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Article

Influence of Mechanical, Thermal, Oxidative and Catalytic Processes on Thickener Structure and Thus on the Service Life of Rolling Bearings

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Abstract: Constant further developments in application technology with the aim of higher economic efficiency and power density place ever greater demands on mechanical components and construction elements and thus on the lubricating greases used. This is particularly true in the area of roller bearings, in which lubricating greases are sometimes used with high mechanical stress and in wide temperature ranges. A current example is the rolling bearings in the assemblies of hybrid vehicles, which are subjected to extreme thermal and mechanical loads due to engine downsizing, high speeds and the radiant heat from the combustion engine. Investigations at the Competence Center of Tribology Mannheim (KTM) show that the grease service life for roller bearing lubrication, even at high temperatures, does not only depend on classic oil aging. In numerous roller bearing tests and by means of rheological measurements, it could be shown that the loss of the lubricating effect is a consequence of the change in the thickener structure. Mechanical, thermal, oxidative and catalytic processes play a decisive role here. In this article, a scientific method is presented for the first time as to how these individual influencing factors can be examined and evaluated independent from one another. For this purpose, the first results of an ongoing DGMK project are presented and evaluated.

Keywords: grease lubrication; roller bearings; thickener degradation; aging; screening tests

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1. Introduction

Constant further developments in application technology with the aim of higher economic efficiency and power density place ever greater demands on mechanical components and construction elements and thus on the lubricating greases used. This is particularly true in the area of roller bearings, in which lubricating greases are often used with high mechanical stress and in wide temperature ranges. A current example is the rolling bearings in the assemblies of hybrid vehicles, which are subjected to extreme thermal and mechanical loads due to engine downsizing, high speeds and radiant heat from the combustion engine (Figure 1).

Figure 1. Challenges for greases in EV roller bearing applications [Source: KTM].

Investigations at the Competence Center of Tribology Mannheim (KTM) show that the grease service life for roller bearing lubrication, even at high temperatures, does not only depend on classic oil aging. In numerous roller bearing tests and by means of rheological measurements, it could be shown that the loss of the lubricating effect is often a consequence of the change in the thickener structure. Mechanical, thermal, oxidative and catalytic processes play a decisive role here.

1.1. Economic Importance of the Topic

If roller bearings fail, this can lead to a total loss of the entire technical system or to long downtimes. Rolling bearing failures can have several causes. In addition to overloading or fatigue of the components as well as assembly errors and contamination, a malfunction due to inadequate lubrication is often found (approx. 50%) [1,2]. In most cases, an incorrect selection of the lubricant with regard to the specific application can be cited as the cause [3,4].

A better understanding of these mentioned relationships, the influencing factors, and the influence on lubrication would help companies to lower development costs, reduce development times, and develop high-performance products for niche markets.

1.2. Aim of the Public Funded Project DGMK 820

The calculation of the service life of grease-lubricated rolling bearings is based on the fatigue strength of the bearings in accordance with ISO 281. However, under critical operating conditions, such as high temperatures, failure due to a lack of lubrication occurs even before this fatigue limit is reached. Since many roller bearing systems are lubricated for life in practice, the service life of the bearing depends on the service life of the grease and not on the fatigue life of the bearing. The service life of the grease, however, is not a clearly determinable characteristic value that can easily be determined by a standard test [5]. For this reason, various laboratory aging processes and endurance runs in roller bearing test rigs are usually used in development in order to obtain information about the expected service life of a component (e.g., FE8-test, FE9-test, ROF-test). These tests are time-consuming and costly, such that the industry is constantly looking for new, innovative and meaningful screening tools [6].

In the finished DGMK project, 788 "Screening test method for lubricating greases", it was shown that the loss of the lubricating effect of a grease is strongly influenced by the thickener degradation (DGMK, German Society for Sustainable Energy Carriers, Mobility and Carbon Cycles e.V.) [7]. Recent publications by other scientists confirm this hypothesis and reinforce the need for research (e.g., [5,8–10]). In the case of soap-thickened greases, this effect has been shown to occur well before the actual base oil aging and accordingly limits service life. The catalytic effect of the cage material is apparently different—and previously unknown—than on classic oil aging (Figure 2). The current running research project aims to clarify which influencing factors ultimately play the decisive role and how the effect can be positively influenced.

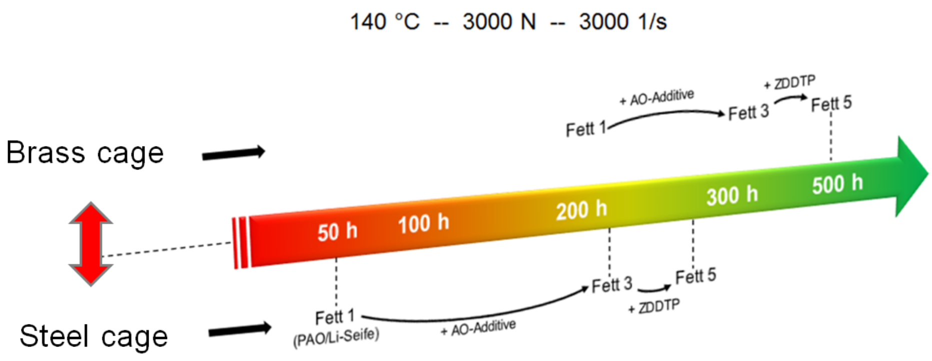

Figure 2. Lifetime of the various grease samples in DGMK project 788 in an FE9-run (140 °C, 3000 N, 2000 rpm).

In technical applications, a wide variety of causes can lead to irreversible damage to the lubricants. Thermo-oxidative degradation depends strongly on the ambient conditions. In non-encapsulated systems, the oxidation of the lubricant leads to the formation of acids, polymers, condensates and deposits. This process depends on the temperature, the presence of catalysts such as metal surfaces or wear debris, the oxygen supply and the aging products produced. Furthermore, coking effects can occur due to the aging of the lubricating grease and thus the degradation and polymerization of the lubricating grease, but also due to insufficient lubrication, especially at elevated temperatures and high speeds [1,4]. In addition to thermo-oxidative aging, a lubricating grease is also subject to high mechanical–dynamic stress in use. The importance of the individual influencing factors was clearly shown in the recent DGMK project 788 [7].

The characterization of the lubricating greases with regard to their resilience and the change of the chemical–physical properties before the actual technical use is an important part of lubricating grease development. In order to simulate the corresponding requirement and to carry out a characterization, there are a large number of tribological test apparatuses and methods used, such as the FE8 (DIN 51819) or FE9 (DIN 51821) methods [6]. These tests are mainly used to check a fully developed and therefore marketable product for its suitability in the end system as well as to examine wear and friction behavior and possible component fatigue. Furthermore, the determination of the upper grease usage temperature is an essential part of the FE9 test.

