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A FEW INSIGHTS INTO GREASE TESTING

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Introduction:

What we all know about our products we learned from testing. Laboratory tests are used for research and development, quality control, and to determine the chemical and physical properties of greases and oils. Although various standards organizations such as ASTM, DIN, and JIS do an excellent job in defining exactly how tests should be conducted, experienced laboratory personnel often gain insight into streamlining test procedures, interpreting results and developing new test methods that further our understanding of lubricants. This paper discusses some of these "tricks of trade" learned in the author's laboratory along with two novel methods developed to assess grease characteristics. Bomb oxidation, dropping point, grease permeability, and thickener content by controlled S^2 rheometry are discussed.

Bomb Oxidation Stability Test:

ASTM D942 has been used for many years as a method to determine the oxidation stability of lubricating greases. The advantages of the test are: it requires relatively inexpensive equipment, it is easy to operate, and data interpretation is usually straightforward. What I would like to present today are some of the techniques that have been adopted in my laboratory over the last twenty years. It is hoped that these insights will help eliminate some of the inherent pitfalls in performing the test and facilitate data interpretation.

Based on the ASTM D942 procedure, the bomb must be pressurized to 110 +/- 2 psi (758 +/- 14 kPa) with reagent grade oxygen. In our laboratory, the source of oxygen is a lecture-size bottle of gas fitted with a two stage pressure regulator. If my assumption is correct, many of you have the same difficulty in delivering the required quantity of gas to the steel bomb at ambient laboratory temperatures. This problem could be easily solved by using a regulator with higher delivery side pressure. But if that solution is not an option, the bomb can be filled with the aid of dry ice. The procedure is as follows: Connect the bomb to the O_2 delivery cylinder in the usual manner and then place the bomb in a metal beaker large enough to accommodate the bomb and a few pounds of dry ice. Pack the dry ice around the base of the bomb and open the regulator valve to fill the bomb. Purge air from the bomb in accordance with the ASTM standard, and allow the bomb to remain in the ice bath connected to the oxygen source for approximately 10 minutes. Then remove the bomb from the dry ice bath and place it in a secure location. A keyed fixture can be fabricated inexpensively that can serve as a bench top holder for the filled bomb and can also be a convenient means of securing the bomb during bolt tightening. Vent oxygen from the bomb as the gas begins to reach room temperature.

This procedure simply takes advantage of the gas laws in that a given volume of gas increases in pressure as a function of rising temperature. If we assume that the bomb is -40C after ten minutes in the dry ice bath, the gas pressure at 25°C (298 °K) is about 127 psi. The ASTM procedure states that the bomb pressure must be 110 psi at the test temperature. However, for the example that follows, let's use 100°C which is easier mathematically than the 99°C required by the standard. The minimum delivery pressure can be determined as follows:

$$\mathbf{P_1/ T_1 = P_2/ T_2}$$

P_1 = the required O_2 delivery pressure

T_1 = room temperature in degrees Kelvin, 298 °K, 25°C

P_2 = 110 psi

T_2= test temperature in degrees K, 373°K, 100°C

Solving for P_1 we have:

$P_1 = P_2\ T_1/T_2$ = 110 psi x 298/373 = 87.8 psi

Therefore, if the temperature in your lab is 25°C, the low pressure side of your O_2 regulator needs to deliver about 88 psi(605 kPa). Lower the temperature with dry ice and your regulator becomes a virtual pressure powerhouse.

Perhaps one of the more frustrating aspects of conducting ASTM D942 is the realization that a leak has occurred during an extended test interval. Some tests run for 500 hours. Minor gas leaks if undetected provide misinformation about the thermooxidative stability of a test candidate. Based on experience gained in our laboratory, major areas for leak trouble are the lead gasket and the pressure release valve. To reduce the likelihood of the lead gasket serving as a leak path surface oxide films should be removed with a metal laboratory spatula. Moreover, a thin film of a non-oxidizing PFPE grease applied to the gasket will assist in the formation of a gas tight seal. This approach can also be effective with the new polymeric gaskets now being used. As for the pressure release valve, a brass plug is screwed into the female valve fitting. PTFE pipe tape provides added assurance against leakage. If like me, you do not have the patience to wait twenty-four hours to determine if the bomb is leaking, immerse the bomb in water and look for bubbles!

