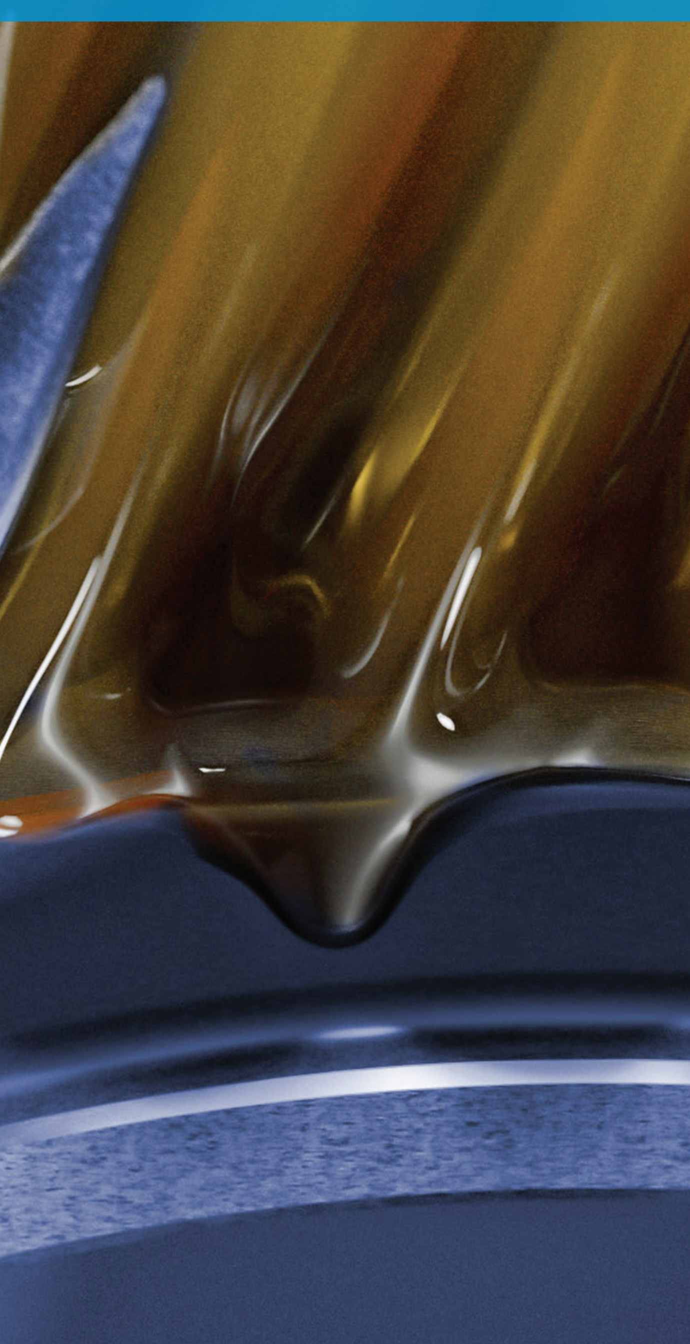
NEW TEST METHOD FOR MEASURING THE OXIDATION STABILITY OF LUBRICATING GREASES – RAPID, SIMPLE, PRECISE



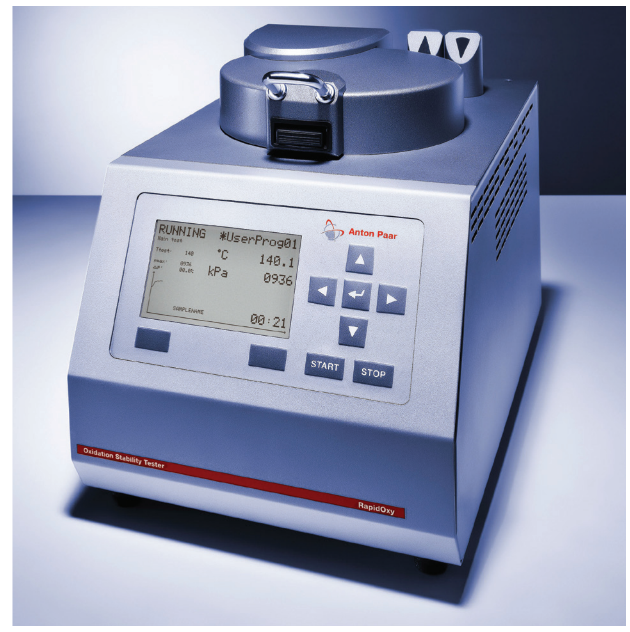
RapidOxy is a fast, safe and user-friendly alternative to traditional stability test methods for determining the oxidation stability of lubricating greases. The instrument measures the induction period, which can be used as an indication of the oxidation and storage stability. Compared to other oxidation and storage stability test methods like ASTM D942, the RapidOxy procedure requires only a small amount of sample. Additionally the measurement of lubrication greases gives an exact test result in a short period of time.

