The Effect of Graphite Type, Purity, and Concentration on the Performance of a Clay Filled Polyalphaolefin Grease, Based on Four Ball Wear (ASTM D2266) with Coefficient of Friction, and Load Wear Index (ASTM D2596).

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Abstract: The performance of six different graphite powders, as wear additives, was evaluated in clay filled polyalphaolefin (PAO) grease base. Neat PAO and PAO blends with each of four types of graphite were evaluated. Friction and wear performance were evaluated using ASTM D2266 and ASTM D2596. In addition to the variation in graphite type, the purity of two graphite powders was varied to determine if ash content affected the performance measured by either of the two procedures. Testing was performed on blends in which the graphite content was varied at 5, 10, and 20 weight percent. Results from ASTM D2266 were augmented with graphs of coefficient of friction plotted as a function of time and optical micrographs of four-ball wear scars for each sample tested. Four-Ball Wear testing (D2266) shows that grease performance is a function of graphite type. There is very limited evidence of the positive correlation between graphite purity and grease performance. Load Wear Index (D2596) shows that grease performance is a strong function of graphite concentration and not a function of graphite type or purity.

Introduction: Although the use of graphite as a solid lubricant probably dates to the Middle Ages, it was not until the late 1800's that true scientific inquiry into graphite and oil lubricating blends began. Initial investigations into graphite-containing fluid lubricants indicated results that varied in an unpredictable manner. Then, in the late 1860s, the correlation between the variation of lubricant properties and graphite particle size was made (Cirkel, 1907). Subsequent work by scientists and manufacturers has shown that the friction properties of lubricants containing graphite may also vary as a result of the type and purity of graphite in a formulation. The purpose of this paper is to provide some basic information on the effect that graphite type and/or purity may have on the performance of polyalphaolefin grease evaluated using ASTM 2596 and ASTM 2266 test methods.

Graphite Type, Purity, and Size: Four types of graphite were evaluated for this study, synthetic, natural flake, natural amorphous, and natural vein. Extensive data on the physical differences between the four types of graphite studied is available in the literature so only a brief description of each type will be presented here.

Synthetic Graphite: Synthetic, also known as artificial graphite, is a manufactured graphite which is made by the high temperature heat treatment of calcined petroleum coke. Crystallite size is generally much smaller than the crystallite size of natural flake or vein graphite. The macroscopic morphology of synthetic graphite is generally granular or needle-like. However, fine-grinding results in the formation of the flake-like particles of which all graphite is based. Commercial material is available in purities from 95-99%

Natural Flake Graphite: Flake graphite forms from the geologic metamorphism of organic material. Primordial deep-ocean, deep-lake, or deltas provided the depositional environment where pre-graphitic carbon was deposited. Post deposition high-grade metamorphism resulted in the conversion of amorphous carbon to crystalline graphitic carbon. The physical condition in such high-grade metamorphic environments was typically 750 C and 75,000 PSI (Granulite facies). Flake graphite has a flaky morphology regardless of particle size. Commercial material is available in purities from 80-99%

Natural Vein Graphite: Vein graphite is the most geologically unique form of graphite. The current popular theory of the formation of this material is from the direct fluid-to-solid deposition of pyrolytic graphitic carbon from a pegmatitic or pegmatite-like geologic fluid. Pegmatites are high-pressure, erosive, subterranean fluids that form as a result of some geologic agent. In the case of vein graphite, a pegmatitic fluid may have invaded a previously deposited flake graphite formation, or other carbonaceous deposit, mobilized the carbon as CO_2, CO, CH_4, etc., and finally re-deposited the mobilized carbon, remote from the original "solution" point, as graphitic carbon. Vein graphite has a needle-like macro morphology and flake-like micro morphology. Vein graphite is considered to be the most crystallagraphically ordered form of natural graphite. Commercial material is available in purities between 90 and 99%.

Amorphous Graphite: Contrary to the name, amorphous graphite is a cryptocrystalline form of carbon and not an amorphous substance. Amorphous graphite is formed from the geologic metamorphism of anthracite coal seams and is therefore considered a seam mineral. Amorphous graphite is the least "ordered" of the natural graphites, and may be more or less crystalline than synthetic graphite depending upon the petrology of the ore body in question. The macroscopic morphology is granular, however the microscopic morphology is flake-like. Commercially available amorphous graphite is available from 70-85% purity.

