An Advanced Technique for Grease Oxidation Measurement

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Abstract

Oxidation stability is a very important property of lubricating greases. Any bench test capable of measuring this property is thus important to the degree that it is capable of predicting either or both the shelf and service life of greases. A well-known test method used to assess oxidation stability of grease is ASTM D942, which was introduced by the ASTM in 1947 and has become a standard. The method is routinely used to measure batch-to-batch grease oxidation stability.

However, the Test Method states that it is not suitable for comparing the relative oxidation stability of different greases. Moreover, Test Method D942 is a very time consuming and labor intensive test requiring a comparatively large sample size thus making it non-applicable to measuring small sample sizes taken from operating bearings or other applications to determine remaining oxidation resistance.

On the other hand, because ASTM D942 is relatively simple to set up and operate, it was desirable to improve this Test Method by elimination of its liquid bath, reduction of sample size and application of Fourier Transform Infrared (FTIR) analysis to extend the application of the method to comparative oxidation response of greases. Beyond this, it seemed reasonable that simultaneous analysis of several small grease sample sizes could extend the productivity of the bench test in determining grease oxidation resistance.

In this paper, the authors present a modified ASTM D942 Test Method as well as further extension of the method in gaining greater efficiency with reduced sample size and simultaneous evaluation of multiple grease samples.

Introduction

Resistance to oxidation and degradation of lubricating greases under the stresses imposed by high temperatures and thousands of hours of operation has always been an important feature of its performance. Of the bench tests designed to assess oxidation stability of greases, ASTM D942 is one of the most common. The test became an ASTM Test Method in 1947 as a quality-control tool in grease manufacturing.

Presently, this ASTM bench test is conducted on a 20 g grease sample in a small oxygen-containing chamber pressurized to 110 PSI at a temperature of 99

°C in a liquid bath. The published ASTM Test Method has always been limited to determine batch-to-batch uniformity of grease in the manufacturing process, although, in fact, the Test Method has been applied in screening new grease formulations in development work. The test length may be anywhere between 100 to 500 hours. Thus, application of the method is time-consuming and encourages development of ways of increasing the information from such tests.

The opportunity to limit the test configuration of the equipment to a relatively small footprint, to eliminate the need for a liquid bath (and its associated care and safety demands), led the authors to considerably modify and expand application of ASTM D942 Test Method.

Test Techniques

Use of FTIR – One of the main techniques employed for the studies reported in this paper, is the use of modern FTIR equipped with Attenuated Total Reflectance (ATR). It is evident that a technique for oxidation measurement that combines the D942 test with Fourier Transform Infrared (FTIR) analysis would overcome the limitations of the original D942 test. The combination of FTIR with D942, referred to hereafter as the Advanced Technique, would provide much more in-depth information on grease oxidation which would consequently allow comparison of the oxidation stability of various types of grease.

It was found at the initial stages of this study that sufficient information could be obtained from IR of the surface of the grease samples. This led to the consideration of using much smaller grease samples in the pans and, thus the ability of applying the principles of D942 and FTIR to samples having the same surface area in the test, but much less grease mass. This approach would not produce the same oxygen pressure decrease, but the FTIR oxidation information would be the same.

The foregoing study led to an additional test concept in which it was considered that rapid screening of grease or additive formulations based on oxidation resistance should be possible. The Screening Technique uses the D942 test conditions to oxidize grease, however, infrared analysis is used primarily to measure oxidation resistance of the sample. This method can be used to significantly increase the speed of acquiring information on oxidative stability of greases in the development process.

GREASE OXIDATION MEASUREMENT TECHNIQUES

Background

This paper builds upon a previous study from 2013. That study compared the oxidation resistance of several greases of varying oxidation resistance.

The study was performed in a specially modified iso-thermal reactor normally used in determining oxidation resistance of liquid lubricants per ASTM D2272. Figures 1 and 2 show the instrument before and after a modification that permits the instrument to be used alternatively in either test configuration. The advantage of modifying the iso-thermal reactor to conduct the D942 test was that it did not require the care and concerns of a liquid bath as the sample chamber is heated by electrical resistance. A stainless steel insert was used to obtain the appropriate chamber volume for D942. Accessories, including a sample rack and sample pans were designed to comply with the method and are shown in Figure 3. The same test setup was utilized in the current work.

Application of the modified iso-thermal reactor for the D942 method was validated in the previous work by testing multiple grease samples for 100 and 200 hours. Consistent results were obtained from repeat tests and show good agreement with D942 tests run at an external laboratory with standard test equipment. All results were within the method's repeatability and reproducibility.

According to the ASTM D942 Test Method, 20 g of a grease sample is tested in five glass dishes with an exposed surface area of approximately 25 cm2 per dish and a total surface area of 125 cm2 per test. The dishes are stacked with a gap of approximately 5 mm between them. The combined stack of grease-filled dishes are then inserted into a cylindrical pressure chamber and exposed to oxygen of not less than 99.5% purity at an initial pressure of 100 pounds per square inch (PSI) and room temperature which is then increased to 99 ± 0.5 °C. Under the increased temperature, the oxygen pressure is maintained at 110 ± 2 PSI. The test is continued for a chosen period of time and decrease in oxygen pressure resulting from grease oxidation is reported in PSI as the test result.