However, these test methods are not suitable for the basic development of lubricating greases, as the individual tests are too time-consuming and costly and often do not reflect the actual conditions in the application. To make matters worse, several iterative development cycles are typically necessary in an early grease development stage, such that the costs multiply with each cycle. These costs are not easily affordable, especially for small- and medium-sized companies with their innovative and individual products. It is therefore urgently necessary to obtain new findings on the failure mechanisms of grease-lubricated rolling bearings.

The focus of the current research project will be on changing the thickener structure as a result of mechanical, thermal, oxidative and catalytic stress. The chemical and structural changes are detected and examined using the most modern analytics and microscopy (Figure 3):

- Mechanical stress: FE9, shear apparatus according to Klein;
- Structure of the thickener system: scanning electron microscopy, partly "cryo-SEM";
- Rheology: Yield stress, flow curves, elastic and plastic modulus;
- Aging: RapidOxy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), oven aging;
- Analytics: fourier transform infrared spectrometer (FTIR), high-performance liquid chromatography with mass spectroscopy (HPLC-MS), gas chromatography with mass spectrometry (GC-MS), pressure differential scanning calorimeter (PDSC), inductively coupled plasma (ICP).

This research project is based on an empirical approach. This means that numerous laboratory tests on aging dependent on temperature, ambient medium and catalytic elements will be carried out and evaluated. The focus is on the so-called RapidOxy test, as this is becoming increasingly important in the industry (ASTM D8206, DIN 51808) [10,11]. The main part of the tribological tests will be application-oriented roller bearing tests on the multi-station roller bearing test bench (MPWP) based on the FE9 test. Different parameters and bearing types are tested in random trials. These tests are supplemented by high-speed tests in order to meet the special requirements of e-mobility. The aim is to gain knowledge for the first time as to how the thickener structure changes during aging and mechanical stress, and how this can be proven and what influence this has on lubrication and thus on the performance and service life of the rolling bearing.

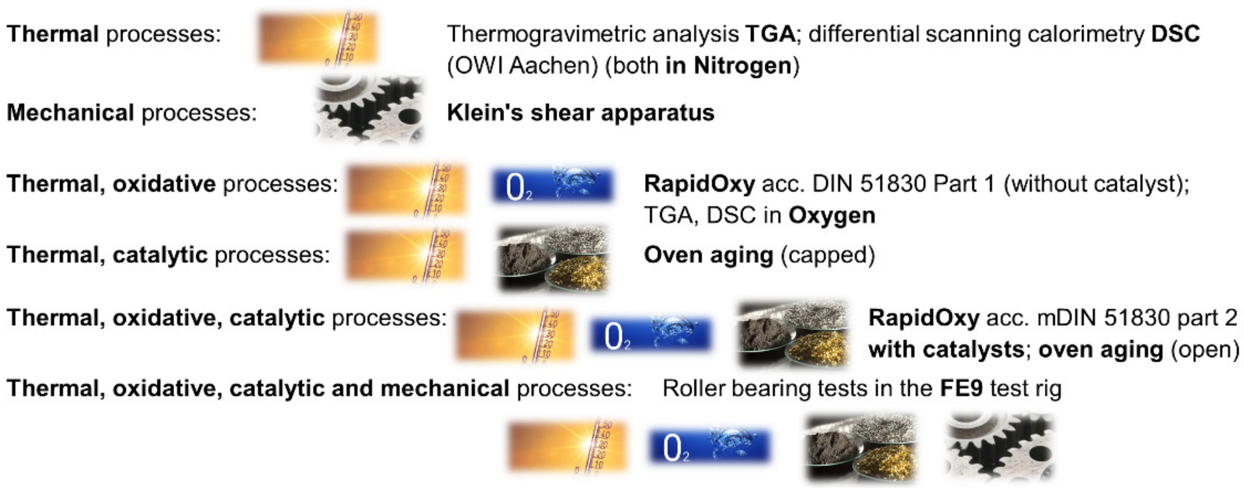

Figure 3. Tests to investigate and clarify individual influences on the loss of the lubricating effect of greases.

2. State of Research

Lubricating greases are used in various applications, with their market share accounting for around 3% of the total amount of lubricant that is processed worldwide. This relatively small proportion may be one of the reasons why the rheology of lubricating greases has received little attention in research until now. The mechanical behavior of a lubricating grease on a lubricated surface is still largely not understood; thus, the need for research is still high. The difficulties in a simple description are due to the complex rheological behavior compared to rheologically simple fluids. A better understanding of the rheological properties of lubricating greases can help to understand how a lubricating grease actually behaves under real operating conditions and how lubrication of the highly loaded contacts works.

Lubricating greases are generally highly structured suspensions made up of a thickener dispersed in mineral or synthetic oil. Of the different types of thickener, the fatty acid soaps of lithium, calcium, sodium, aluminum and barium are most frequently used as thickeners because they are inexpensive and have positive properties for various requirements. The thickener is necessary to increase the consistency of the grease in a targeted manner, to prevent the loss of lubricant under operating conditions, and to prevent the ingress of contaminants such as solid particles and water. The soap thickener forms an interlacing network that binds oil and gives the grease the appropriate rheological and tribological behavior. The performance of lubricating greases depends on the nature of its components and the microstructure achieved during processing. Suitable structural and physical properties can consequently be achieved through a suitable selection of the ingredients, but also through process optimization [12]. It is therefore important to understand how the evolution and change in the grease microstructure affects the functional, tribological and rheological properties of lubricating greases.

In the last few years, there have been a few reports of research projects dealing with the modification of a lubricating grease under thermal–oxidative stress. It is well known that the flowability of a grease increases with increasing temperature, which favors lubricity. However, the risk of oxidative and thermal degradation increases with increasing temperature and residence time [12,13].

As early as 1998, Kuhn investigated the structural breakdown of lubricating grease and found that the variation in rheological properties correlated with the breakdown of the structure [14]. Kuhn defined the term “lubricating grease wear” as a sign of the change due to tribological stress [8].

Cann et al. have found, on the basis of roller bearing tests on the R0F test stand, that grease degradation in the bearing is mainly determined by the bearing temperature [15,16].

Yu and Yang were able to demonstrate the deterioration in the lubricating effect of the grease in the bearings of an electric motor as a result of the increased temperatures and the resulting degeneration of grease [17].

The fiber structure and the inner network are of the greatest importance for the lubricating properties of soap greases. Adhvaryu et al. investigated the change in the fiber structure of lubricating greases as a function of antioxidants [18]. They define the breakdown of the structure as damage to the lubricating properties. Couronne and Vergne found that the fiber length is shortened by thermal aging [19]. Gonçalves et al. found also that the thickener matrix changes with thermal aging [20]. Shen et al. investigated the thickener structure of a lithium–calcium thickened grease and also showed that the network structure is gradually destroyed with a longer thermal aging time and that the stability of the grease structure decreases significantly [21].