Two levels of purity of synthetic and flake graphite were used for this study. Only one purity of amorphous and vein graphite was used. The particle size of each sample was chosen so that all samples tested had particle size distributions that were within a 10-micron spread. Table 1, below, presents the size and purity data on the graphite materials used in this study.

Table 1

Graphite Grade	230U	146	4421	A99	2127	508
Type	High CarbonFlake	Flake	Purified Synthetic	Synthetic	Vein	Amorphous
Carbon Content	99.36	96.94	99.96	99.57	97.30	85.56
MT50thpercentile	15 um	25 um	18 um	21 um	25 um	15 um
BET Surface Area	6.8	4.7	9.2	8.1	4.0	16.6
Weight %+325	0.0	1.84	0.11	0.11	1.6	1.18
Weight %-325	100	98.16	99.89	99.89	98.4	98.82

All of the graphite powders utilized in this study were “off the shelf” commercial grades, which are currently used in many industrial applications including dry and wet friction and lubrication.

Experimental Method: Testing of graphite/grease blends was performed according to ASTM D2266 and D2596. The grease used in all blends was a clay-thickened polyalphaolefin. Petro-Lubricant Testing Laboratories, Lafayette, New Jersey, performed all testing on grease/graphite blends. The technical services laboratory of the Asbury Graphite Mills, Inc., Asbury, New Jersey, tested all powdered graphite samples.

Results and Discussion: Part 1

ASTM D2266 Four-Ball Wear: In addition to Four-ball wear scar measurement, results included the coefficient of friction plotted as a function of time for each test sample. Photomicrographs of all wear scars were recorded and are included. As specified in the method, the test was run at 1200 rpm and 40 kgf for one hour. Figure 1, below, presents the wear scar data and Figure 2 the grand average coefficient of friction for each blend. For Part 1 of this paper, test results are presented in groups corresponding to the graphite concentration in each blend. The coefficient of friction graphs are presented along with the corresponding wear-scar micrographs following the discussion of each test group.

