Shear on the grease, as it happens in a running bearing, does change its bleed *properties*. i.e., its ability to bleed (given by the base oil-thickener affinity and grease permeability). This is important because these properties have changed significantly by the time that oxidation occurs, Akchurin et al. [25]. This means that specifications for bleed need to be revised in the future.

10. Conclusions

In this section we will formulate some conclusions that can be drawn from the experiments described in this paper. These are formulated in a general way. Strictly speaking these are only applicable for the conditions, grease and bearing type that was used here. However, since we used a commercial standard lithium-thickened, mineral base oil grease and a standard ball bearing with temperatures and loads that are commonly applied, we believe that these are applicable in a larger application domain, provided that grease life is much shorter than bearing fatigue life.

The principles of what was presented applies to all bearing types and grease types. However, the absolute numbers will be subject to bearing type, grease and operating condition. For example Komatsuzaki and Uematsu [21] reported that grease loses its lubricating ability when the oil content of the grease mass inside the bearings dropped to about 50%–60%. They did their tests in cylindrical roller bearings.

The general conclusions are:

- Grease life in sealed ball bearings is dominated by oxidation. The probability of failure can assumed to be zero before the oxidation induction time. The start of oxidation (oxidation induction time) corresponds to the L_{10} life, using a conventional Weibull analysis on the tests, showing that oxidation is the main cause of failure at these temperatures for this type of grease
- The oxidation induction time is given by the point in time where anti-oxidants have entirely been consumed. This means that the induction time will be a function of additive concentration and effectiveness but also on the oxygen concentration.
- Oxidation leads to the formation of volatiles, leading to a mass loss of oil in the track
- Oil separation from the grease in the reservoirs (bleed) will start only after oxidation has taken place. As long as there is a layer of oil in the track, no oil flow from the grease reservoirs from the sides of the bearing towards the running track takes place.
- Oxidation will mainly happen in the running track where the temperatures are higher than in the grease reservoirs next to the track.
- The impact of load on grease life is caused by an increase in heat development in the EHL contacts.
- Oxidation increases the acidity of the grease leading to corrosive wear. This again generates iron particles that form a catalyst for further oxidation, accelerating the oxidation process again.
- Mechanical degradation will have an impact on grease life through leakage during the churning phase and by changing the oil separation ability (bleed properties). The latter will have an impact on the oil release during oxidation and therefore on life after the induction time.
- The Arrhenius temperature is not a function of temperature. The Arrhenius temperature for oxidation is similar to that for mechanical degradation (see Zhou et al. [23], who found an Arrhenius temperature of 10 °C where that for grease life in our tests was 11 °C). This makes it difficult to distinguish the degradation modes from grease life tests.
- A location time parameter τ was introduced in the Weibull distribution. Before this time, the probability of failure is zero. The value of this location parameter would be equal to the oxidation induction time. The Weibull slope $\beta \approx 1$. This implies that grease life may be dominated by oxidation but that grease life is not determined only by this. The supply of relatively fresh oil from the reservoir makes it possible to extend grease life after the induction time. The randomness of this is caused by the earlier reported chaotic behavior that results in a random component in the degradation and 'quality' of the grease reservoirs in the bearing

Declaration of competing interest

We the undersigned declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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Data availability

The data that has been used is confidential.

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