Five lithium based greases of varying oxidation resistance were chosen for the current work. Greases 1, 2 and 3 are developmental greases provided by Loadmaster Lubricants LLC, interested in extending the information gained from ASTM D942. Respectively, Greases 1, 2 and 3 are said to be high load-carrying lithium grease, fully synthetic lithium complex grease and high load carrying lithium complex grease. Greases 4 and 5 are commercial lithium-complex greases and the compositions are proprietary.

Advanced Technique for Oxidation Measurement

Infrared spectroscopy has been used for over half a century in the study of grease oxidation[2,3,4,5,6]. The level of oxidation in petroleum-based lubricants in general is measured in the carbonyl region (1670 to 1800 cm-1). Infrared energy is absorbed in this region as a result of the carbonyl group (C=O) stretch from various carbonyl compounds including, ketones, esters, carboxylic acids, carbonates, aldehydes, anhydrides and amides. The FTIR peak around 1715 cm-1, is generally known as the "oxidation peak" results from C=O stretch and indicates breakdown of the lubricant and formation of oxidation by-products.

Combining the ASTM D942 method with infrared analysis seemed to be a solid approach to grease oxidation measurement. The following steps were used in the technique:

1) Response of a grease to ASTM D942 is determined by measuring change in oxygen pressure in 100 hours
2) The grease is sampled from the pans after the test
3) Oxidation resistance of the grease is analyzed using ATR-FTIR spectroscopy

For this study the authors used a PerkinElmer Spectrum 100 FTIR Spectrometer equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory. The latter was indispensable in applying IR to opaque materials by using the reflection from the sample surface. Infrared analysis was conducted using about 2-4 mg sample. Multiple IR taken from the same sample showed no measurable difference in the resulting spectra indicating effects of the small variation in sample size is negligible. Sample was skimmed from the surface of the grease.

Screening Technique

Attempts have been made in the past to design a simple and rapid screening test based on grease oxidation stability that correlates well with in-service oxidation conditions[7]. In this work, a test concept has been developed for rapid screening of grease samples based on oxidation resistance. The concept is similar to the High Throughput Screening (HTS) technique used in drug discovery.

In the Drug Discovery process, biological targets are identified and potential compounds are screened against the target. This was originally an expensive, tedious, and time-consuming manual process termed Low Throughput Screening (LTS), which usually took months. Over the last two decades, innovations in technology transformed the LTS into an automated microprocessor controlled robotic process called High Throughput Screening (HTS). This quantitative step makes it possible to screen 10,000-100,000 compounds within 24 hours.

A Screening Technique similar to HTS may be useful to speed up the grease development process. As the D942 Method requires five sample pans, the authors considered the possibility of evaluating five different greases in the same test. The Screening Technique does not need to be limited to five grease samples. In the initial work, five greases were chosen mainly because the current D942 Test setup is equipped with five sample pans. The setup can be easily modified to test any reasonable number of greases at the same time.

The screening test concept was evaluated in the following two steps.

Step 1: Reduced Sample D942 Test

A modified D942 test with smaller sample amounts was evaluated using Grease 2. Four and five g of Grease 2 was tested in the following two configurations:

1) 5g, 5-Pan Test: five pans, each containing 1g of Grease 2, was tested in the iso-thermal reactor for 100 hours following the D942 test conditions (99 °C and initial pressure of 110 PSI).
2) 4g, 1-Pan Test: one sample pan, containing 4g of Grease 2, was tested in the same way.

Grease 2 was spread out in each pan and the surface was leveled using a clean spatula to minimize the impact of any differences in surface area between pans. Following the 4g, 1-Pan and 5g, 5-Pan Tests, 2-4 mg of Grease 2 was sampled for infrared analysis.

Step 2: High Throughput Screening Test

Next, a Screening Test concept was developed where 5 different greases were oxidized simultaneously under D942 test conditions and then oxidation resistance of the greases was measured by infrared analysis. The Screening Technique uses the D942 test equipment to oxidize the grease samples however oxidation is measured primarily by infrared analysis. The following two configurations were evaluated:

1) 5 grease-5 pan @1g: 1g each of the 5 grease samples was tested in the iso-thermal reactor for 100 hours at the D942 test conditions (99 °C and initial pressure of 110 PSI).
2) 5 grease-5 pan @4g: 4g each of the 5 greases was tested in the same way.

The grease samples were spread out in the pans and the surfaces were leveled using a clean spatula to minimize the impact of any differences in surface area between the pans.

As would be expected, oxygen uptake during the 5 grease tests does not correlate with the oxidation stability of the individual grease samples. The 5 grease Screening Test disregards the change in pressure generated by the oxidation process and utilizes infrared analysis to assess the extent of oxidation of the grease samples.

RESULTS

Standard ASTM D942 Test

Utilizing the iso-thermal reactor shown in Figure 2, each of the five greases was subjected to 100 hours of the standard D942 Test.

Figure 4A shows overlay of pressure vs. time plots for Greases 1, 2 and 3. Greases 1 and 3 show relatively small changes in pressure in 100 hours compared to Grease 2. The results indicate that Greases 1 and 3 are relatively resistant to oxidation. In contrast, Grease 2 appears to be highly susceptible to oxidation as the chamber pressure reduced to an atmospheric level of about 15 PSI as a result of complete oxygen uptake during the 100-hour D942 test.

Figure 4B shows the responses of Greases 4 and 5 to 100-hour ASTM D942 tests. Very small change in pressure was observed for both of the greases indicating that these greases are highly resistant to oxidation. Table 1 below, compares the changes in oxygen pressure for all five grease samples during the ASTM D942 tests.