All it takes for preparation is to fill in 4 g of sample into the sample dish, place the sample dish in the test vessel, tighten the pressure chamber's lid and close the instrument. The test cell is automatically charged with oxygen pressure and heated until it reaches the test temperature. Subsequently the pressure is monitored until a pressure drop of 10 % from the maximum pressure is detected.

This article will provide information on important initial tests and the respective results in regards of measuring the oxidation stability of lubricating greases.

Introduction

Due to the consistency of lubricating greases derived from a lubricating fluid and a thickener these unique products are



predestined to be used for any kind of machinery with sliding or rolling contacts like gears, velocity joints or couplings, to name just a few applications. Around 90 % of all bearings are lubricated by greases to protect them from contaminants like water, dirt or even corrosive gases. One important feature of lubricating greases is a preferably high resistance to oxygen as oxidation products can lead to changes in the chemical and physical properties of the lubricating grease, affecting its lubricating properties. To enhance the oxidation stability antioxidants often serve as additives. However, besides exposure to light, water and acids there are other conditions which accelerate the oxidation process. These include catalysts such as copper, elevated temperatures or high pressure which cannot always be avoided. Therefore, various standard methods have been established for determining the oxidation stability of these kinds of products with the aim of manufacturing greases with as high a resistance to oxidation as possible.

Measuring principle of the new rapid oxidation stability tester for lubricating greases

The development of a new oxidation stability test for lubricating greases has its roots in the Rapid Small Scale Oxidation Test (RSSOT) for determining the oxidation stability of gasoline which was developed as an alternative to ASTM D525 (the "pressure vessel method"). The procedure of the ASTM D525 method is in its essence comparable with ASTM D942, which is the traditional pressure vessel method for greases. The RSSOT method measures the induction period (IP) of spark-ignition fuels. In a typical RSSOT test a small sample volume (5 mL) is introduced into a test cell and charged with oxygen under pressure (500 kPa) at room temperature. Subsequently the measurement starts by heating the test cell to 140 °C. The measurement is finished when the break point is reached. The break point is defined as a pressure drop of 10 % from the maximum pressure of the respective test run. As a result the time elapsed from starting the heating process to reaching the break point (pmax-10%) is reported as the induction period (IP) and can be used as a measure of the oxidation stability (Figure 1).

In comparison to ASTM D525 the break point is reached approximately 20 times faster using the RSSOT. Additional benefits of the RSSOT method are the small sample volume and the simple cleaning process.