Moreover, when testing any grease for an extended interval and there appears to be negligible pressure loss, be suspicious. In my 25 years of experience, I have seen only one false negative. But even one can be quite alarming. Many lubricants are made using water as a vehicle for rapid saponification or water may be a by-product from the chemical reaction. If incompletely removed during the dehydration process, residual water can cause problems with ASTM D942. Consider this scenario. As the bomb achieves thermal equilibrium with the heating bath, the vapor pressure of the water becomes significant. Since water does not oxidize, its partial pressure contributes to the total pressure in the bomb in accordance with Raoult's law. In essence, the pressure on the gauge is kept artificially high by water vapor. Although water is a prime suspect, volatile decomposition products may also contribute to false negatives. The strategy used in our laboratory to overcome this problem is to read the pressure on the bomb at the completion of the test, at the test temperature, and again when the bomb has reached room temperature. Table 1 outlines this procedure and its interpretation.

TABLE 1

Temperature	**Time = 0**	**Time = 168 Hours**	**ΔP**	**Comments**
100°C	$P_0 = 110$ psi	$P_{168} = 105$	5	Pressure change at test temperature.
25°C	$P_0 = 88$ psi	$P_{168} = 83$	5	Same ΔP at both temperatures implies a valid test.
25 °C	$P_0 = 88$ psi	$P_{168} = 78$	10	Different ΔPs implie an invalid test.

Note: The fill pressure changes by approximately 1 psi for a +/- 4°C change in room temperature. Therefore, for the invalid test above only 1 psi could be attributed to a new room temperature of 29 °C. The additional 4 psi is probably due to the oxidation of the sample.

What Table 1 illustrates can be understood by a simple gedanken experiment. You fill the bomb in your laboratory at ambient temperature and reach a stable pressure of 88 psi. The bomb is placed in a heated bath and the new pressure is 110 psi and the test in run for 168 hours. At the completion of the test, the drop in pressure is 5 psi at 100 °C. The bomb is removed from the heated bath and allowed to reach room temperature. If the pressure difference, from 88 psi, is greater than 5 psi and it can not be accounted for by a shift in room temperature, a false negative occurred.

Now suppose the bomb is pressured to 90 psi at 25°C. How many moles of oxygen does this represent? Since we wish to use the universal gas equation to calculate the number of moles, let's convert the pressure in psi to atmospheres. Given that one atmosphere is 14.69 psi, we have:

90 psi / 14.69 psi atm^{-1} = 6.1 atm

The universal gas equation is: PV = nRT

P = pressure in atmospheres
V = volume of the bomb = 0.185 liters
R = universal gas constant = 8.02×10^{-2}-atm deg^{-1} mole^{-1}
T = degrees K
n = number of moles

Rearranging the equation and solving for n we have:

$$n = PV/ RT$$

$= 6.1 \times 0.185/ 8.02 \times 10^{-2} \times 298$
$= 4.6 \times 10^{-2}$ mole of oxygen

That is only 0.046 mole of oxygen is contained in the bomb.

The method requires 4.00 +/- 0.01 grams of grease in each of five dishes for a total of 20 grams. If we assume that the molecular weight of the grease is 800 g mole^{-1}, then we have 2.5×10^{-2} mole of grease. The mole equivalents for oxygen and grease are presented in Table 2.

TABLE 2

Component	Moles x 100	Mole Equivalents
Oxygen	4.6	1.84
Grease	2.5	1.00

Based on this analysis, there is more than enough oxygen to oxidize the entire quantity of grease. But we need to ask what is the smallest hydrocarbon target that would interest a molecule of oxygen? It could be the whole hydrocarbon molecule, but a more likely candidate is the CH_2 moiety. If we now divide the molecular weight of the grease by the weight of the CH_2 moiety (800 /14), we find that there are 57 such moieties per molecule or 57 moles worth. This is more than sufficient to stave off total oxidation of the grease if we assume that each molecule experiences multiple strikes by oxygen. Oxidation cannot be eliminated but the onset to oxidative degradation can be significantly extended by the judicious choice of effective antioxidants.