Figure 1: Four Ball Wear Scar

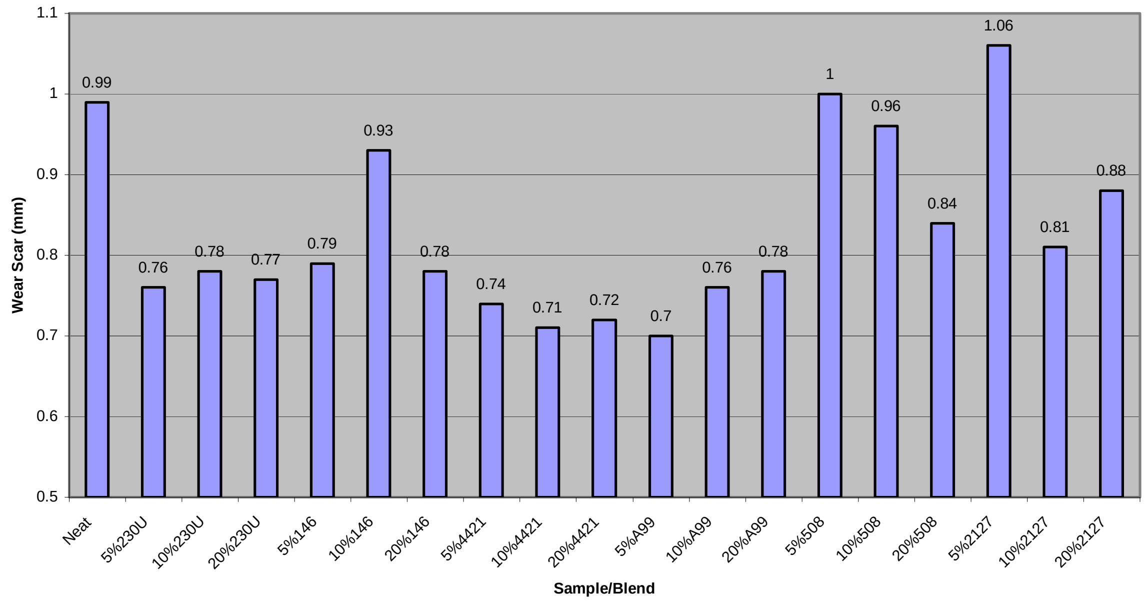
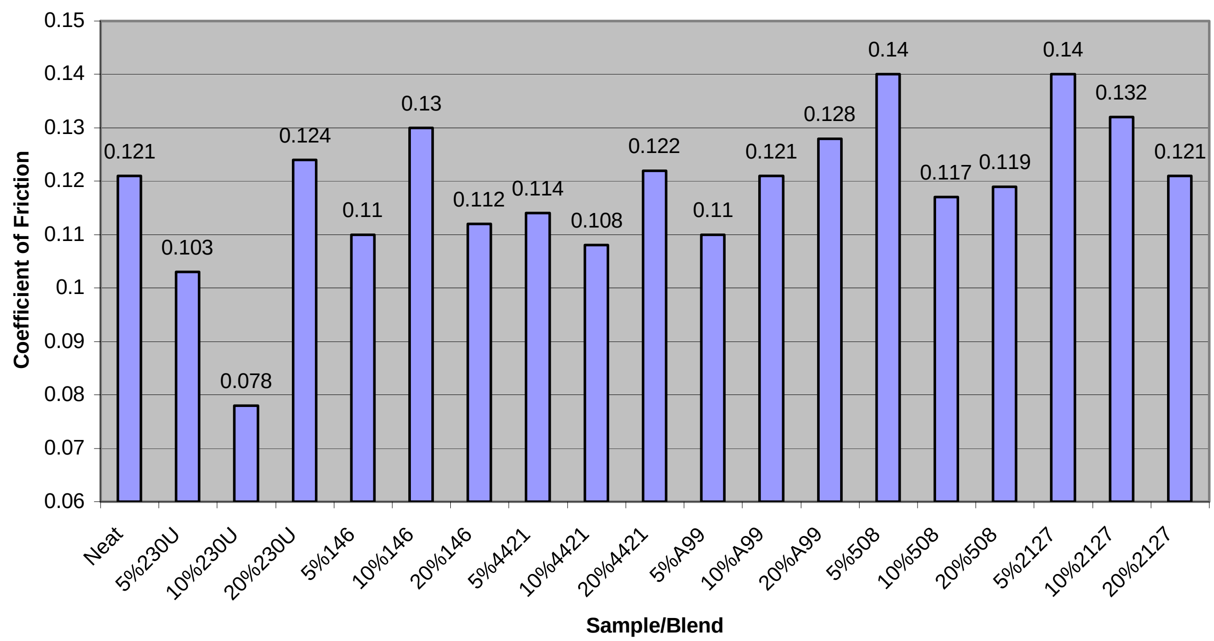


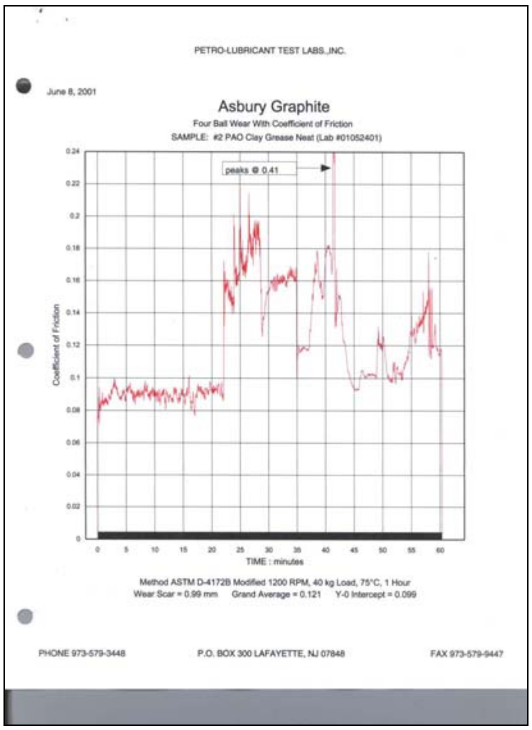
Figure 2: Four Ball Coefficient of Friction



Neat Grease:

Clay filled polyalphaolefin was used as the base grease for this study. The test grease consisted of Albemarle Durasyn #166 filled with Rheox Baragel 3000, organically treated smectite. The plot of coefficient of friction vs. time and the micrograph of the 4-ball wear scar are presented below. The wear scar of the neat grease was 0.99mm. The grand average coefficient of friction was 0.121.