Pan et al. investigated the structural change of a lithium soap grease when stored statically at 120 and 150 °C [22]. To do this, they analyzed the microstructure and infrared spectra of grease samples using field-emission scanning electron microscopy (FESEM) or Fourier transform infrared spectroscopy (FTIR). So-called frequency sweep and controlled stress tests were carried out using a rheometer in order to assess the change in the thickener structure. In addition, the mechanical reversibility (thixotropy) was examined by means of three-stage shear strength tests. The investigations showed that when the lithium soap grease was stored for 24 h at 120 °C, no structural degradation or chemical changes occurred. However, the 24 h exposure at 150 °C led to significant structural changes, which could be detected both by scanning electron microscopy and by changes in the rheological parameters. Oxidative changes were also found in the FTIR spectra.

The effect of the type, size and distribution of soap fibers was analyzed by Delgado et al. [23]. Scanning electron microscopic and rheological analyses during the production process of the lithium soap grease show how the typical network structure and the rheology typical of grease only develop fully at the end of the process steps. They were also able to demonstrate that the thickener structure degrades with thermal aging. In another project, the researchers also examined the rheological behavior and microstructure of lithium greases as a function of the soap concentration and the viscosity of the base oil [24].

A current publication on the subject complex, which did not emerge directly from the previous DGMK project [7], was conducted by Yuxin et al. [9]. The research team examined the shear degradation of a lithium soap grease under shear stress in the rheometer at room temperature. It was found that the grease loses its original consistency during use and shows two-phase aging behavior. In the first phase, the main effect is a realignment and breakage of the thickener network, which leads to a progressive decline in the rheological properties of the grease. After that, aging is dominated by the breakage of smaller fiber fragments, and the grease structure is broken down more slowly. Based on this observation, an aging equation based on an entropy approach was formulated by Rezasoltani and Khonsari [25] to describe the aging behavior of lithium-thickened grease. The results of atomic force microscopy of the fresh and aged grease showed that the change in the thickener microstructure is a good explanation for the mechanism of lithium grease degradation: Under shear, the original fiber network is gradually destroyed and fragmented, which leads to a loss of consistency and a change in the rheological properties. Although the researchers only focused on mechanical aging and therefore did not consider the thermal, catalytic and oxidative effects, this work shows that all individual stresses contribute to changes in the microstructure. These results confirm the theses from the DGMK project 788. In another study, this structural degradation of lithium soap-based grease, which can be measured in the rheological parameters, was also visualized using scanning electron microscopy (Figure 4) [26,27].

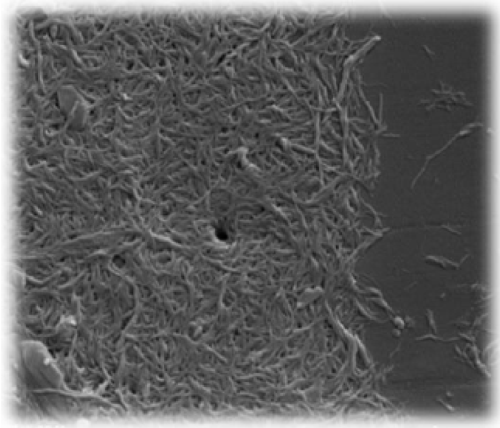

Figure 4. Thickener structure of a lithium soap grease (SEM picture) [Source: KTM].

3. Materials and Methods

3.1. Model Greases

In order to be able to scientifically examine the different influencing factors, model lubricating greases were developed for the project. Mineral oil and Polyalphaolefines (PAO) were used as base oils. These were thickened with a lithium soap (Li-12-hydroxystearate) or with a diurea. Lithium-saponified lubricating greases account for by far the largest market share (simple lithium soaps: 53.7%; lithium-complex soaps 20.65% in 2020 [28]). For this reason, they represent the basis of the investigations. For high-temperature applications, polyurea greases with synthetic base oils represent the gold standard. Two different anti oxidation additives (AO) additives were added to protect against aging (0.5% aminic or 0.5% phenolic). In addition, a classic zinc dithiophosphate was added to some samples as an extreme pressure (EP)/antiwear (AW)/AO additive (1%). These formulations thus represent good and commercially available basic formulations. The variations result in 16 model greases in the first step (Table 1). All greases have been adjusted to an NLGI grade of 2.

Table 1. Composition of the 16 basic model greases of the current DGMK project.

Sample	Base Oil	Thickener	NLGI	Quantity	Additive
Grease 1	Mineral oil	Lithium soap	2	-	-
Grease 2	PAO	Lithium soap	2	-	-
Grease 3	Mineral oil	Diurea	2	-	-
Grease 4	PAO	Diurea	2	-	-
Grease 5	Mineral oil	Lithium soap	2	0.50%	aminic
Grease 6	PAO	Lithium soap	2	0.50%	aminic
Grease 7	Mineral oil	Diurea	2	0.50%	aminic
Grease 8	PAO	Diurea	2	0.50%	aminic
Grease 9	Mineral oil	Lithium soap	2	0.50%	Phenolic
Grease 10	PAO	Lithium soap	2	0.50%	phenolic
Grease 11	Mineral oil	Diurea	2	0.50%	phenolic
Grease 12	PAO	Diurea	2	0.50%	phenolic
Grease 13	Mineral oil	Lithium soap	2	1.00%	ZnDTP
Grease 14	PAO	Lithium soap	2	1.00%	ZnDTP
Grease 15	Mineral oil	Diurea	2	1.00%	ZnDTP
Grease 16	PAO	Diurea	2	1.00%	ZnDTP

3.2. Structural Degradation

Two methods are usually used to investigate the structural breakdown of greases: One is the mechanical roll stability test, in which the grease is stressed under load and shear. A typical mechanical stability test is the "Shell roll stability test" (ASTM D 1831 [29]), in which the grease is sheared between a heavy roller and a hollow rotating cylinder at an elevated temperature (generally 80 °C). According to the literature, this test shows good transferability for wheel bearings in motor vehicles [30] and roller bearings in railroad cars [31,32]. The other test is the shear strength test, in which only a shear stress but no high contact pressure is given. This is considered important for bearings that run under relatively stable working conditions. With continuous shear, it is observed that the shear degradation of the lubricating grease leads to the release of oil and thus provides additional lubricant [33,34]. In the "grease worker" (ASTM D 217 [35]), which consists of a closed cylinder and a piston plate with a number of holes, the grease is sheared through the holes during a precisely defined number of strokes (usually 10,000 or 100,000 strokes). The disadvantage of both of the aforementioned ASTM aging methods (ASTM: American Society for Testing and Materials) is that the shear rates tend to be rather low and not precisely defined, which makes it difficult to use these methods for developing predictive aging models. For this reason, a different method of shear stress is used in the current project. With the help of the Kleins shearing apparatus (Figure 5), greases can be sheared under well-defined conditions. The grease is pumped in a circle, which works similarly to a gear pump. The change in the rheological parameters (yield point and loss modulus) is then determined using rheometer measurements.

Figure 5. Shear tester acc. Klein.

