A Comparative Study of Grease Oxidation Using an Advanced Bench Test Technique

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Summary

Grease oxidation resistance has always been an important aspect of its performance. However, because of its nature as a gelatinous colloidal dispersion in oil, understanding and improving this aspect of grease performance continues to be a technical challenge. Moreover, the wide range of components used to formulate this most ancient of blended lubricants, makes it difficult to devise bench tests that will accelerate grease response to oxidation conditions without loss of correlation with actual applications. This paper applies a combination of an advanced version of a test method that has been used for decades but with virtually no ability to compare greases. Precise control of test temperature and measurement of change in moderately high oxygen pressure is combined with infrared analysis of the grease after the test period of 100 hours. The technique has shown significant differences among greases common in lubrication.

1. Introduction

As the most ancient of lubricants – said to extend back into the later Stone Age of man – grease is nonetheless perhaps the least understood and yet most widely used form of lubrication. This situation is not for want of effort to more clearly understand its response to operating conditions but more because of the wide range of those operating conditions and the range of components that over the millennia have been found to make it more usable.

A property having a major effect on the utility of grease is its resistance to oxidation and the consequences of this resistance to the ability of grease to maintain its level of effective lubricate. This property has been a particular focus of grease use and development over the years. As a consequence, increasingly advanced bench techniques have been developed to improve the understanding of both how the oxidation resistance can be enhanced by formulation and how this resistance can be lost in service.

1.1 Grease Oxidation Test

In the 1940's the desire for a readily applicable bench test for quality control of a grease formulation by measuring its oxidation resistance led to the development and publication of ASTM Test Method D942 in 1947 – a test method which continues to be applied [1, 2].

This test requires exposure of 20 grams of a grease to be tested in five glass dishes with an exposed surface area of approximately 25 cm^2 per dish and 125 cm^2 per test. The dishes are stacked with a gap of approximately 5 mm between them as shown in Fig. 1.

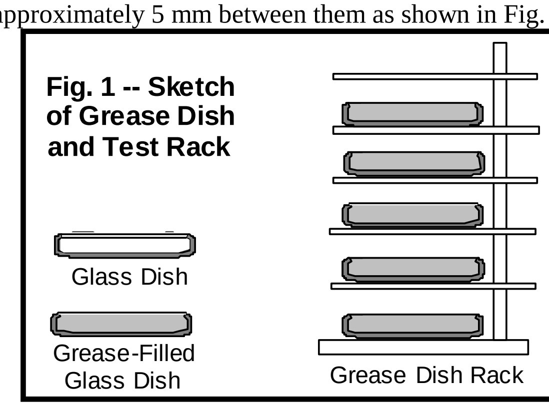

Fig. 1 -- Sketch of Grease Dish and Test Rack

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 = 690 kPa) and room temperature which is then increased to 99 ±0.5°C. Under this increased temperature, the oxygen pressure is carefully released to maintain no more than 110 ±2 PSI).

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The test is normally continued for a chosen period of 100 or 200 hours and the resultant decrease in oxygen pressure as a result of grease oxidation is taken as the test result.

1.2 Limitations of ASTM D942 – Despite being relatively simple and straight-forward, it is clearly stated in the ASTM D942 method [3], that the test is severely limited in application to any other use than quality control of a grease formulation.

For example, it is stated that the test should not be applied to compare the oxidation stability of the tested grease to actual behaviour in service. Similarly, because of differences among grease formulations and the effects of oil volatility, comparison of oxidation resistances of different greases for a given application is also not recommended. Nor should the test be used to predict the stability of grease stored in containers or the oxidation stability of greases used in bearings and motors since only controlled oxidation of a physically stable surface of grease is used in the test.

2. ASTM Method D942 Tests Using the Bath-Free Quantum RPVOT Instrument

The authors considered that the physical configuration of the ASTM D942 test and grease oxidation exposure, coupled with subsequent analyses of the grease by Fourier Transform InfraRed (FTIR) had considerable merit if some way could be found to eliminate the need for the awkward and difficult-to-maintain oil bath. Fortunately, such a test instrument was available for adaptation.

2.1 Quantum Iso-Thermal Reactor – In the last few years a new approach to meet ASTM Test Method the Rotating Pressure Vessel Oxidation Test (RPVOT) D2272 [4], was developed [5]. This instrument, called the Quantum, does not use a liquid bath to heat the pressure chamber. Thus, in essence, it is a bath-free isothermal instrument first applied to the RPVOT method and incorporated into D2272 in 2009 after an extensive round robin [6].