The CoF plot indicated consistent friction for the first 22 minutes of the test procedure, after which time the friction becomes and remains unstable throughout the remainder of the test. The micrograph of the wear scar appears to indicate galling, which is supported by jump in the CoF plot to 0.41 about 42 minutes into the test.


PETRO-LUBRICANT TEST LABS.,INC.

June 8, 2001

Asbury Graphite

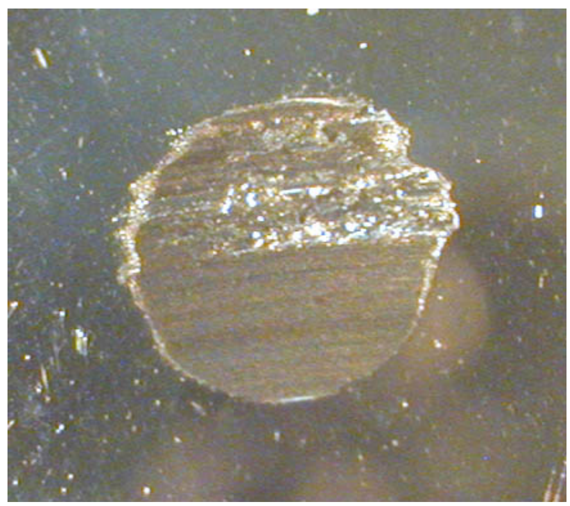
Four Ball Wear With Coefficient of Friction

SAMPLE: #2 PAO Clay Grease Neat (Lab #01052401)

Method ASTM D-4172B Modified 1200 RPM, 40 kg Load, 75°C, 1 Hour

Wear Scar = 0.99 mm Grand Average = 0.121 Y-0 Intercept = 0.099

PHONE 973-579-3448 P.O. BOX 300 LAFAYETTE, NJ 07848 FAX 973-579-9447



5% Blends

The blend containing #A99 at 5% addition showed the smallest wear scar diameter (0.70mm) of all blends tested at all concentrations. The wear scar for this particular blend was smooth and showed no abrasive wear in the high-pressure, high turbulence region adjacent to the wear scar. The grand average coefficient of friction for this sample was 0.11.

The wear scar measurement of all 5% blends varied from 0.70-1.06mm. The average wear scar for the group was 0.842mm. The flake graphite and synthetic graphite blends varied only between 0.70-0.79mm. Wear scar micrographs of #230U (99% carbon flake), and both synthetic graphite blends did not show evidence of wear in the turbulent region adjacent to the wear scar. The wear scar formed in the sample containing #146 (95% carbon flake graphite) showed a slight indication of wear in the turbulent area. The blends containing #508 amorphous graphite, and #2127 vein graphite, in addition to having significantly larger wear scars, showed wear adjacent to the wear scars. Grease containing #508 and #2127 actually showed an increase in the wear scar diameter above that in the neat grease.

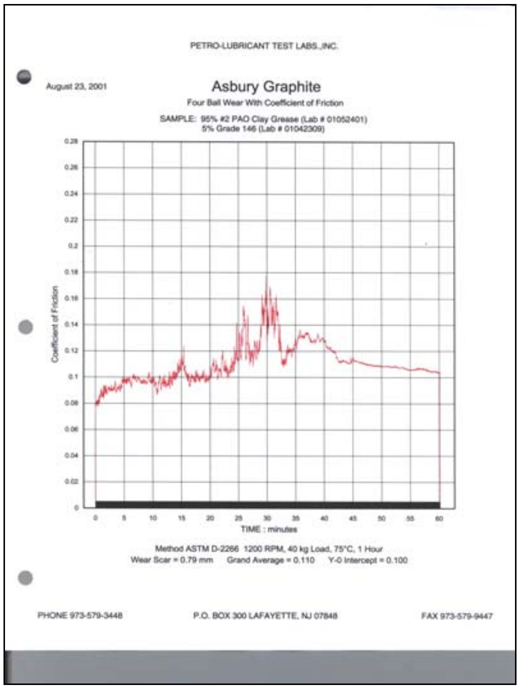
Examination of the CoF graphs for the 5% blends indicates some variation during what appears to be an approximately 35 minute “break in” time, for the #A99, #146, and #230U blends. The CoF graph for the #508 blend is erratic throughout the test time with CoF peaks as high as 0.22. Grade #2127 showed stable friction between zero and 25 minutes and then again between 45 and 60 minutes.