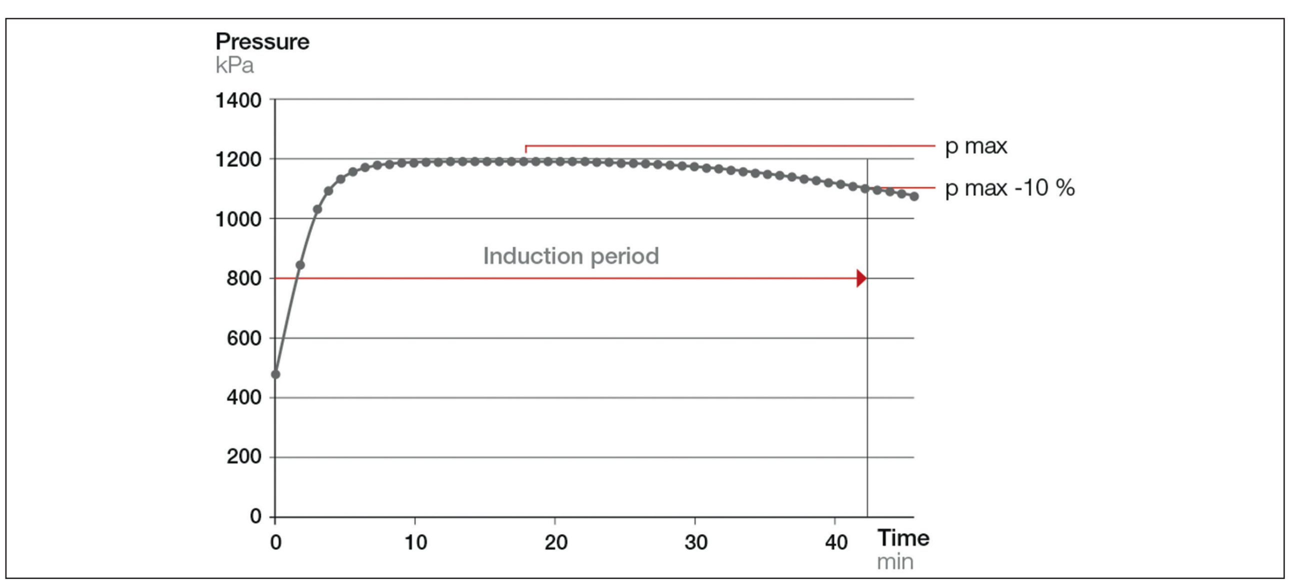


Figure 1: RSSOT / ASTM D7525 induction period - time elapsed between starting the heating procedure and a pressure drop of 10 % from the maximum pressure.

To transfer these clear advantages of the RSSOT to testing lubricating greases for their resistance towards oxidation, the RapidOxy device was developed. It differs from the test equipment of ASTM D7525 (PetroOxy) as it has a stainless steel cup into which the sample is introduced in a sample dish. The measuring principle of the induction period is identical. However, due to the fact that lubricating greases are not highly volatile it is possible to employ a higher pressure of oxygen (700 kPa) when measuring the oxidation stability of these products. Only 4 g of sample is required, resulting in a fast, cost-effective and ecological measurement.

Repeatability and reproducibility of determining the oxidation stability of lubricating greases with the new test method

To find appropriate test methods to measure the oxidation stability of bio-based lubricating greases a joint ELGI-NLGI Working Group has been formed. The focus of this working group is the evaluation of new test methods and comparison of these with the older methods. The goal is to find new suitable standard methods applicable for quality control purposes and product specification. As a member of the ELGI Test Methods and Bio Working Groups, Steve Nolan from RS Clare examined the repeatability and reproducibility of the new RapidOxy test method for lubricating greases. Repeatable results are one major criterion for a testing equipment to be applicable. To evaluate the RapidOxy, studies on the repeatability precision measurement (r) were carried out at RS Clare using one of their bio-based greases. For that purpose five different temperatures were tested twice (Table 1) to demonstrate the very good repeatability at every implemented temperature. As expected, the high precision already achieved with the previously studied RSSOT was transferred to the new instrument which is used for examining the oxidation stability of lubricating greases.

Table 1: Repeatability of the RapidOxy when measuring the oxidation stability of a bio-based grease at five different temperatures.

Temperature	IP 1 (min)	IP 2 (min)
130	101.20	102.08
140	65.06	63.56
150	45.31	46.40
160	34.61	34.95
170	28.18	29.68

To show that the RapidOxy additionally delivers an effective reproducibility (R) ELGI round-robin (RR) grease samples were tested with the new test equipment by two different laboratories. Introducing these specific samples also allows for verification of the induction period as an effective method to determine the oxidation stability of lubricating greases, since the oxidation stability of the employed greases was already defined by an interlaboratory study. It was confirmed that all eight greases were discriminated equally in terms of their oxidation performance. The good level of reproducibility was substantiated by this study (Figure 2).