3.3. Aging Method

As part of the cooperation project DGMK 820, various aging methods are being investigated. The Oel-Waerme Institut (OWI) in Aachen carries out measurements with the RapidOxy device, the TGA and the DSC (see Figure 3). At the KTM, we focus on what is known as oven aging. This method has already been used in a similar form at the Bosch company for many years [5]. What is new is that two different methods are now used for the lubricating grease to interact with the catalyst sheet and the oxygen (Figure 6). With the open method, a 1 mm thick layer of grease is applied to the previously cleaned catalyst sheet and is placed in the oven for a defined period of time and temperature. With the capped method, a 2 mm thick layer of lubricating grease is applied, and then another catalyst sheet is placed on top ("sandwich"). Thus, the interaction with the catalyst material is comparable. However, almost no atmospheric oxygen can interact with the grease. The standard test times are 24 and 72 h for both methods.

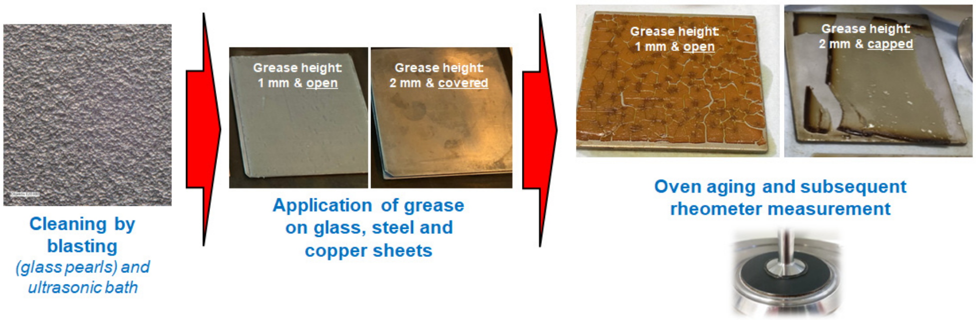

Figure 6. Procedure for so-called oven aging using both methods (open/covered) [Source: KTM].

3.4. Test Methods for Tribological Performance

Tribological tests can be divided into different types (categories). There are various intermediate stages between the so-called field test (field test, Category I) and the model test (Category VI). Together, they result in the so-called tribological test chain [36]. Category IV includes, for example, the standardized FE8 and FE9 test benches that are indispensable in connection with grease testing. In category VI, well-known model test stands are found, such as the four-ball apparatus (VKA, DIN 51350) and the translatory oscillating tribometer (SRV, DIN 51834), the results of which are of almost no significance for roller bearing applications [7].

While the FE8 test bench is used to determine the wear protection and friction behavior of lubricants (oils and greases), the FE9 test bench is used to investigate the high-temperature suitability of lubricating greases for rolling bearings. An angular contact ball bearing is filled with a defined but small amount of grease, which is axially loaded and operated at a fixed speed. Depending on the thickener and base oil, the test is carried out at +100 °C to a maximum of +250 °C. The majority of the tests are carried out in the area around 140 °C. It is possible to carry out the test on open bearings (procedure A), but it is also possible to run the bearing with sealing plates on both sides or with a grease deposit. According to DIN 51821-2, the test is carried out with open bearings with an axial load of 1500 N at a speed of 6000 rpm. Usually, five tests are carried out simultaneously on the five test heads of the test stand (Figure 7). The runtime until failure is determined by a significant increase in friction torque. With the five downtimes, the statistical test runtimes B10 and B50 are then determined by means of a Weibull evaluation. In requirement standards such as DIN 51825, it is specified which running times must be achieved at certain temperatures.

Figure 7. Modern MPWP test rig at the KTM [Source: KTM].

3.5. Rheological Test Methods

Various rheological measurements are suitable for demonstrating changes in the grease structure. For this purpose, a modern rheometer is used (Figure 8) with which, in addition to flow curves, oscillation measurements are also possible to determine the storage and loss modulus. In the context of this publication, however, only the flow curve measurements are discussed.

Figure 8. Rheometer with cone/plate configuration acc. DIN 51810-1.

With this measuring method described in DIN 51810-1, a pre-shearing takes place first (2). After a certain relaxation time (3), the shear rate increases linearly to 500 1/s (4). There, it is then kept constant for 5 min (5). In order to determine the thixotropy, in step 6 (no standard), the shear rate is then linearly reduced to 0 again (Figure 9).

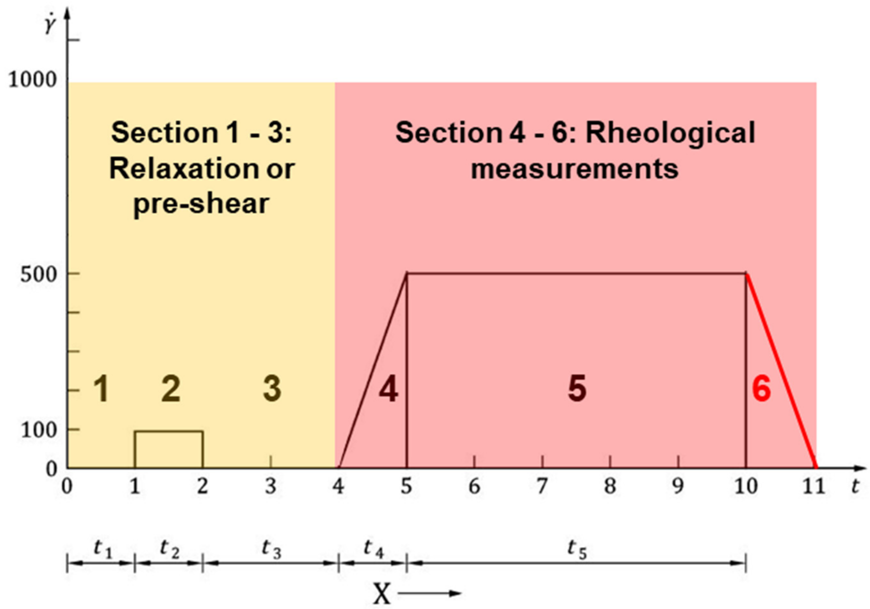

Figure 9. Test procedure for greases acc. DIN 51810-1.

For reasons of clarity, only the curves at level 5 with a constant shear rate are considered in the following graphics. All data will be analyzed as part of the project. Various statistical approaches (DOE) and types of representation are used for this purpose.

Measurement of grease samples are carried out:

1. In fresh condition;
2. After different times of exposure to Klein's shearing;
3. According to the different types and periods of oven aging (variable duration, catalysts, open/capped).

4. Working Hypothesis and Work Packages

In the previous project, DGMK 788, it could be clearly shown that the loss of the lubricating effect of the grease in a rolling bearing is not only dependent on pure aging [6]. Instead, the thickener structures of greases change under certain thermal and mechanical boundary conditions. This can lead to the properties that are essential for a grease, such as the flow limit and structural viscosity, being almost completely lost. The lubricant then behaves similar to a pure oil and flows out of the bearing. In many cases, this thickener degeneration occurs before the oil actually ages and therefore clearly limits service life. This effect seems to be particularly pronounced with soap thickeners, which make up by far the largest part on the market [28]. The catalytic effect of the cage material evidently has a different (previously unknown) effect on these effects than on classic oil aging (see Figure 2). The findings obtained in project 788 as well as the most recent investigations by the KTM in 2019 [26,27] correlate well with the current results of other researchers [1,5,8].