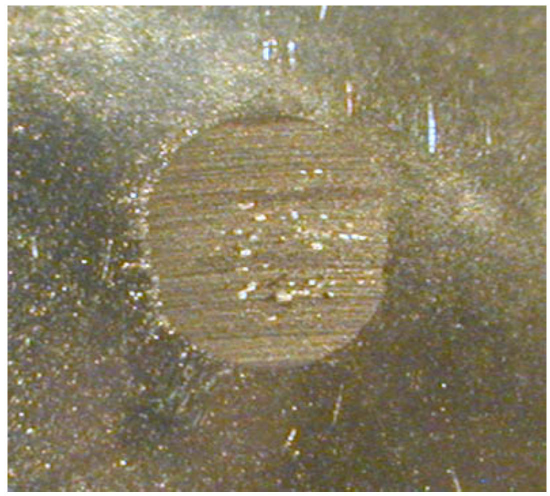
The Grand Average coefficient of friction varied between 0.103-0.140. The CoF of the blends containing flake and synthetic graphite varied between 0.103 and 0.114 (neat grease = 0.121). The CoF of the blends containing amorphous or vein graphite were equal at 0.14, and were higher than the CoF of the neat grease.

In the 5% blends, flake and synthetic graphite showed improved friction and wear characteristics over the amorphous or vein graphite. At 5% concentration, the type of graphite used appears to have an effect on the performance of the grease. The effect of purity, based on the performance of the different flake and synthetic graphite samples, was inconclusive. This statement is based on wear scar diameter, optical microscopy of the wear scar, grand average coefficient of friction, and the somewhat subjective interpretation of the friction vs. time graphs.

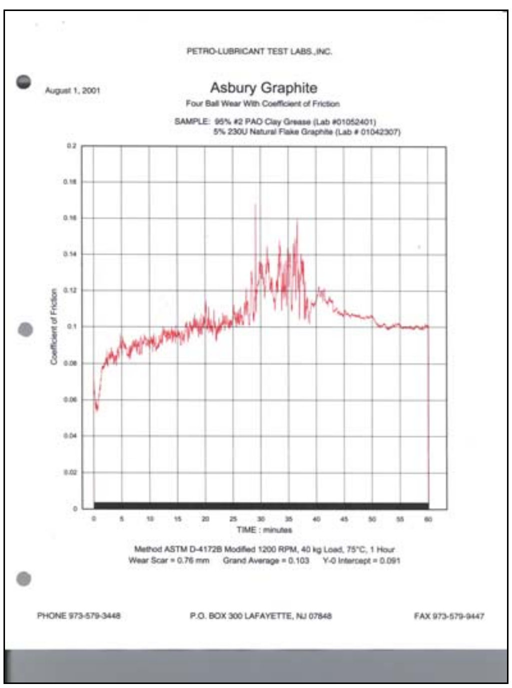
Coefficient of Friction vs. Time Plots, and Micrographs for the 5% Blends