Table 1. 100-hour ASTM D942 Oxidation

	Grease 1	Grease 2	Grease 3	Grease 4	Grease 5
Pressure Drop (PSI)	14.4	95.0	13.5	6.0	2.8

Advanced Technique

In the advanced technique, the grease samples oxidized by 100-hour D942 test were analyzed by FTIR-ATR. Initially, each of the five dishes of grease from the D942 test was sampled for infrared analysis. No significant differences were observed between the dishes from the five-dish rack. In subsequent tests, only the top dish was sampled for IR analysis.

The infrared peak around 1715 cm-1, known as the "oxidation peak", was evaluated to measure the extent of oxidation in the five greases following individual 100-hour D942 tests. Figure 5A compares the ATR-FTIR spectra from Greases 1, 2 and 3 following oxidation by 100-hour D942 tests. Intensity of the oxidation peak is higher for all three greases after the D942 tests compared to the fresh grease samples. The infrared analysis clearly indicates oxidation of the grease samples, however, the level of oxidation is substantial for Grease 2 compared to the other two greases. As observed previously in Figure 4A, the change in oxygen pressure for Grease 2 during the 100-hour D942 test was also much higher compared to Greases 1 and 3.

Figure 5B compares infrared spectra of fresh and oxidized Greases 4 and 5. No oxidation peak is observed in either grease before or after 100-hour D942 test. As discussed previously, both of these greases produced very little change in pressure during the 100-hour D942 tests.

Infrared analysis, therefore, agrees well with D942 test results confirming that Grease 2 is highly susceptible to oxidation, Greases 1 and 3 are moderately stable and Greases 4 and 5 are extremely resistant to oxidation under similar oxidative conditions.

The results also support the approach of using infrared analysis as an alternate way to measure grease oxidation stability. The combination of ASTM D942 method and the subsequent FTIR analysis evidently enhances the relatively simplistic information provided by ASTM D942 alone. Moreover, the limitations of ASTM D942 when used alone are overcome with the more in-depth information provided by infrared analysis.

Reduced Sample-D942 Tests

Figure 6A shows a comparison of the responses of Grease 2 to the standard D942, 4g, 1-Pan and 5g, 5-Pan Tests, where each test was conducted for 100 hours. Five g of Grease 2 distributed in five sample pans were evaluated in the 5g, 5-Pan Test whereas only one sample pan containing 4g of Grease 2 was evaluated in the 4g, 1-Pan Test. As observed in Figure 6A, the standard D942 produces a pressure loss of 95 PSI for this grease, which is significantly higher compared to 56.9 and 32.7 PSI obtained during the 4g, 1-Pan and 5g, 5-Pan Tests respectively.

The results clearly indicate a correlation between the change in pressure during these tests with the volume of oxygen available per mass of sample grease. Table 2 compares the results of the standard D942 test with 4g, 1-Pan and 5g, 5-Pan Tests on Grease 2.

Table 2. 100-hour Oxidation of Grease 2

	Standard D942	5g, 5-Pan	4g, 1-Pan
Pressure Drop (PSI)	95.0	56.9	32.7

FTIR spectra taken from Grease 2 following the standard D942 and the 4g, 1-Pan and 5g, 5-Pan tests are compared in Figure 6B. The modified tests with reduced sample mass caused a higher level of oxidation in Grease 2 compared to the standard D942 test. Infrared analysis clearly shows that the standard D942 does not completely oxidize Grease 2 during the 100 hours.

It is apparent in these results that the standard D942 test leaves Grease 2 partially oxidized, because of complete exhaustion of oxygen in the reaction chamber before the test ends, whereas the reduced sample tests allow further oxidation of the grease. The ratio of oxygen volume in the chamber to the sample mass is higher in case of the latter.

Incomplete information is likely obtained from the standard D942 test for greases that are highly susceptible to oxidation. The results demonstrate another limitation of the ASTM D942 method, as well as, the significance of coupling the test with infrared analysis.

Screening Test

As discussed previously, there was considerable agreement between the test results obtained by the standard D942 test and the Advanced Technique.

In an effort to develop a Screening Test concept, the five greases were tested simultaneously in the following two configurations: 5 grease, 5-pan Test (@1g) and a 5 grease, 5-pan Test (@4g).

Figure 7A compares the effect of oxidation on Grease 2 for the standard D942 test, 5 grease, 5-pan (@1g) and 5 grease, 5-pan (@4g) Screening Tests where each test was conducted for 100 hours. The Screening Tests clearly obtained a higher level of oxidation of this sample compared to the standard ASTM D942, as measured by infrared analysis. Both the standard D942 test and the Screening Tests found Grease 2 to be highly susceptible to oxidation compared to the other four greases.

As observed in Figure 7B, infrared analysis detected no oxidation of Grease 4 after the standard D942 test, however, a minimal level of oxidation was measured in the same grease after the Screening Tests. Both tests indicated that Grease 4 is highly resistant to oxidation. The results imply that the 5-Grease Test creates a relatively harsh oxidative environment compared to the standard test, which is designed to measure oxidation of a single grease sample.

The preliminary results obtained in this work demonstrate that the Screening Test concept may be useful in rapid selection of grease or additive formulations. This approach could significantly reduce the time needed for grease research and development.