We acknowledge the work of RS Clare and in particular Steve Nolan in supporting the RapidOxy as suitable test equipment for determining the oxidation stability of lubricating greases

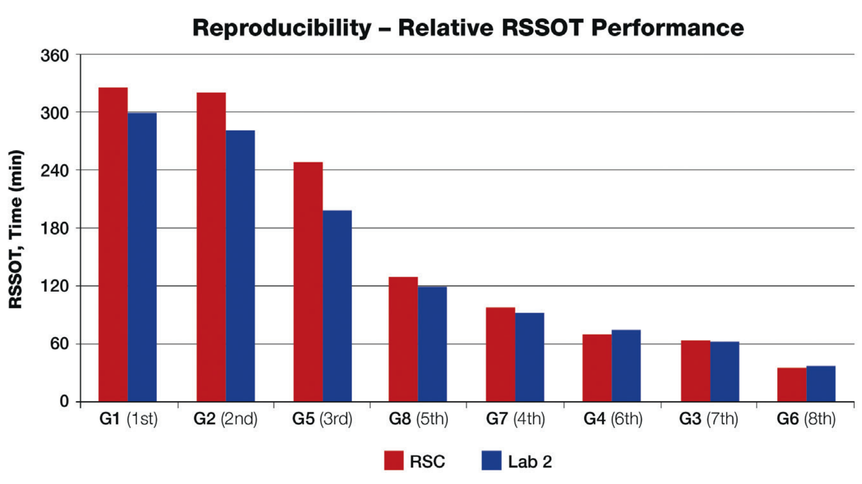


Figure 2: Studies concerning the reproducibility of the RapidOxy: Measuring the oxidation stability of 8 ELGI Rail WG 2012 RR greases in two different laboratories.

Table 2: Measured induction periods of 11 grease samples with two different instruments (1 and 2)

Sample	Thickener System	IP 1 (min)	IP 2 (min)	IP$_{mean\ value}$ (min)	ASTM D942 100 h (kPa)	ASTM D942 400 h (kPa)
Grease 1	Calcium	184.71	-	184.71	18.00	39.00
Grease 2	Clay-based	403.91	399.26	401.59	35.00	119.00
Grease 3	Lithium	225.93	229.81	227.87	27.00	-
Grease 4	Lithium	195.91	190.66	193.29	62.00	189.00
Grease 5	Lithium Calcium	266.91	258.43	262.67	33.00	136.00
Grease 6	Lithium	465.00	460.73	462.87	19.50	60.50
Grease 7	Lithium Complex	404.48	404.10	404.29	34.00	90.00
Grease 8	Polyurea	779.30	-	779.30	10.00	27.00
Grease 9	Lithium Complex	168.98	163.71	166.35	58.00	154.00
Grease 10	Calcium	320.26	322.53	321.40	14.50	41.00
Grease 11	Lithium	404.23	412.68	408.46	29.00	88.00