A picture of this instrument is shown in Fig. 2 as used for the RPVOT test.

Fig. 2

The design of the bath-free Quantum also permits access to the test substance in the pressure chamber during test to extract a small sample [7].

2.1 Configuration of Quantum Instrument for Grease Oxidation Test – Since the Quantum instrument – which actually is an isothermal reactor capable of many uses, has all of the necessary geometry, heating, and availability of pressurized oxygen as a test condition, it was very easily adapted for running the ASTM D942 grease oxidation test.

Accordingly, a steel insert to reduce the inner volume of the Quantum's pressure chamber and a vertical rack for the five grease samples were designed. These are shown in Fig. 3 with one of the grease-filled dishes.

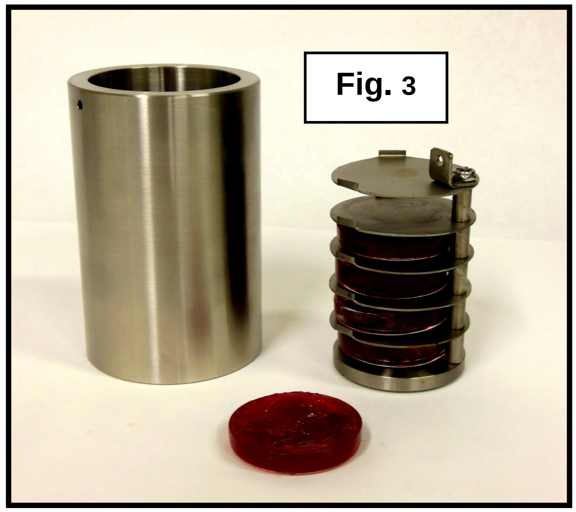


Fig. 3

To further simplify this alternative use of the Quantum instrument, simple steel shelving was designed that permitted the Quantum instrument to be tipped to a vertical position for use in grease oxidation tests or to set in its normal orientation for RPVOT tests. These are shown in Fig. 4a and 4b.

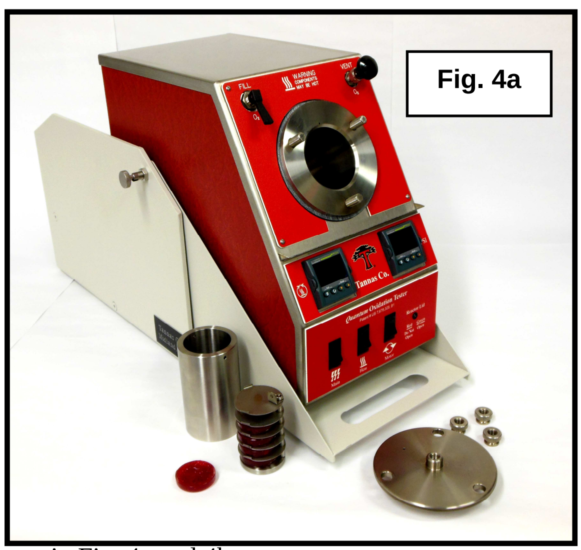


Fig. 4a

In Fig. 4a, the Quantum instrument is set into the rotatable shelf to permit the operator to use it for the RPVOT test or for the grease oxidation test.

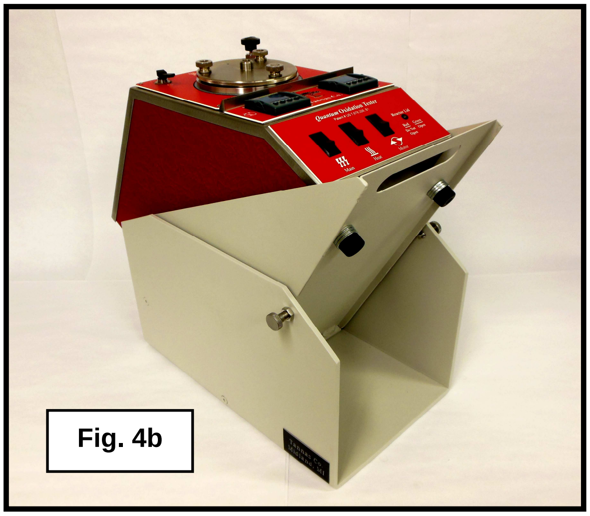


Fig. 4b

In Fig. 4b, the shelf holding the Quantum is tipped up to the position in which the pressure chamber within the Quantum is vertical and the steel sleeve and rack of grease-containing dishes are installed awaiting sealing the lid and pressuring the closed chamber with oxygen.