As a final comment, any grease that forms a polymer skin must be disqualified since such behavior would result in a favorable pressure drop due to the static nature of the method. However, under dynamic testing surface polymerization would offer little if any long term protection.

Dropping Point:

One lesson that I had hoped each student would learn during my tenure at the helm of the NLGI grease education program, was that dropping point is **NOT** the same as the maximum service temperature of a grease. ASTM D566 or D2265 determine the lowest temperature a drop of material (oil, thickener, or both) separates from the grease structure under the conditions of the test. Grease made to a high NLGI penetration i.e. a soft grease will exhibit a low dropping point even if formulated from a relatively non-melting thickener. For example, lubrication grade PTFE has a melting point of 324°C. However, a PTFE thickened NLGI Grade 1 grease may have a dropping point below 200°C. The drop of oil that flows from the thimble must be considered thermal separation and is not caused by appreciable softening or melting of the PTFE thickener. Similar behavior is expected for other non-melting thickeners such as organo-modified clay and amorphous silica.

One approach that may be used to delineate the heat resistance of a grease that is susceptible to thermal separation is to report the temperature at which successive drops fall from the dropping point thimble. If the thickener has good heat resistance, each successive drop will occur at higher temperatures with considerable spread between the first and third drop. The information is not as technically tidy as reporting a fixed dropping point; but, it can be useful data in convincing customers about actual heat resistance of a soft grease.

Moreover, the NLGI and ELGI are surely the world's best forum to launch a serious debate about the technical merit of reporting dropping points above 260°C. Let me propose that we consider any dropping point above 260°C as simply >260°C. This implies that if during a dropping point test, the temperature reaches 261°C, the test be stopped and the dropping point be reported as >260°C. Doing so, in my judgment, would help educate customers about the high temperature limitations of grease, improve the credibility of our literature, and eliminate laboratory time spent in a temperature realm beyond the oxidative stability of all but a few exotic greases.

Grease Permeation:

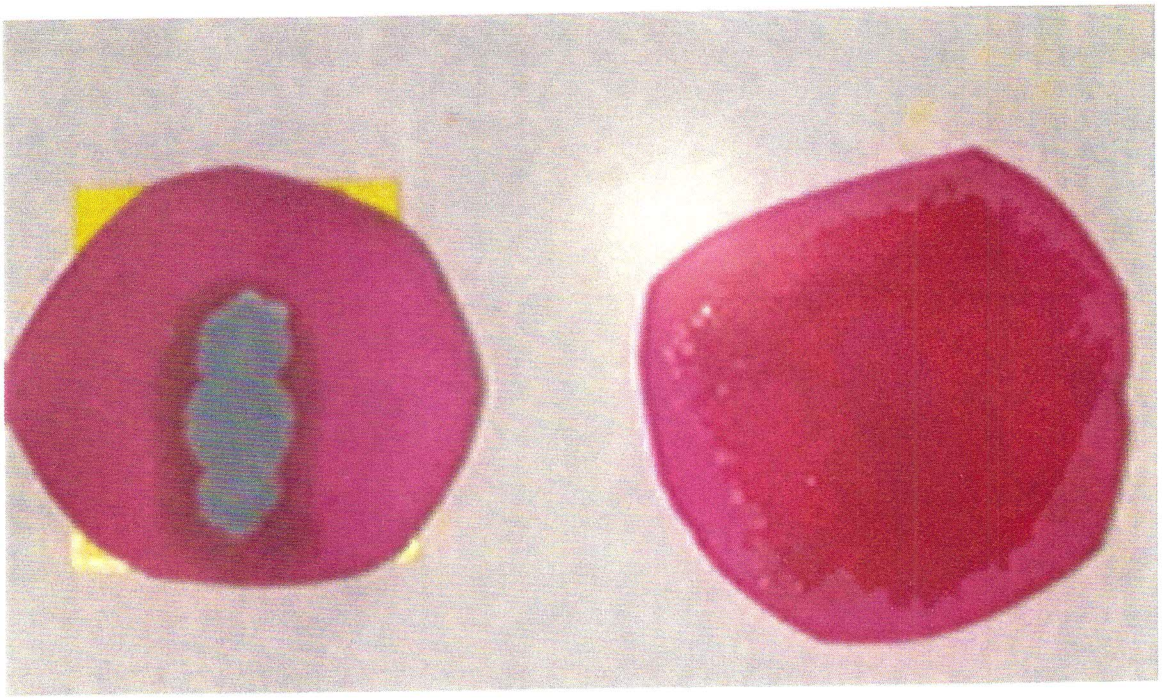
In addition to their tribological duties, an ancillary function of grease is to protect vulnerable metal surfaces from the ravages of atmospheric corrodants. Non-noble metal electrical contacts exemplify an application requiring a grease to function in this dual role. Unless formulated with special fillers to make them conductive, lubricating greases are dielectrics. A grease's ability to function in an electrical switch or contact is dependent on sliding motion. During actuation, the contact wiper moves in relation to the terminals and a film of lubricant forms in accordance with hydrodynamic principles. However, when the wiper comes to rest, the normal load on the wiper displaces grease from the real area of contact and electrical continuity is established. If the contacts are susceptible to oxygen, sulfur, or some other atmospheric pollutant, electrical performance degrades due to the formation of surface films. Film formation can be greatly reduced or sometimes eliminated with the judicious selection of the appropriate grease, one that can serve as a physical barrier to the transport of small molecules or ions.

A diagnostic test recently developed in our laboratory uses a dilute mineral acid to probe a grease's permeability. The technique consists of treating circular filter paper with an aqueous 0.1N solution of sodium hydroxide followed by impregnation with phenolphthalein indicator. The base color of the indicator is red. Using plastic motor mounts as templates, grease is applied to the chemically treated filter paper. One half, 1mm, and 1.5 mm thick grease films are good starting dimensions. A 0.2N solution of Hydrochloric Acid is applied to the exposed upper grease surface. Transport of the H^+ ion through the grease changes the red basic color of the filter paper to white. The variable recorded is time to permeation. Units may be minutes, hours, or days. Care must be taken to prevent evaporation of water from the solution of hydrochloric acid from stalling the transport mechanism. Since the chloride ion is a powerful salt former, soap thickened greases are particularly vulnerable to degellation and early failure in this test.

The hydrogen ion, H^+ and the hydrated hydronium ion H_3O^+ are very useful probes due to their small ionic dimensions compared to the molecular dimensions of typical atmospheric, metal contaminates. If a proton can be stopped, SO_2, O_2, and CO_2 should be also.

Figure 1 shows the condition for a fail and pass grease sample.

Figure 1



FAIL **PASS**

Thickener Content from Rheology:

A difficult problem in any lubrication laboratory is to determine the amount of thickener in a field return sample of grease. Customers often report that a particular grease looks dry after fewer hours of operation than expected. Since base oil loss due to oxidation, oil separation, and evaporation can produce the " dry look", finding a suitable method to determine the amount of thickener in a limited quantity of grease would be of value. Infrared analysis has many advantages in terms of sample preparation, sample size, and time for analysis. However, problems with poor quantitation due to soap agglomerates scattering the infrared radiation severely limit the use of IR analysis.

Several years ago, our laboratory purchased TA Instruments TA 1000N control stress/control shear rheometer, S^2 for short, which has been used extensively for the elucidation of the viscoelastic properties of various lubricating greases. More recently the rheometer has been used to measure the apparent viscosity of a series of clay thickened polyolester greases of known thickener concentration in order to determine if a calibration curve could be plotted of apparent viscosity versus thickener concentration. A mathematically sound correlation would allow the determination of approximate thickener content from field returned grease. Such information would be useful for monitoring grease condition and determining relubrication intervals.