Conclusion

ASTM D942 is severely limited in its applications to any other use than quality control in grease manufacturing processes. The goal of this work was to improve the ASTM D942 Test Method, by combining precise control of test temperature and measurement of oxygen pressure with infrared analysis. The in-depth information provided by FTIR analysis expands the applications of the original method. The extended test is capable of comparing oxidation stability of various types of grease. Based on this analysis, we believe that the ASTM D942 should be extended to include the use of infrared analysis.

In addition, a Screening test concept was developed in this work. The concept involved simultaneous oxidation of multiple grease samples under ASTM D942 conditions and measurement of oxidation resistance by infrared analysis. The results indicated that the Screening Test and the standard ASTM D942 Test Method measure comparable oxidation tendency of the grease samples. The Screening Test can be useful in selecting preliminary formulations in the grease development process by significantly shortening the analysis time.

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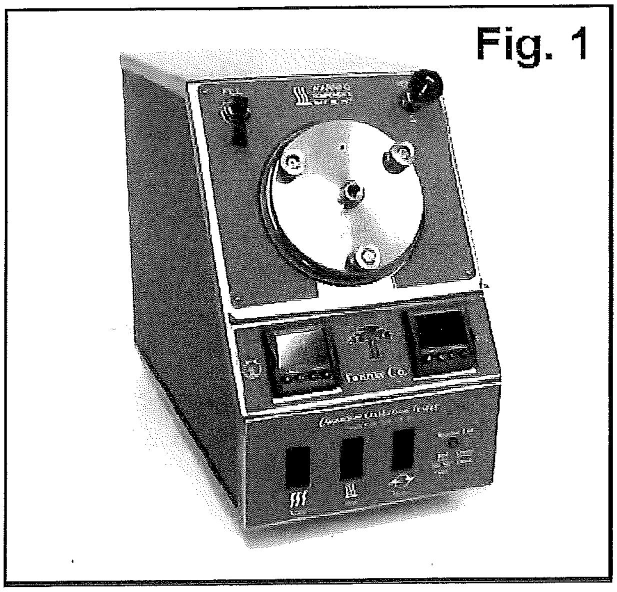

Figure 1. Iso-thermal reactor before modification

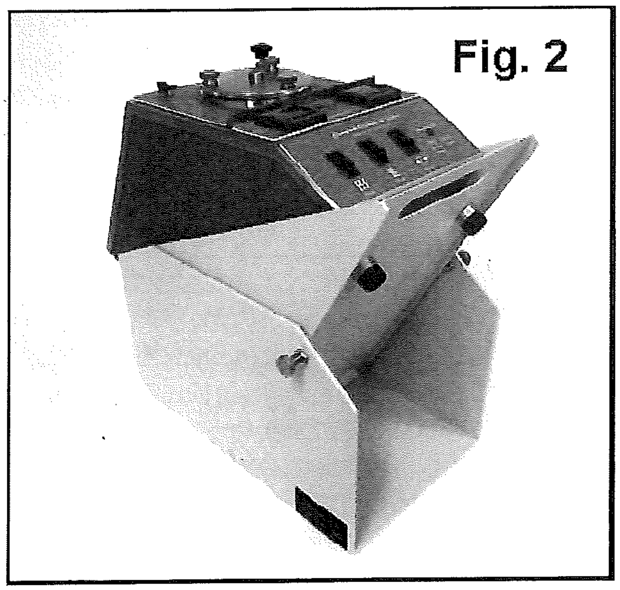

Figure 2. Iso-thermal reactor after modification

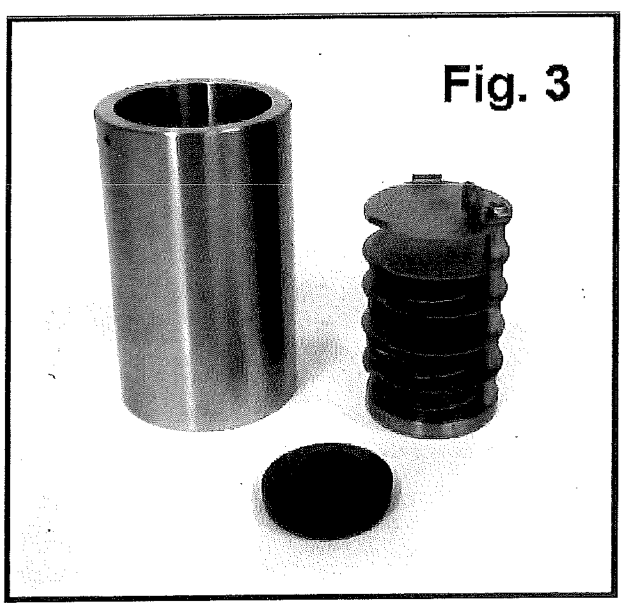

Figure 3. Accessories for the iso-thermal reactor specially designed for D942 test