2.2 Application of Attenuated Total Reflectance Infrared – Infrared spectroscopy has been used for more than a half-century in the study of grease oxidation [8, 9] starting with the work of Rappoport in 1952 [10].

The introduction and development of Fourier Transform InfraRed (FTIR) spectroscopy was a major development permitting creative comparison of infrared spectra. More recently the use of Attenuated Total Reflectance (ATR) infrared has again further extended the use of infrared to materials which are not very amenable to transmitting infrared light through the sample to generate spectra.

For greases, with their colloidal, gelatinous, and otherwise heterogeneous dispersion of components, ATR using only the reflective surface of the sample is a desirable comparative source of IR spectra.

2.3 Combined Analytical Technique to Compare the Oxidation Resistance of Greases – A test protocol was developed for

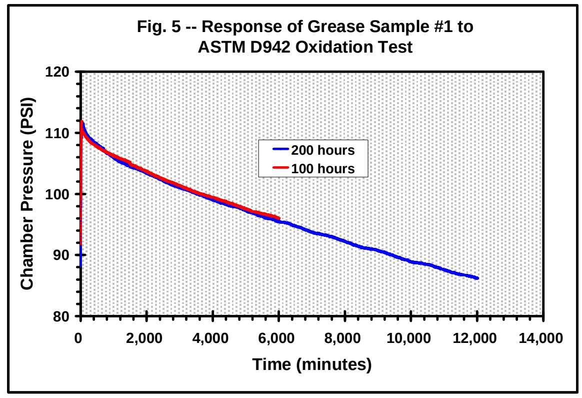
1) First determining the response of a grease to ASTM D942 using oxygen pressure decrease, then
2) Sampling the grease in the dishes from the test, and finally
3) Comparing the oxidation resistance of the greases using ATR FTIR spectra.

3. Results of ASTM D942 Tests of Five Greases Using the Quantum Instrument

Applying the modified Quantum instrument shown in Figs. 3, 4a and 4b, ASTM D942 grease oxidation tests were run for 100 hours and additionally, in some cases, 200 hours. For each test, pressure change with time was continuously recorded.

Following each test, the five dishes of grease were sampled for infrared analysis on an ATR equipped FTIR. In first tests, it was found that there were essentially no differences between individual dishes from the five-dish stack. Consequently, only the top dish was sampled for subsequent IR analyses

3.1 Grease #1 – Tests using the ASTM D942 method were run for both a 100-hour and a 200-hour test period under this test method. Fig. 5 shows the closely similar pressure traces obtained during these tests.



Grease #1 was run at both 100 hours and 200 hours for comparison of both:

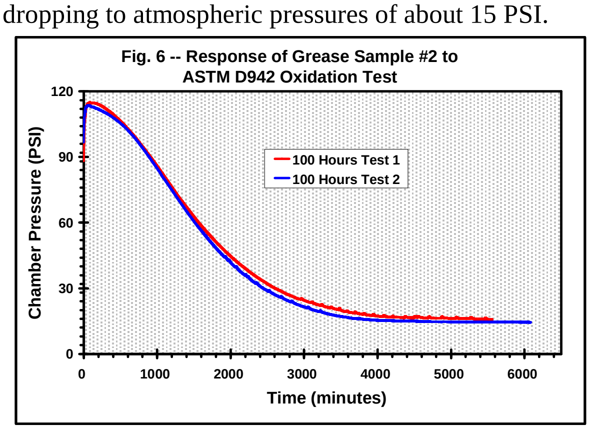
1. The repeatability of the pressure-decrease curves in the first 100 hours and
2. The continuing rate of oxidation for the next 100 hours of exposure.

It is evident that the oxidation curves are quite similar and that ASTM Method D942 as applied by the modified Quantum instrument is capable of providing reproducible information.

The oxygen pressure in Test 1 at 100 hours was 96 PSI. At 200 hours of test it was 86 PSI.