In this follow-up project, the focus will be on changing the thickener structure of the grease. Using state-of-the-art analytics and practical tribological tests, factors influencing the change are to be examined in detail. The aim of the project is to gain a deeper understanding of the factors that limit the service life of grease-lubricated roller bearings. These findings can then be used for a much more targeted grease development or lubricant selection. Thus far, numerous standard methods have been used both in the field of laboratory aging and tribological laboratory testing. The characteristic values are used to be able to compare the lubricating greases with one another and to fill out data sheets. It is widely known that many of these methods are not effective and do not allow for any statements about the behavior in real application [6,7]. It is therefore imperative to know what happens to a lubricating grease under thermal and mechanical stress, how it changes, what influence that catalyst materials and the surrounding medium have, and how exactly these effects and influencing factors can be checked in laboratory tests.

The discussion with the members of the project-accompanying committee as well as with other experts resulted in numerous ideas and hypotheses about the catalytic effect of metals on the thickener structure. One hypothesis is that organic copper compounds, such as copper oleates, copper stearates and possibly iron oleates, are formed during operation through friction, and these are then entered into the grease. Since organic acids (carboxylate groups) and ketones (keto groups) can arise through oxidation of the hydrocarbon chains of the base oil, these could be ionic organic "salts" with copper in the + I or + II oxidation states and with iron in the + II and + III oxidation states (e.g., copper stearate). The grease modified in this way would have different (lubricating) properties than the original soap grease made from alkali/alkaline earth metals (lithium, sodium, calcium). Since in the tests in DGMK project 788, the bearings with the brass cages ran significantly longer than those with the steel cages, it could be that the "copper soaps" that are produced in vitro improve the lubricants in terms of wear or that the iron soaps that are produced worsen the lubricants performance. In this project, the element contents (copper, iron) of the lubricating greases from the tribological tests are to be measured by means of ICP. In addition, it should be investigated whether the elements are present in the form of debris or in the form of organic salts/complexes.

In order to scientifically investigate this question, organic copper compounds such as copper oleates or copper stearates and possibly iron oleates are added in small quantities to the grease samples. It can be used to specifically investigate the extent to which copper soaps structurally or chemically influence the properties of lubricants. Should the copper actually have a positive effect, typical copper inhibitors would have a counterproductive effect. The classic EP/AW additives, which mainly act on the steel, should not have any influence on this effect. In this part of the project, it can be demonstrated whether the registered wear elements (copper and steel) can actually explain the different running times observed or whether only the different cage geometries for sheet metal (steel) and solid cage (brass) are decisive. However, there are statements from the rolling bearing industry that under standard conditions, bearings with brass cages usually have shorter running times than bearings with sheet metal cages. Only at higher speeds are the more precisely manufactured solid brass cages better suited than cold-formed sheet metal cages.

Another hypothesis to be examined is that the aging products of the oil destroy the soap fibers. Here, too, there can be contradicting effects: Initially, the thickener degradation seems critical, as there is a risk that the oil will bleed out quickly and there will be insufficient lubrication. Should the thickener break down more quickly due to the copper contact, however, additional oil will also be released from the grease, which could never be released with a stable thickener structure. The residual oil content of a grease that no longer releases any oil is still approx. 50%. The thickener degradation would therefore have to be assessed as positive, at least in the sense of the working hypothesis, since it virtually triggers an emergency lubrication process. In the context of this question, the gradient of the change between the proportion of grease that is in contact and that of which is only next to the friction point is to be investigated. If the thickener decomposes primarily only in contact with the cage (sliding friction), the rest of the grease remains in its structure and can later age more quickly and spontaneously when it comes into contact with the cage. In order to scientifically investigate this question, the greases are to be examined by means of FTIR after different storage periods. The band ratios can be determined precisely with modern evaluation methods such as peak/array integration. At the same time, the oil extract should also be analyzed in order to show the changes in the base oil. Measurements in the SKF FTG2 test stand provide information about the ratio of oil to thickener and thus about changes in the internal structure.

5. Results

The research project has been running for a year now. Therefore, we can only present the initial results here. However, these already show the first interesting trends and interactions, which then have to be worked out and explained in detail as the project progresses.

5.1. FE9-Tests

The tests on the FE9 (Figure 10) test stand are carried out under standard conditions (axial load 1500 N, speed 6000 rpm). The temperatures differ for the two thickener types. The lithium soap greases are set at 140 °C, whereas the urea greases are tested at 160 °C, since the run times are otherwise over 1000 h, which would go beyond the scope of the project.

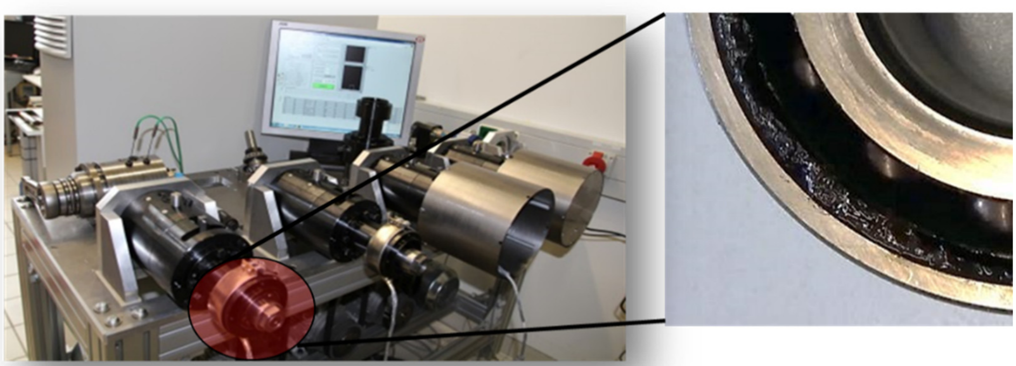

Figure 10. FE9-test bench and bearing with ageded grease [Source: KTM].

A significant rise in temperature or a friction torque greater than 0.9 Nm are set as abort criteria.

Figure 11 shows the results of the first duplicate determinations. The inscription above the bars indicates whether the test was switched off due to excessive temperature (Temp.) or excessive frictional torque (Mr). All greases with diurea as a thickener (white background) have a significantly longer test run time (despite a 20 °C higher test temperature). Mineral oil with diurea thickener (#3) shows the third longest lifetime even without additives. Surprisingly, used AO additives reduce lifetime (#7, #11). Zincdialkyldithiophosphate (ZnDTP) only works optimally for greases with diurea thickener (#15, #16).