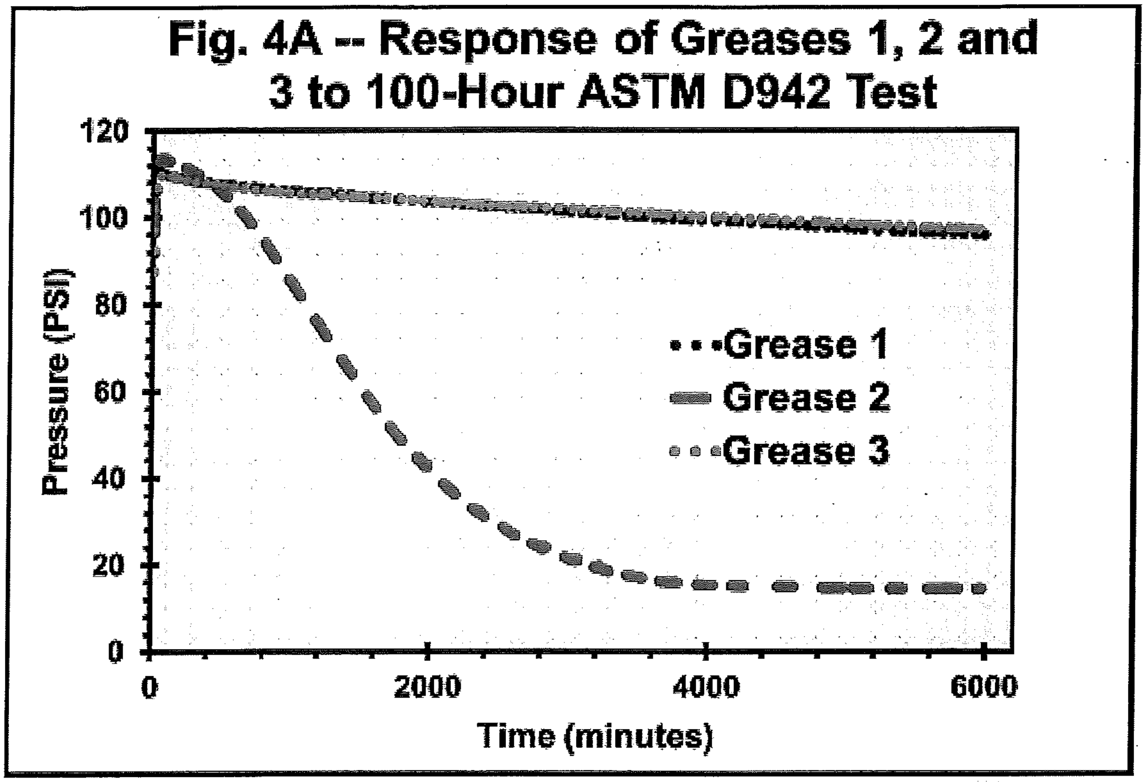

Figure 4A. Responses of Greases 1, 2 and 3 to 100 hours D942 Test

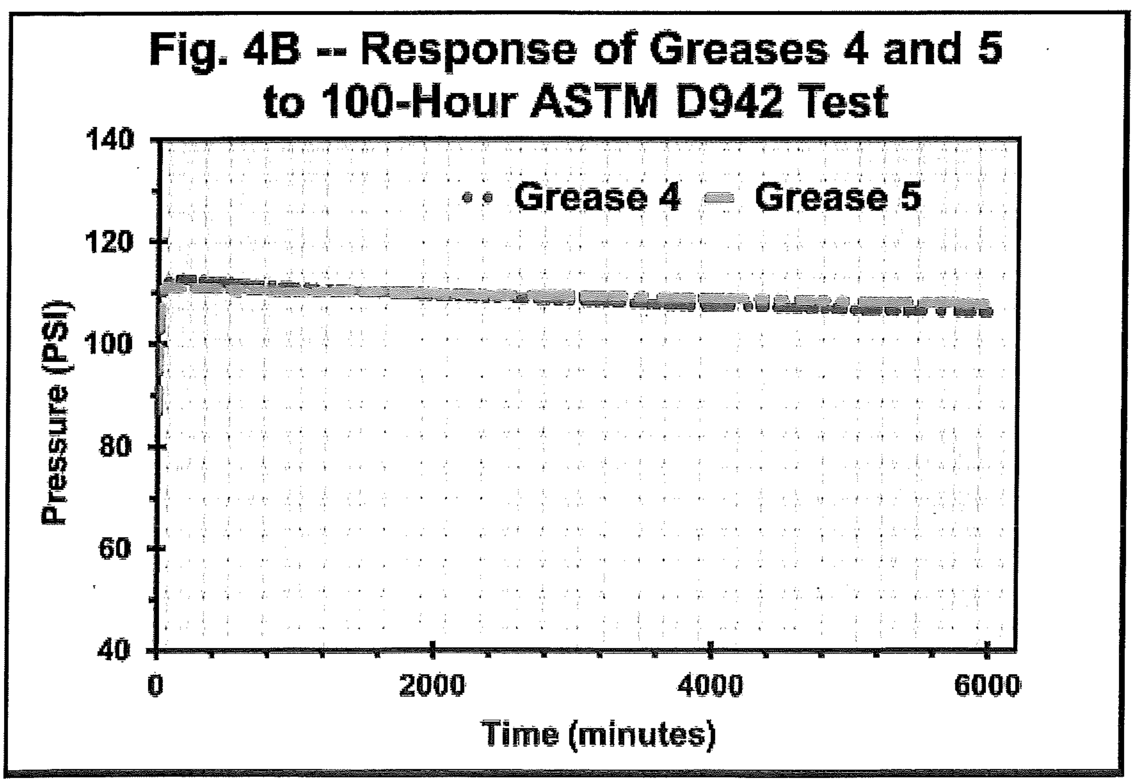

Figure 4B. Responses of Greases 4 and 5 to 100 hours D942 Test

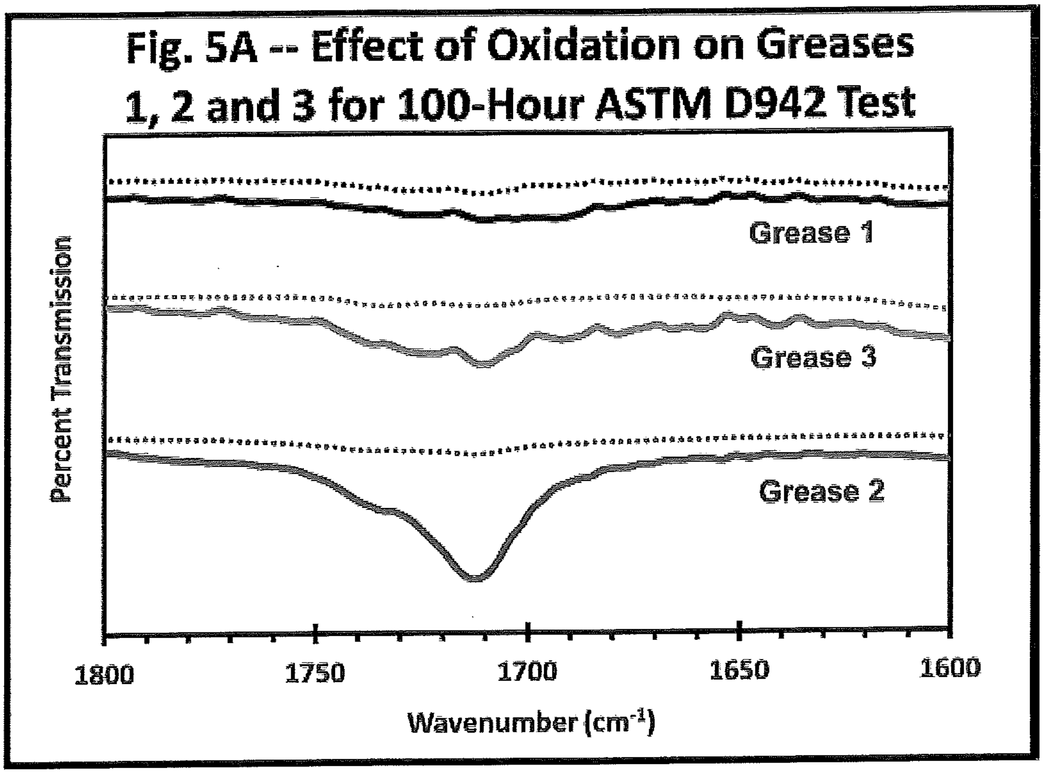