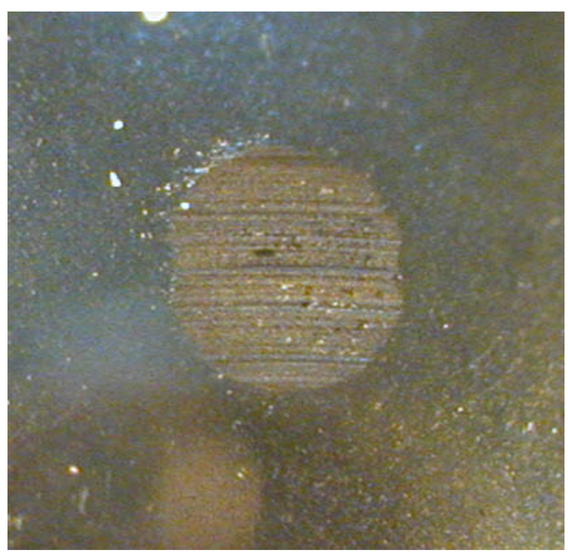
Grade 146, 5%





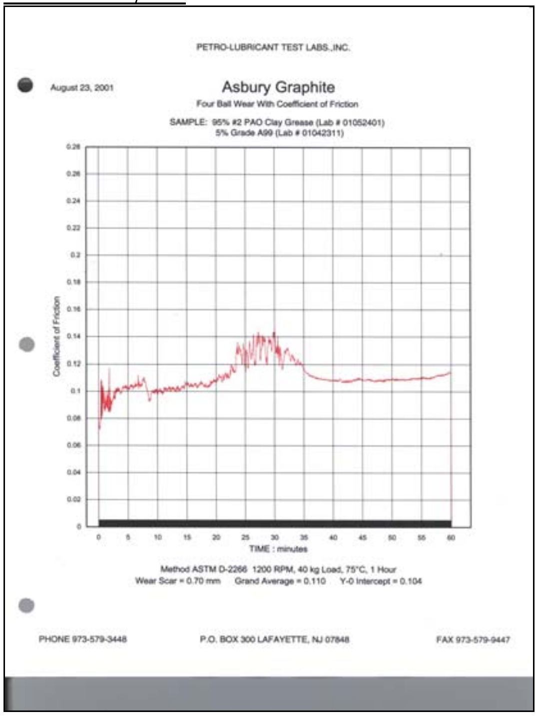
Grade 230U, 5%

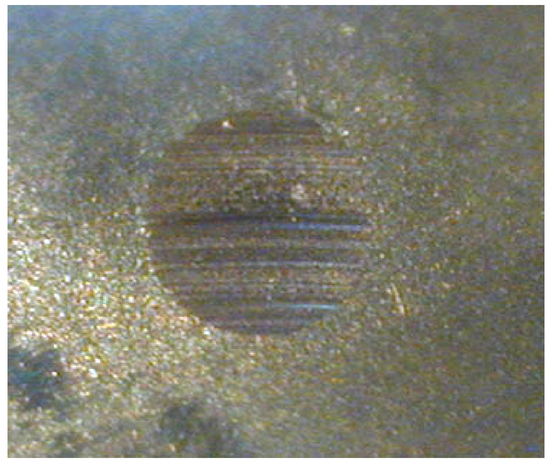




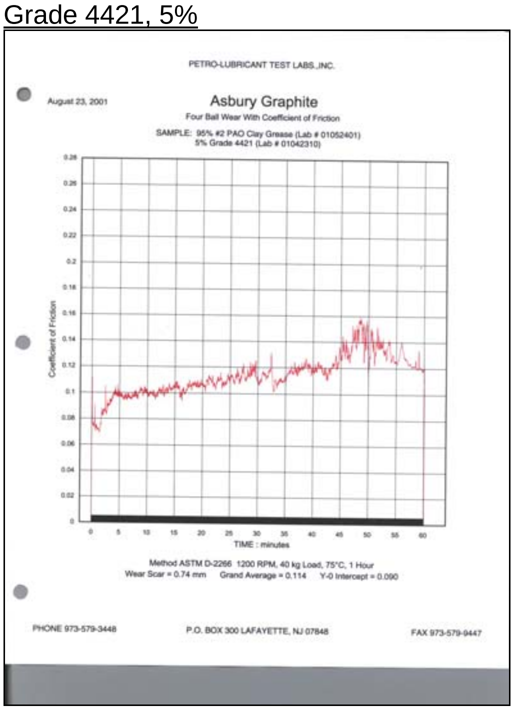
Coefficient of Friction vs. Time Plots, and Micrographs for the 5% Blends