3.2 Grease #2 – ASTM D942 tests were conducted in replicate for 100 hours on Grease #2 and results are shown in Fig. 6.

The response to ASTM D942 was quite strong but highly repeatable. This grease may have begun oxidizing even before the chamber temperature reached its maximum of 99°C. Interesting, the final pressures in the chamber showed total oxygen uptake during test by dropping to atmospheric pressures of about 15 PSI.



3.3 Grease #3 – As mentioned earlier, according to the protocol of ASTM Test Method D942, when the oxygen pressure rises to 110 ±2 PSI, the oxygen is carefully released to keep it at this level until oxidation of the grease begins.

Figure 7 suggests the consequences of not relieving the oxygen pressure in Test 1 for almost 2½ hours. The data indicate that additional grease oxidation may occur under such preliminarily higher oxygen pressure.

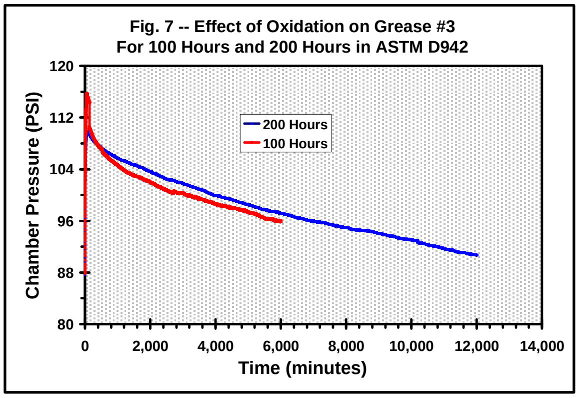


Fig. 7 -- Effect of Oxidation on Grease #3 For 100 Hours and 200 Hours in ASTM D942

Final oxygen pressures were 96 PSI after 100 hours for Test 1 and 91 PSI after 200 hours for Test 2.

3.4 Grease #4 -- Grease #4 was found to be highly resistant to oxidation in the D942 test as shown by the three replicate tests in Fig. 8. In these three tests, the lowest oxygen pressure after a 100-hour test was only 107 PSI.

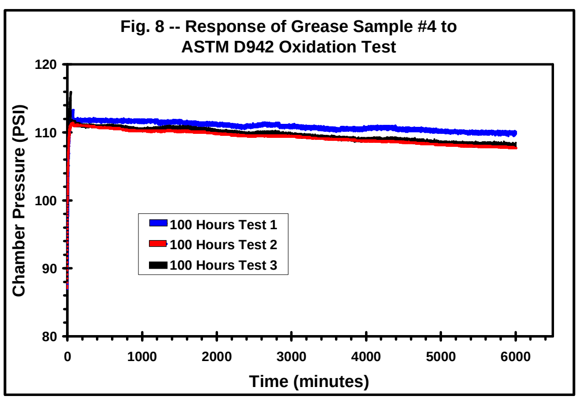


Fig. 8 -- Response of Grease Sample #4 to ASTM D942 Oxidation Test

3.5 Grease #5 – Evaluation of Grease #5 shown in Fig. 9 indicated this grease to also be fairly resistant to oxidation over 100 hours of test.

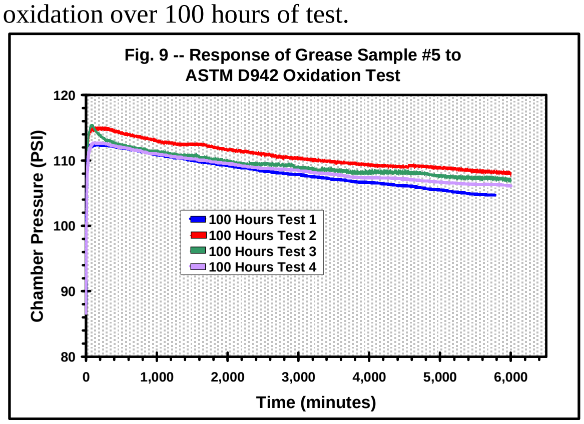


Fig. 9 -- Response of Grease Sample #5 to ASTM D942 Oxidation Test

4. ATR-FTIR Analyses of Greases Oxidized in the Quantum Adaptation of ASTM D942 -- Technique

Following exposure of each of the foregoing five greases to ASTM Method D942 for 100 or more hours, the oxygen pressure is released. When the pressure chamber is sufficiently cooled, the instrument is opened and the rack of dishes removed.