Figure 5A. Effect of Oxidation on Greases 1, 2 and 3 to For 100 hours 942 test

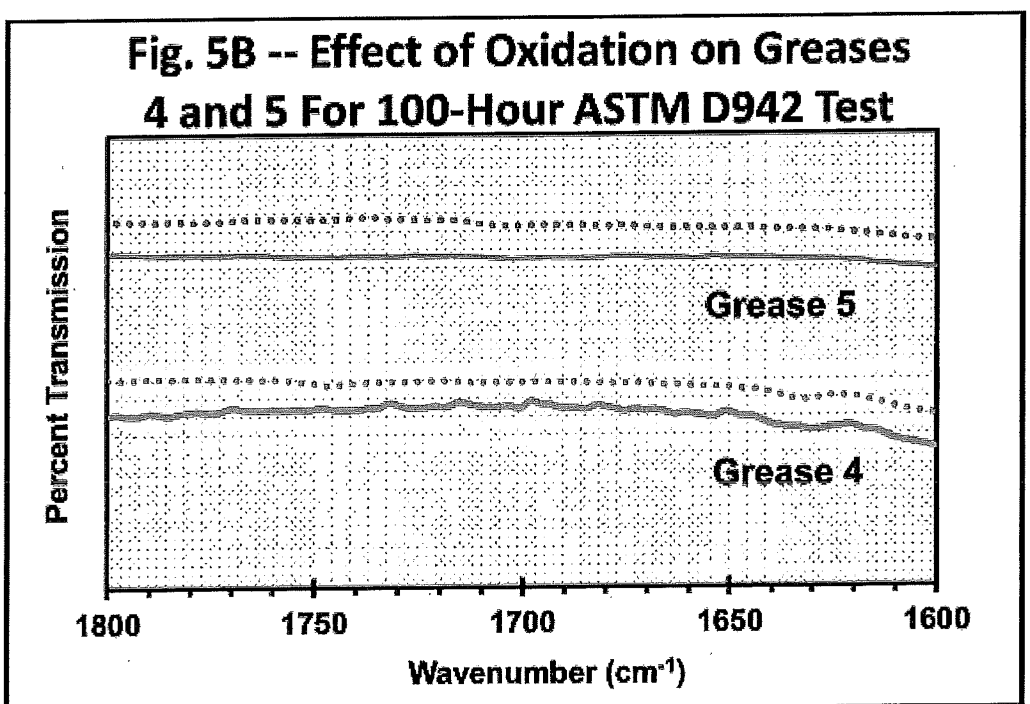

Figure 5B. Effect of oxidation on Greases 4 and 5 for 100-hour D942 test

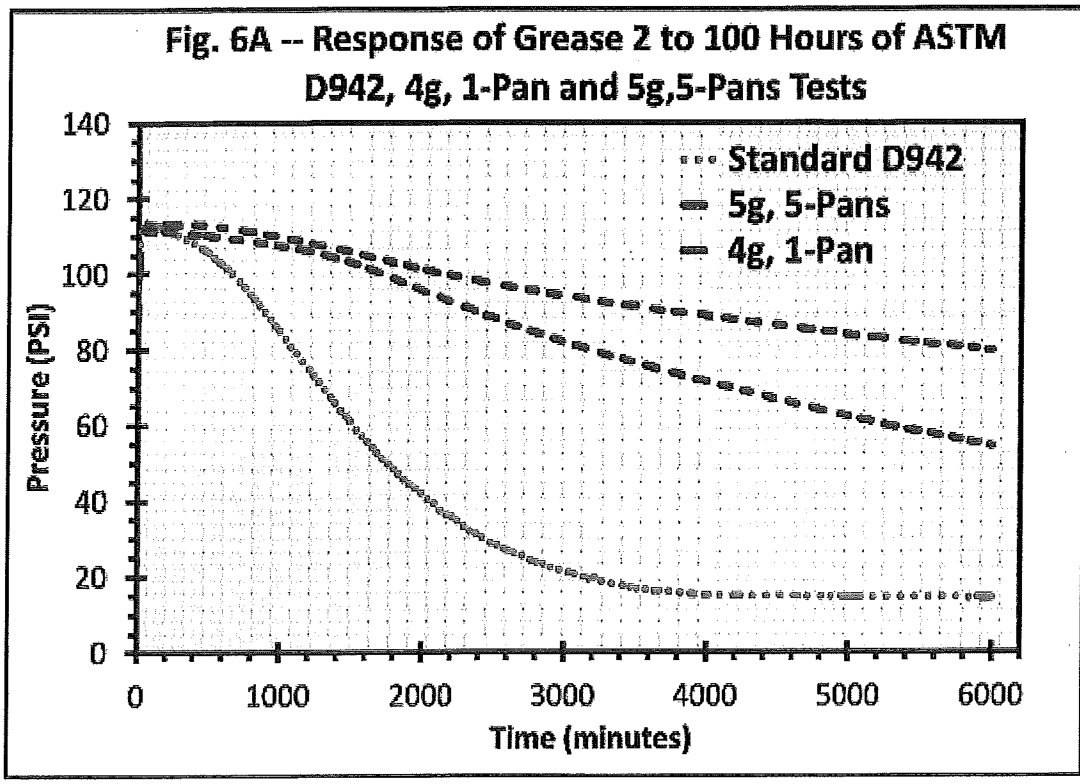