All testing was done with a TA Instruments 1000N rheometer using a 2°, 4 cm, stainless steel geometry. Apparent viscosity was measured at 5 s^{-1} intervals to a maximum of 30 s^{-1}. The Williamson model was used to determine the apparent viscosity at zero shear to assure repeatable data acquisition. Table 3 gives the viscosity of the base oil and greases in milliPascal seconds, mPa.s.

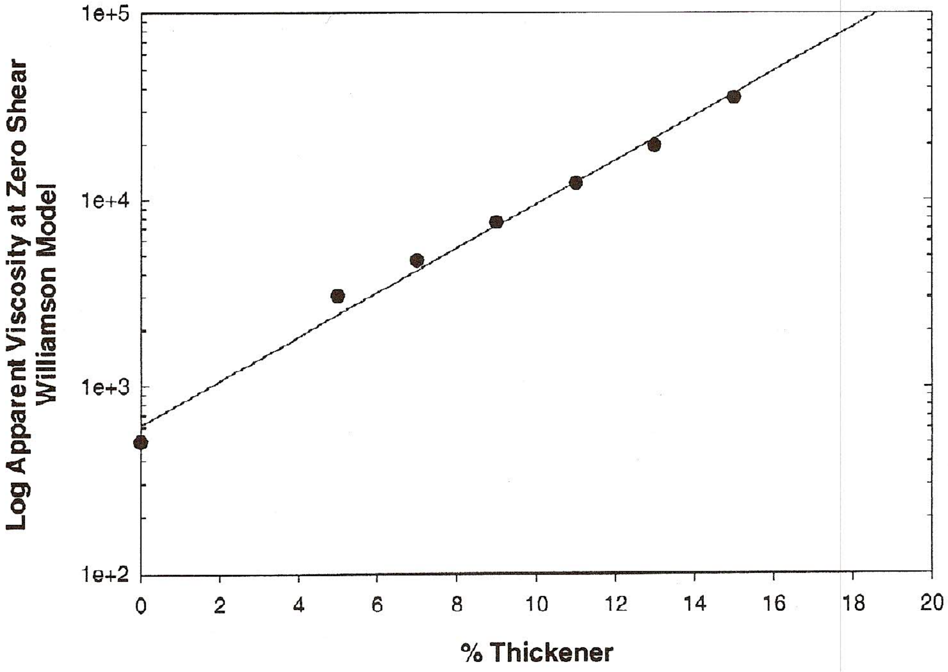
TABLE 3

Sample	% Clay Thickener	Apparent Viscosity, mPa.s	Comments
Base Oil	None	502.2	Newtonian Behavior
Grease-1	5	3,052	Non-Newtonian Behavior
Grease-2	7	4,704	"
Grease-3	9	7,558	"
Grease-4	11	12,250	"
Grease-5	13	19,620	"
Grease-6	15	35,270	"

Graphical representation of the data is presented in Figure 2.

Figure 2

Apparent Viscosity Versus % Clay Thickener



A first order linear regression of the data resulted in the following coefficients: slope of 0.1186, y-intercept equal to 2.792 (619 mPas) and a correlation coefficient of 0.994.

From this data, an equation was generated equating percent thickener to apparent viscosity:

$$\% T = \frac{\log n^* - 2.792}{0.1186}$$

%T = the percent thickener

n* = the apparent viscosity of the grease at zero shear as determined using the Williason model.

Although the equation has not been put to use yet, we're optimistic in our laboratory that this work will be fruitful in helping us estimate the continued serviceability of grease in service. Future plans call for determining if other thickener types can also be similarly characterized by rheometry.

Conclusion:

Insights acquired from twenty-five years of experience in a lubrication laboratory have been shared with you. It is hoped that some of the insights can be put to good use in other laboratories.

References:

1. ASTM Method D942-90, Standard Test Method for Oxidation Stability of Lubricating Grease by the Oxygen Bomb Method.

2. ASTM D2265-94a Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range.