About 2-4 milligram of grease sample was needed in analyzing its FTIR spectrum using the ATR. For consistency in the study, the grease sample was skimmed from the surface of the grease in the top plate.

4.1 ATR-FTIR Analysis of Grease #1 – As shown in Fig. 5, Grease #1 was subjected to 100 and 200 hours oxidation exposure in ASTM Method D942 run in the modified Quantum instrument.

Fig. 10 shows an analysis of the spectrum of fresh Grease #1 from a wavenumber of 1600 to 2200 cm^{-1}. Values of the Percent Transmittance of only the fresh Grease #1 are shown on the left-hand ordinate.

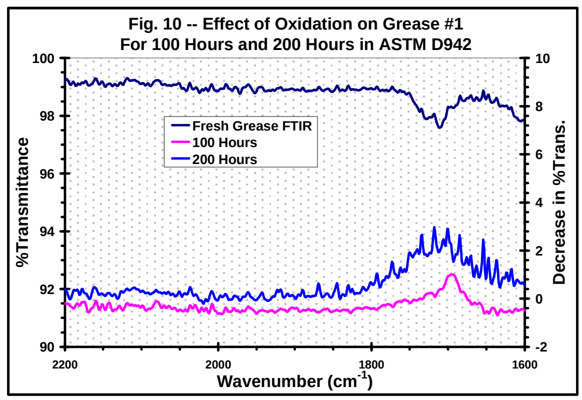


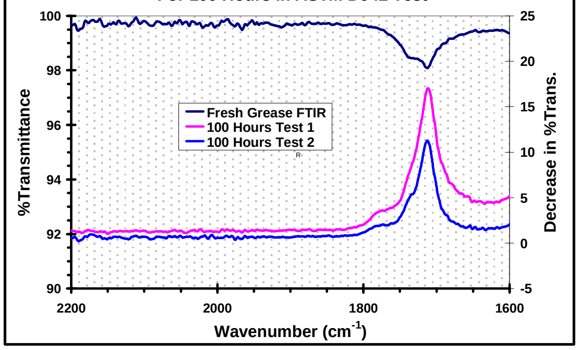
Fig. 10 -- Effect of Oxidation on Grease #1 For 100 Hours and 200 Hours in ASTM D942

On the right-hand ordinate, the FTIR values of Percent Transmittance for the oxidized grease samples are subtracted from those of the fresh grease (in this case Grease #1). This shows the effects of oxidation on the fresh test grease by the increase in concentration of oxidized grease components and thus a decrease in Percent Transmittance.

It is evident and confirming that at the wavenumbers between approximately 1700-1750 cm^{-1} associated with carbonyl oxidation products (carboxylic acids, ketones, aldehydes, etc.) there is, as would be expected, substantial increase as a consequence of oxidation. Moreover greater oxidation is shown in the 200-hour test compared to that of 100 hours. Interestingly, even in the fresh grease, there are evident peaks shown in the vicinity of 1700-1750 cm^{-1}. This suggests that the formulation of this grease may contain carbonyl additives components or that the grease may experience some oxidation in formulation.

4.2 ATR-FTIR Analysis of Grease #2 – As discussed in Section 3.2 and shown in Fig. 6, Grease #2 was very oxidation susceptible in the ASTM D942 oxidation test protocol. The three curves shown in Fig. 11 resulted after the grease was tested twice and the resulting FTIR spectra subtracted from that of the fresh Grease #2.

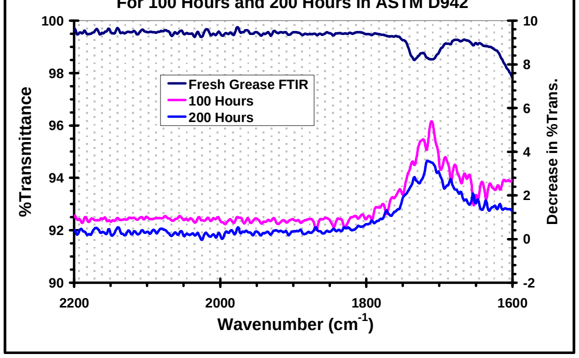
Fig. 11 -- Effect of Oxidation on Grease #2
For 100 Hours in ASTM D942 Test



The peaks of Test 1 and Test 2 are both at 1710 cm^{-1} with reduced Percent Transmittance of 17% and 11% respectively at this wavenumber closely associated with hydrocarbon oxidation.