Figure 6A. Response of Grease 2 to 100 hours of ASTM D942 and 4g, 1-pan and 5g, 5-pans

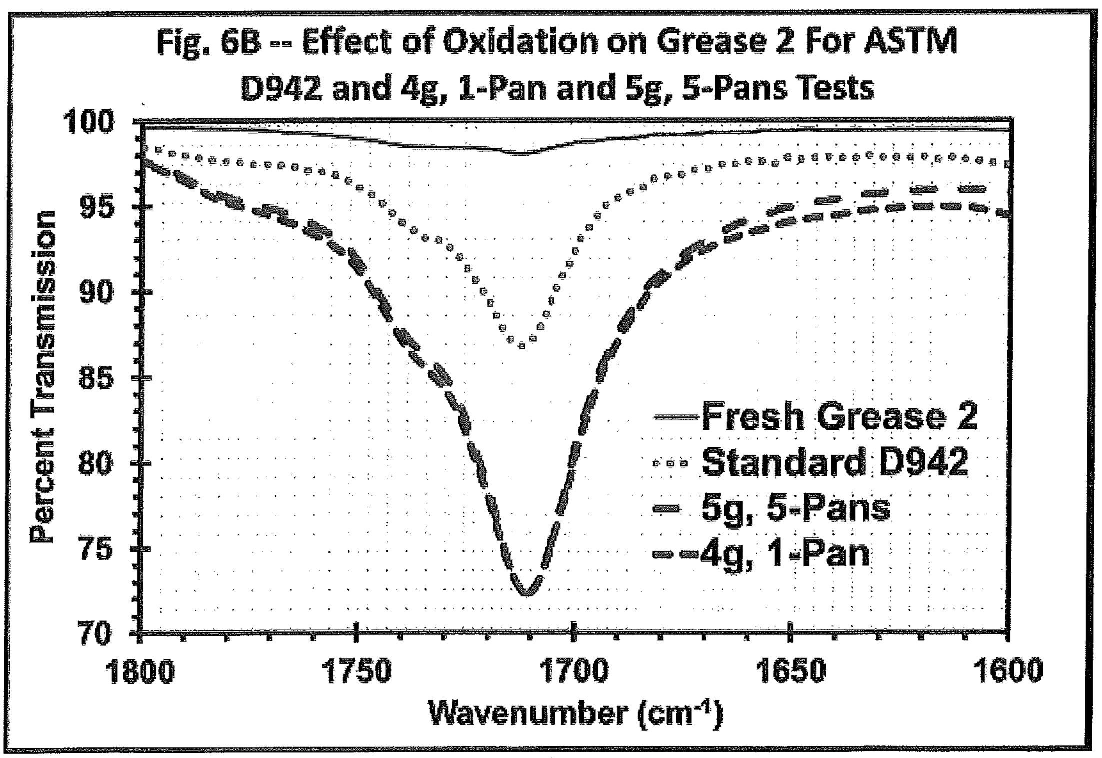

Figure 6B. Effect of oxidation on Grease 2 for 100 hours of standard D942, 4g, 1-Pan and 5g, 5-Pan tests