Grade A99, 5%



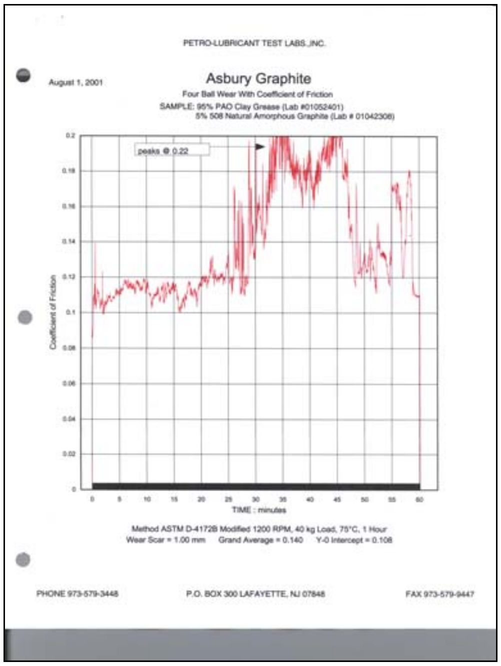


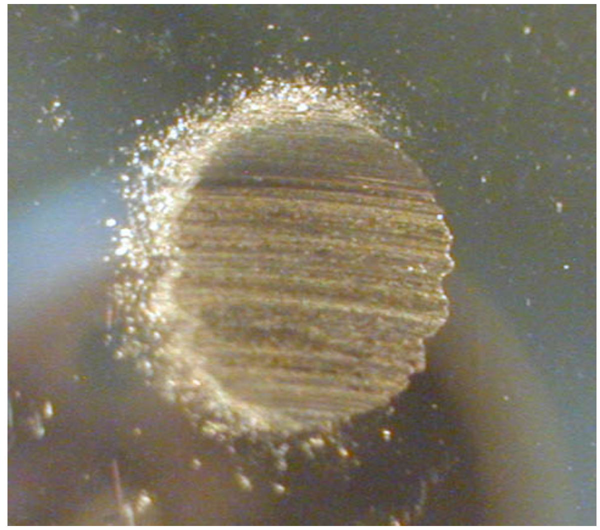
Grade 4421, 5%



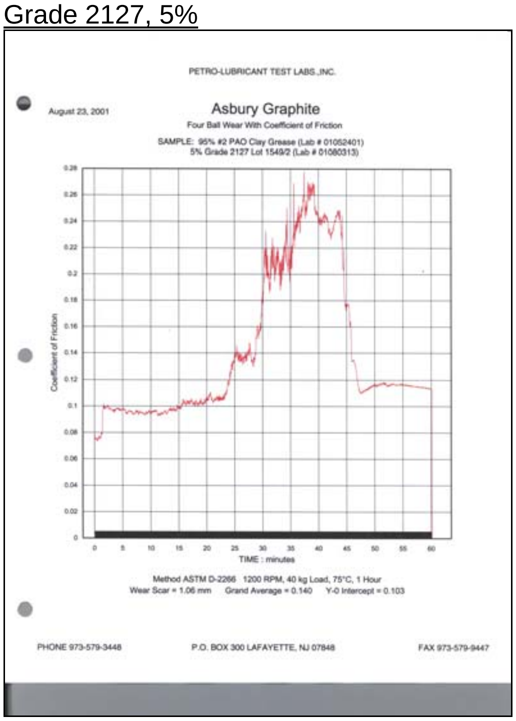
Coefficient of Friction vs. Time Plots, and Micrographs for the 5% Blends

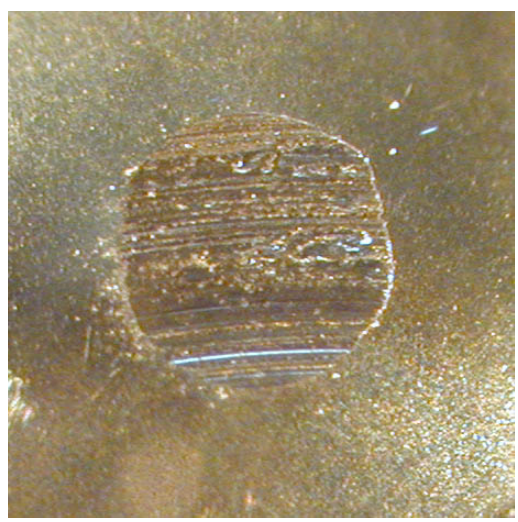
Grade 508,5%





Grade 2127, 5%





10% Blends:

The wear scar diameters in this sample group varied between 0.71 and 0.96mm, with an average wear scar of 0.825. Less variation in scar diameter was seen in this group as apposed to the 5% blends, and all were smaller than the neat grease. The blend containing 10% #4421, high purity synthetic graphite, had the smallest wear scar of this group.