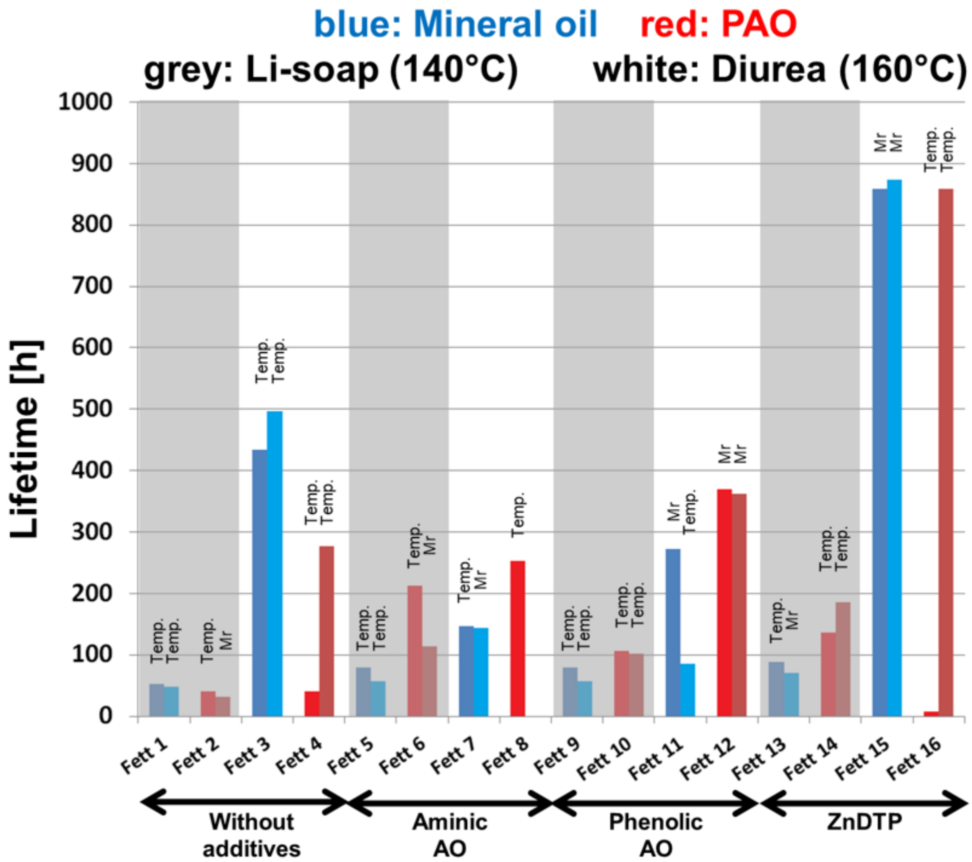

Figure 11. Reached life times for the investigated modeled greases #1–#16.

The aminic additive shows an increase in the service life of greases based on lithium soap (#5, #6). Conversely, adding the aminic additive to diurea greases actually has a disadvantageous effect (#7, #8). The characteristics shown above are partially reversed for the phenolic additives (i.e., with PAO as the base oil). The tests with high scatter (grease #4, #11 and #16) and grease #8 will be repeated.

These results already show that the effect of the additives differs significantly in the different base greases. In addition, the significantly higher performance of PAO compared to mineral oil becomes clear.

In the following aging and shear tests, only greases 1–8 have been examined thus far.

In order to evaluate the results objectively and scientifically, all data are statistically evaluated. Figure 12 shows, for example, an interaction plot in which the interactions of the influencing factors can be evaluated. However, the number of repetitions is currently not sufficient. Therefore, this graphic is intended to illustrate the visualization and evaluation method as an example.

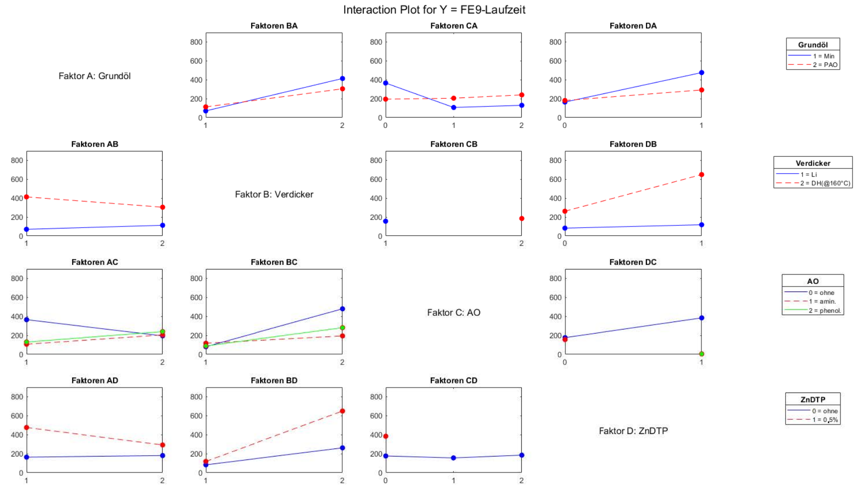

Figure 12. Statistical evaluation of FE9-lifetimes by interaction plot (MatLab 2021b®), exemplary representation. A high slope of the curve means a large positive influence of the factor on the running time in the FE9; a falling curve shows a negative impact.

5.2. Shear Test Acc. Klein

The experiments in the shear test according to Klein show that the lubricating greases are already significantly damaged after 24 h. This can already be seen in the visual inspection of the lubricant samples after the test. The subsequent rheological investigations confirm the strong change after a relatively short test period. Tests with shorter running times are currently being carried out here.

5.3. Rheology

As already mentioned, all greases from the Kleins shearing show a significant change and (nearly) a Newtonian flow behavior and a quite low viscosity near to the base oil viscosity (blue curves in Figures 13 and 14). The grease seems to have lost nearly the complete thickener structure. This shows that this type of mechanical stress has a significantly more detrimental effect on the grease structure than aging. Further into the course of the project, tests with shorter runtimes will therefore also be added. In the diagrams, however, the same stress times should always be compared with one another.

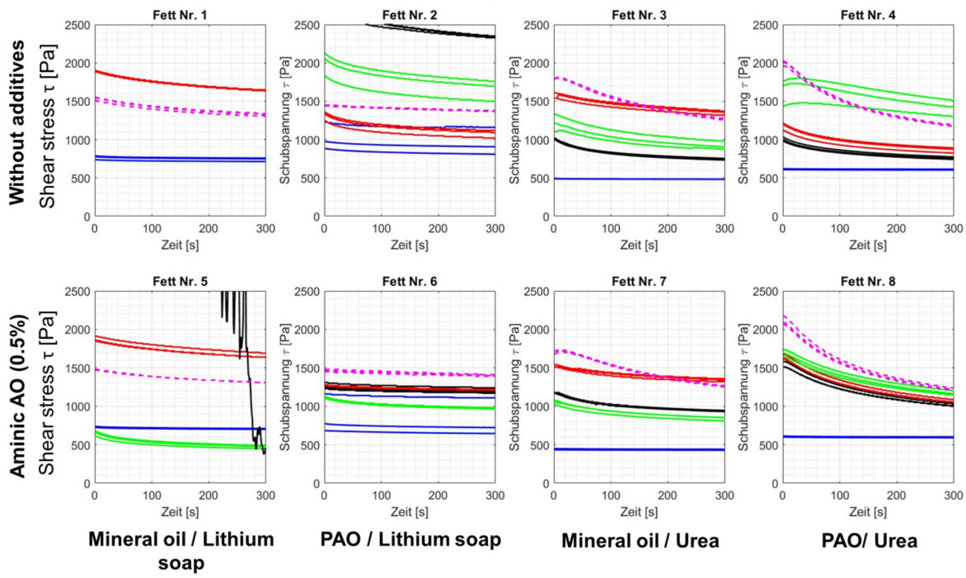

Figure 13. Shear stress curves at constant shear rate (stage #5) after 24 h open oven aging and Kleins shearing (blue); red: on glass; black: on steel; green: on copper; magenta: fresh.