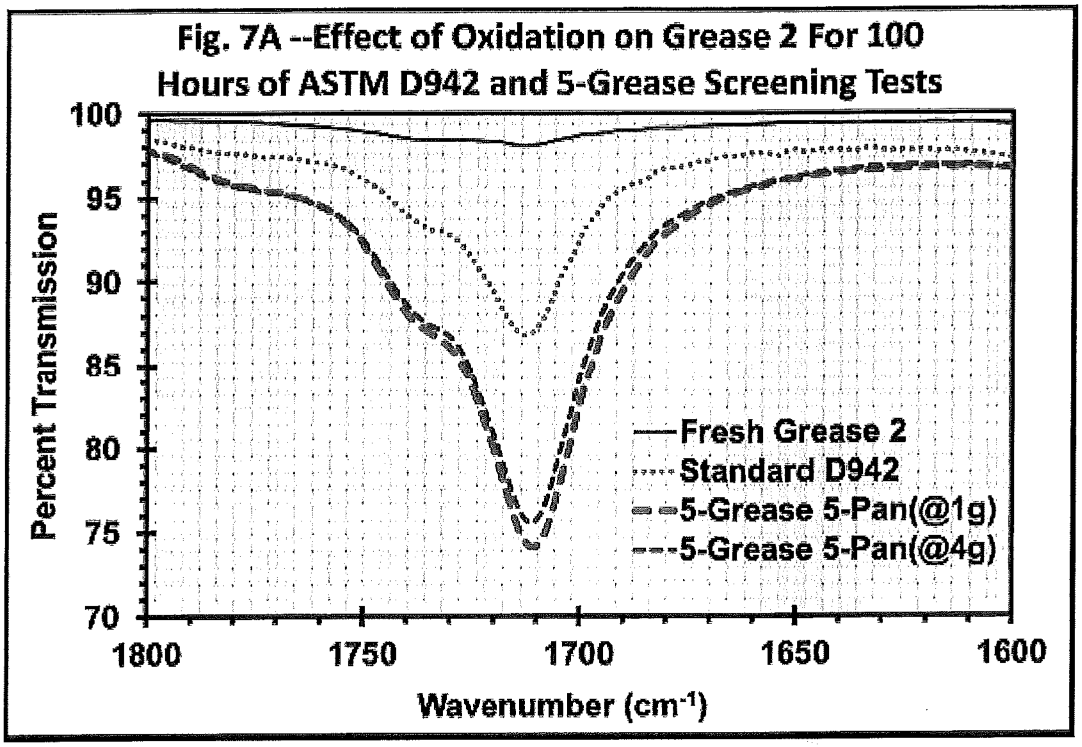

Figure 7A. Effect of oxidation on Grease 2 for 100 hours of ASTM D942 and 5 Grease tests

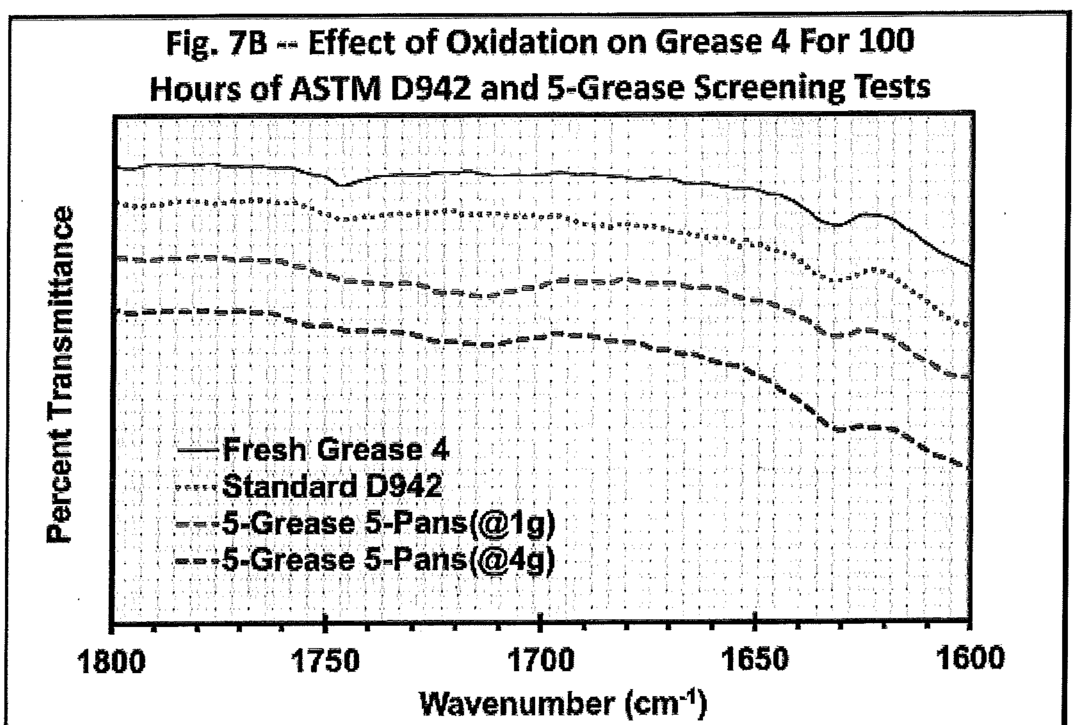

Figure 7B. Effect of oxidation on Grease 4 for 100 hours of ASTM D942 and Five-Grease tests