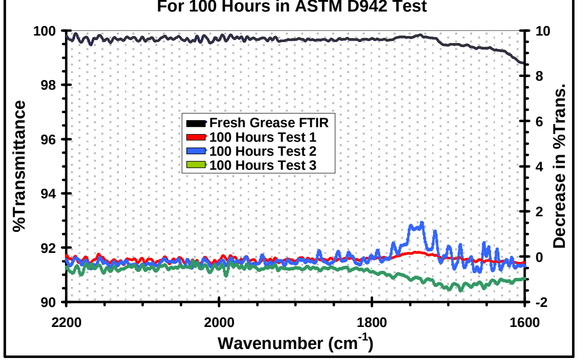
4.3 ATR-FTIR Analysis of Grease #3 – Grease #3 demonstrated oxidation susceptibility in Fig. 7. In this, it is similar to Grease #1. However, as shown in Fig. 12, when the FTIR spectra were obtained, the degree of oxidation shown by the decrease in Percent Transmission was somewhat greater than Grease #1.

Fig. 12 -- Effect of Oxidation on Grease #3
For 100 Hours and 200 Hours in ASTM D942



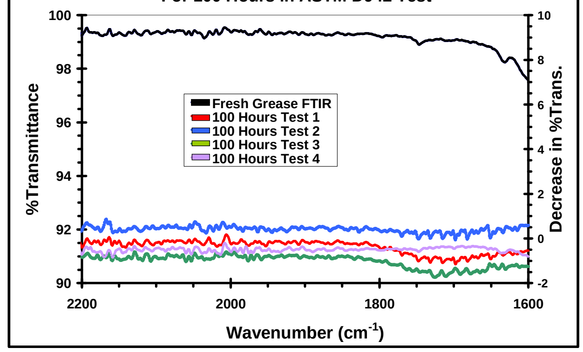
4.4 ATR-FTIR Analysis of Grease #4 – As expected from Fig. 8, in Fig. 13 Grease #4 shows high oxidation resistance. The three tests run at 100 hours show some variability in the oxidation wavenumber region indicating a sensitive antioxidant.

Fig. 13 -- Effect of Oxidation on Grease #4
For 100 Hours in ASTM D942 Test



4.5 ATR-FTIR Analysis of Grease #5 – From the ASTM D942 oxidation tests, Grease #5 also seems resistant to oxidation. This becomes clear in Fig. 14. Essentially, no oxidation is shown by Grease #5. Moreover, in some distinction to Grease #4, the four tests on Grease #5 are fairly similar.

Fig. 14 -- Effect of Oxidation on Grease #5
For 100 Hours in ASTM D942 Test



5. Discussion

As virtually the most ancient form of man-made lubricant, grease has been unique in its complex forms and the nature of its tribological contributions.

Grease is subject to many forms of stress in providing lubrication. One of the more important of these is oxidation. This is particularly the case since, in many applications, the grease is very exposed to the environment composing and surrounding the lubrication site – however varied that environment may be. Moreover, unlike forms of liquid lubrication, there is seldom much that can be done to protect the grease from its often harsh environment.

As a consequence of the complex chemistry and composition of greases, and the variable nature of the environment in which given grease is applied, standard bench tests of the chemical performance of greases such as ASTM D942 are infrequent. This is in contrast to the more commonly employed physical bench tests for wear and physical degradation in service.

It was for this reason that the authors chose to extend the application of ASTM D942 by improving its instrumental simplicity and heating control and removing its stated interpretive limitations mention earlier in Section 1.2.

Results of this study showed clearly that among the five greases studies, the combination of ASTM Method D942 and the subsequent FTIR analysis of the spectra of the original grease compared to the grease after oxidation showed that the FTIR information supported the relatively simplistic information of ASTM D942 alone. Moreover, the limitations of ASTM D942 when used alone were overcome with the sharper information provided by the FTIR analysis.

6. Conclusions

On the basis of this study, it would seem reasonable that the ASTM Method D942 should be extended to include the use of FTIR analysis. With such information the ASTM Method could be used to show correlation with field experience and to also permit selection of better additives for specific applications.

The use of the FTIR spectrum subtraction technique shown in this paper was helpful in more clearly discriminating the changes in different greases brought about by oxidation.

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