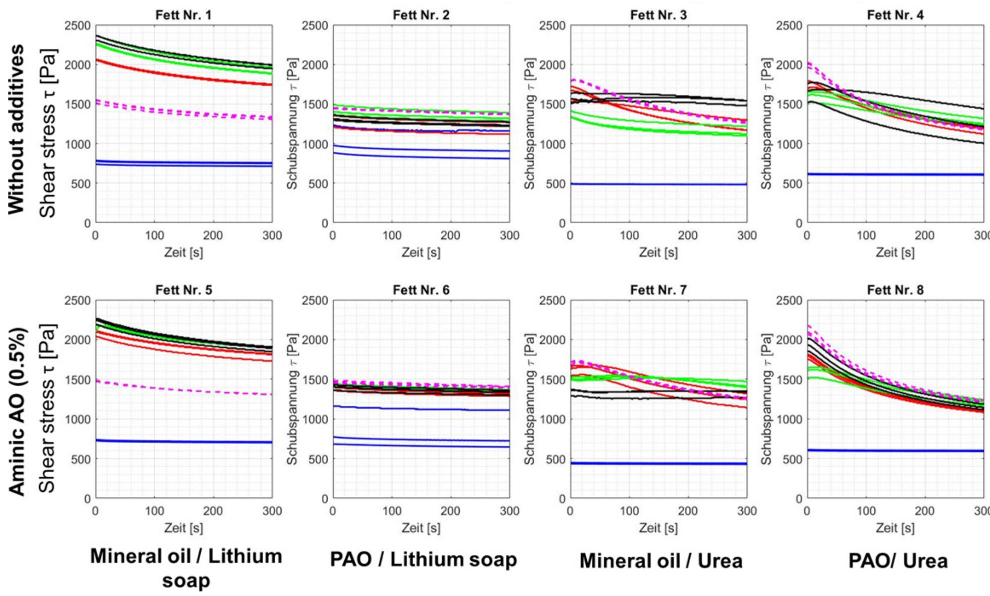

Figure 14. Shear stress curves at constant shear rate (stage #5) after 24 h capped oven aging and Kleins shearing (blue); red: on glass; black: on steel; green: on copper; magenta: fresh.

Figure 13 shows the course of the shear stress over 5 min at a constant shear rate in stage 5. Because of this constant shear rate in this segment, the viscosity curves are similar The course of the curves and the level are decisive for scientific interpretation. This graph shows the results with the grease that were subjected to 24 h in the open oven aging test. Figure 14 then shows the results of a capped system in comparison.

With grease #1, the grease that has aged on steel or copper can no longer be measured in the open system (polymerization). The aminic AO is able to prevent greases from polymerization (except #5 on steel) but not from thickener degradation (viscosity decreases). The effect of the catalyst depends heavily on the base oil and the type of thickener. However, there are no consistent trends. With the combination of PAO + urea (#8), the aminic additive responds well.

In the capped system, i.e., without direct contact with the oxygen in the air, the changes in the flow behavior of the lubricating greases are, as expected, significantly less (Figure 14). All test combinations can be measured after the treatment in the capped arrangement. In the case of greases #1 and #5, the shear stress increases during thermal/catalytic aging, with little to no detectable additive effect. The curves for the greases with and without additives are always similar. The catalytic effect of the different metal sheets is not pronounced without the access of oxygen.

The measurements clearly show that all lubricating greases first liquefy before the apparent viscosity increases again due to the polymerization effects. In the case of curves that are in the area of the starting level, you have to pay attention to the progression over time, since it is possible that the sample has already passed the liquefaction phase and the viscosity has increased again such that it is at the starting level, although the grease is already severely degraded. Here, too, statistical methods and types of representation are used in order to be able to evaluate the large number of results. Figures 15 and 16 show the results as so-called heat maps. This type of graphics helps to present the large number of measurement results in a clear and concise manner.

Test combinations with a green or even yellow background (Figure 15) indicate tests in which the grease has solidified (polymerization): viscosity increase. Black fields after 24 or 72 h indicate that the lubricating grease could no longer be rheologically measured due to strong polymerization. Test combinations with a blue background indicate tests in which the grease structure has softened (thickener degradation): viscosity reduction. Combinations with a turquoise background represent good test results: see grease #8. The ranking for steel and copper varies strongly depending on the grease composition (note the two bottom rows).