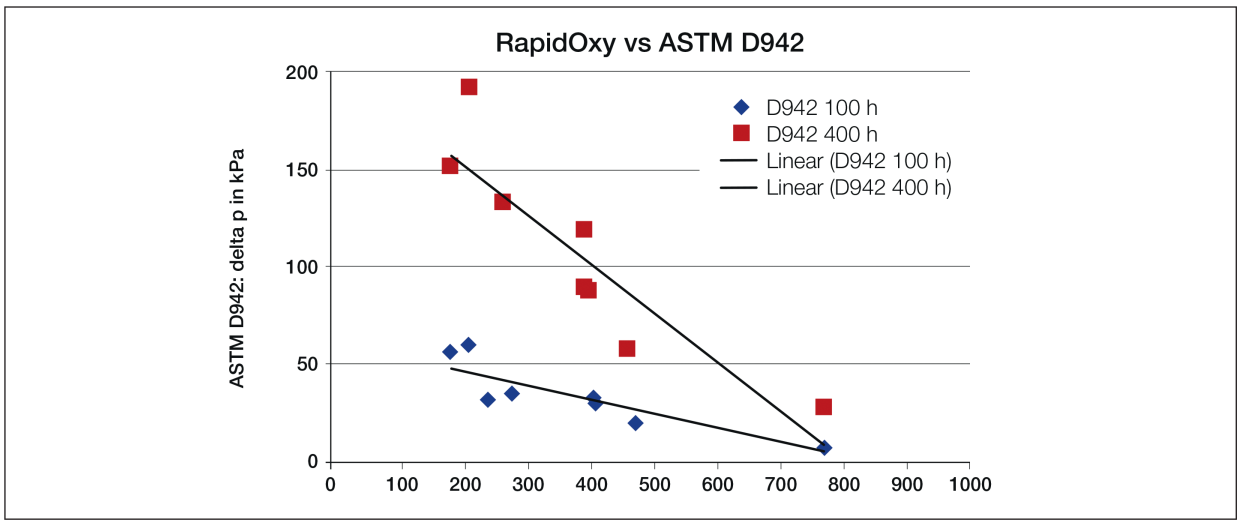


Figure 3: Correlation between the RapidOxy at 160 °C and ASTM D942 at 99 °C after 100 hours (blue spots) and 400 hours (red spots).

Measuring the oxidation stability of lubricating greases – Comparison to traditional method ASTM D942

The probably most frequently used method to determine the oxidation stability of lubricating greases has many parallels to ASTM D525 for determining the oxidation stability of spark-ignition fuels. Also called the "pressure vessel method", ASTM D942 is commonly used in laboratories to examine the resistance of lubricating greases. The method examines the oxidation behavior of a grease sample when stored statically in an oxygen atmosphere in a closed system at elevated temperature.

The major drawbacks of this method are the very long test times (100 hours), the large amount of sample (20 g) required and the tedious cleaning procedure. The information received is the pressure drop after 100 hours often without any additional information about when the pressure drop occurred. To test the stability of modern greases often 400 hours or more are required when this method is employed.

Besides ASTM D942 additional standard methods exist: ASTM D2272 is also based on a pressure vessel ("rotating pressure vessel oxidation test"). It avoids the long test times of ASTM D942 by employing higher temperatures. However, with this particular method there are concerns due to the poor precision. The pressure differential scanning calorimetry (PDSC) method is described in ASTM D5483 and is used to test the oxidation stability of greases. However, these tests are costly and require highly trained operators. In addition, these tests are often unreliable due to poor repeatability and reproducibility.

To prove that the RapidOxy can be used to estimate the relative oxidation resistance of different grease types comparable to ASTM D942, 11 different lubricating greases were measured using the new test method (Table 2). Additionally all samples were measured with two different instruments in the same laboratory to manifest the high precision of the test method. With a test temperature of 160 °C the induction period was measured and reported in minutes. All test results showed a good repeatability (see Table 2).

These results clearly show the very good repeatability for the results derived when using the RapidOxy for the oxidation stability measurement. In case of the calcium-based greases (Grease 1 and Grease 10) the applied temperature of 160 °C led to the liquefaction of these two specific samples, whereas all other grease samples stayed solid. The examination of the oxidation stability of the greases according to ASTM D942 was also carried out to enable a comparison of these two methods. The degree of oxidation of the eleven greases was determined after 100 hours and 400 hours of oxidation time by the corresponding decrease of oxygen pressure in kPa (see Table 2). This comparison of the methods showed a good correlation between the RapidOxy at 160 °C (and 700 kPa) and ASTM D942 at 99 °C after both 100 h and 400 h test times. The calcium-based greases were left out at correlation due to their liquefaction during the measurement (Figure 3).

These very promising results led to the decision to approach ASTM for creating a standard method with the RapidOxy. The respective work item (WK5571) has already been created. The corresponding interlaboratory study (ILS#1383) is currently in preparation and will be initiated before the end of this year.

Conclusion

The new measuring principle for testing the oxidation stability of lubricating greases showed a very good repeatability and reproducibility independent of whether the lubricating grease is bio-based or derived from mineral oil. Additionally a very good correlation to ASTM D942 was found in initial studies. The benefits of this method are the small amount of sample, the fast measuring times and the very simple cleaning procedure. The process for achieving a standard ASTM method for determining the oxidation stability of lubricating greases has already been initiated. The respective work item has been created and the interlaboratory study will begin in the near future with the goal to achieve a new modern standard test procedure which eliminates the drawbacks of the existing methods.

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