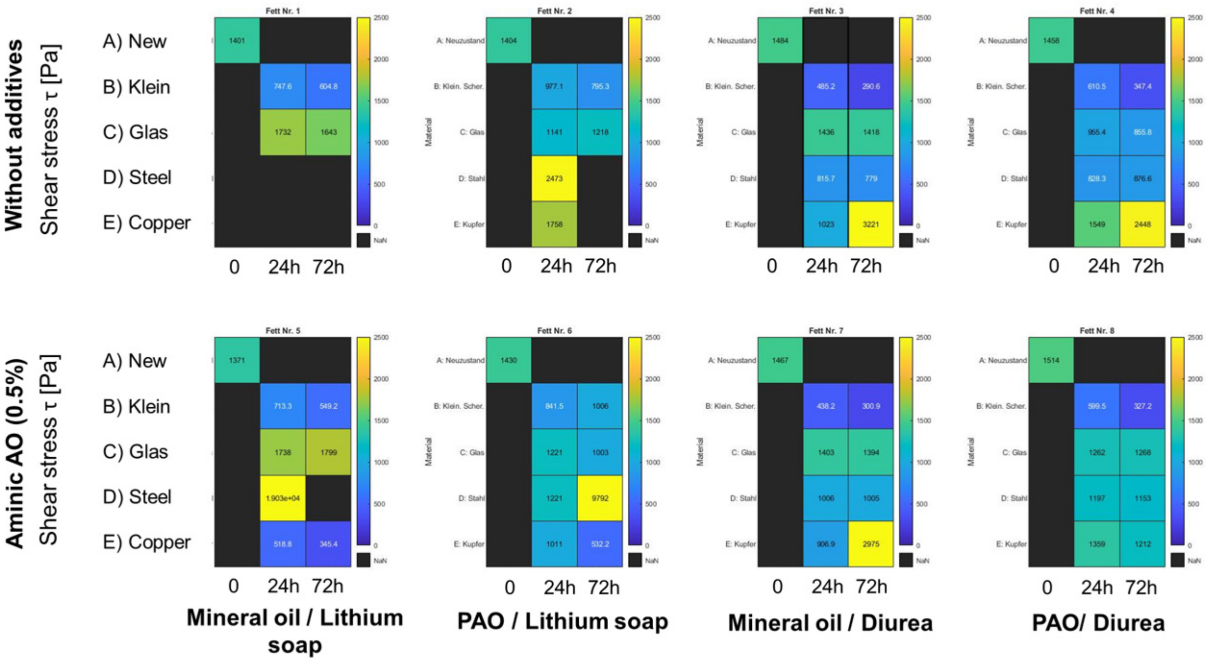

Figure 15. Overall evaluation of the test of open oven aging (with oxygen influence) with so-called heat maps. Top row from left to right: greases 1–4 (without additives); bottom row from left to right: greases 5–8 (with 0.5% aminic AO); top left square in a single diagram represents the new condition, 2nd column after 24 h, 3rd column after 72 h of aging/shearing.

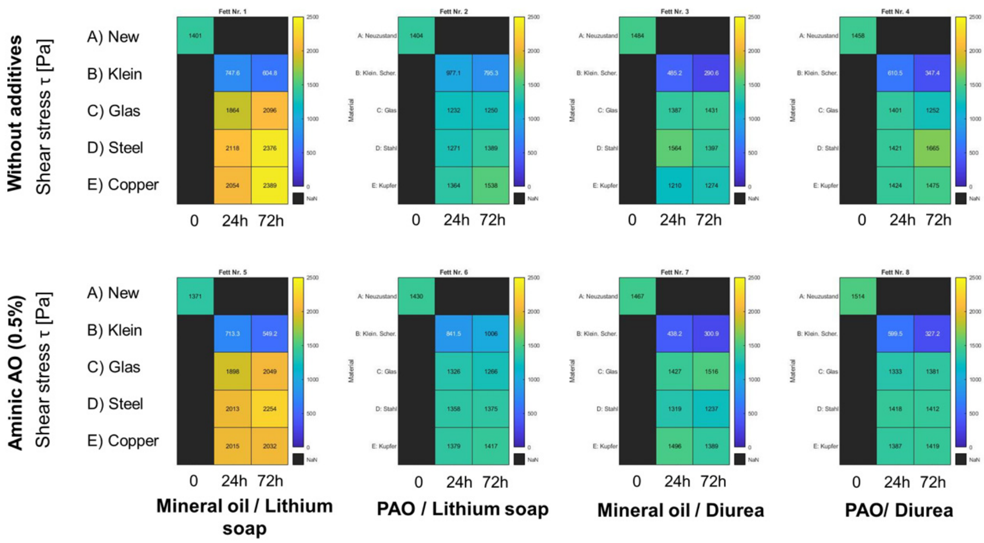

Figure 16. Overall evaluation of the test of capped oven aging (nearly without oxygen influence) with so-called heat maps. Top row from left to right: greases 1–4 (without additives); bottom row from left to right: greases 5–8 (with 0.5% aminic AO); 1st column in a single chart new condition, 2nd column after 24 h, 3rd column after 72 h of aging/shearing.

Without oxidative processes (“capped system”), the changes are, as expected, smaller (Figure 16). In the case of the mineral oil-based lithium soap grease (#1 and #5), the influence of temperature is particularly high. Here, we are the only ones to see significant changes in the capped system. The catalytic effect is quite low. The aminic AO additive has no function under these conditions. For the three other base grease formulations, only relatively small changes can be detected in the capped system. Even after 72 h, the levels are still in the fresh grease range.

As already mentioned, the scientific connections and interactions are not easy to work out. With the different formulations, we see different connections with regard to the catalyst and the additives used. Here, we hope for clearer and possibly more general statements through the statistical evaluation using DOE.

6. Discussion, Conclusions and Outlook

The main focus of this publication is on presenting the procedure and the methods used with which individual factors influencing grease degradation can be examined separately. The results only represent a first milestone and must be supplemented by further tests and accompanying chemical and visual investigations. However, it can already be confirmed that the methods used help to significantly increase the understanding of the changes in the lubricating greases in use.

The first results from the current project confirm the working hypothesis that, in addition to classic lubricant aging (radical formation, polymerization), structural changes in particular are responsible for a reduction in the lubricating effect in the rolling bearing. This leads to bearing failures before the actual aging of the lubricant occurs. The rheological measurements clearly show that all lubricating greases first liquefy before the apparent viscosity increases again due to the polymerization effects. The rheological investigations after oven aging and Kleins shearing show that this effect is much more pronounced with soap greases than with diurea greases. Therefore, the characteristic values determined by laboratory lubricant aging tests often do not correspond to the service life in real applications.

The innovative approach of finding out the influence of the different factors of temperature, oxidation, catalytic effect and shear through detailed and separate individual tests on the model lubricants seems to be successful and helps in the long term to build a mathematical explanatory model with which the influence of these factors can be better predicted for known load collectives. In the first part of the project, which has now been completed, different furnace aging methods have been carried out thus far. Catalytic, oxidative and thermal processes play a role here. In addition, the model greases were subjected to purely mechanical stress using the shear apparatus acc. Klein. The extent of the influence of these individual factors on the structural change can be demonstrated using numerous rheological measurements. These results were then correlated with the results of the rolling bearing tests in the FE9 testing machine. For example, the short run times for both lithium soap greases #1 (mineral oil) and #2 (PAO) can be predicted from the results of open oven aging with steel as the catalyst. It can also be seen from the aging tests that the aminic AO additive in grease #1 is not effective. However, there are still results here that cannot be derived easily.

Initial statistical evaluations show that the influence of the individual factors depends heavily on the base oil, the type of thickener and the respective additives. Thus far, no generally applicable relationships have been identified; thus, it can be assumed that the complex interplay cannot yet be reliably predicted using simplified tests. In the further course of the project and with the help of the project data from the partner OWI in Aachen, further investigations are to be made.

Currently, the change in the thickening structure of the greases that are stressed in different ways is also visually documented. For this purpose, a digital microscopic method was developed, which makes it possible to quickly make initial statements. In the next step, the samples are examined in the scanning electron microscope. Using cryo-REM investigations, the extent that the thickener structures change as a result of the dissolving of the base oil and whether this is significant will also be investigated. Further chemical analyses such as FTIR are carried out and evaluated by our project partner.

In the further course of the project, these relationships are to be further clarified. Here, we will also use other statistical methods such as DOE and ML to work out the correlations more clearly. The main goal is to use targeted chemical/physical experiments to reduce the number of time-consuming endurance tests on roller bearing test benches and, overall, to enable a safer design and a good prediction of lifetime.

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Appendix A

Figure A1. Funding by DGMK within AiF based on a resolution of the German parliament.

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