Optical examination of the wear scars of the #4421 and #230U blends showed an even wear surface with no erosion apparent in the high pressure, high turbulence region adjacent to the wear scar. These two micrographs appear to have the smoothest textures of all the wear scars in all sample groups. The #146 scar showed slight wear in the high turbulence region with deviation of the scar diameter toward an ellipse. The #A99 also showed slight wear in the high turbulence region and seizure galling which may be indicated in the friction graph as a 0.30 CoF peak. The #508 and #2127 blends both show apparent wear in the high pressure, high turbulence region. Wear adjacent to the scar is most significant in the #508 blend.

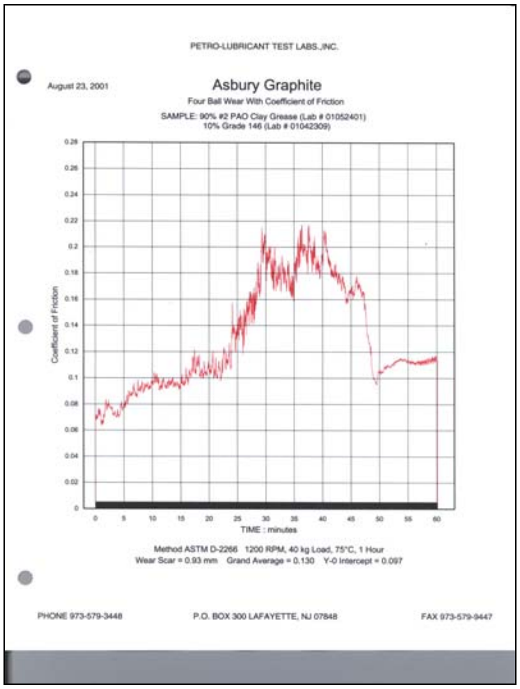
The grand average CoF for this sample group varied from 0.078-0.132 (neat grease = 0.121), averaging 0.825. The lowest grand average CoF for this sample group, 0.078, was measured in the #230U blend. Three of the blends, #146, #A99, and #2127 have a CoF equal to or above the neat grease. Five of the six graphite blends evaluated had CoF values within 0.024 points of one another.

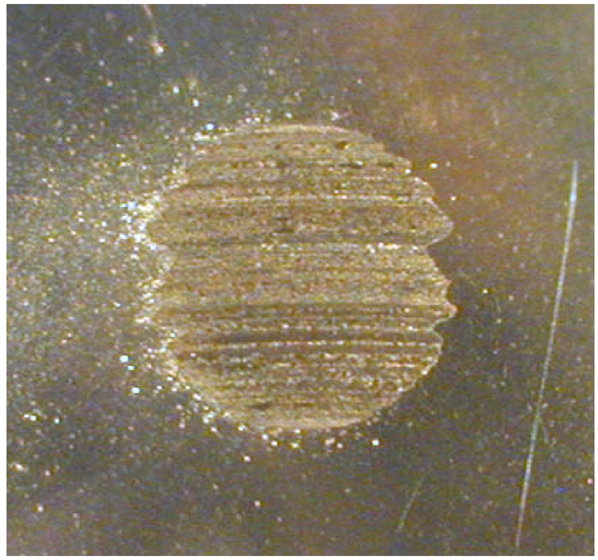
The plotted coefficient of friction vs. time is relatively smooth, after an initial “break in” period for the #146, #230U, 4421, and 2127 blends. Both the #A99 and #508 blends show somewhat erratic friction behavior throughout most of the timed test (see attached plots).

Only slight variation in wear scar diameter was observed in the 10% graphite blends. However, subjective (no standards for reporting optical observations are available to the best of the author’s knowledge) optical examination showed significant differences in scar contour, which varied from smooth with no wear adjacent to the scar, to seizure galling, to very well defined wear adjacent to the scar. Based on interpretation of wear scar, the friction vs. time graph, and optical examination of the wear scar contour, Grade #230U and #4421 showed the best friction and wear behavior in this sample group. This observation may support an improvement in wear performance in the samples containing 10% graphite, as a function of graphite type and purity.

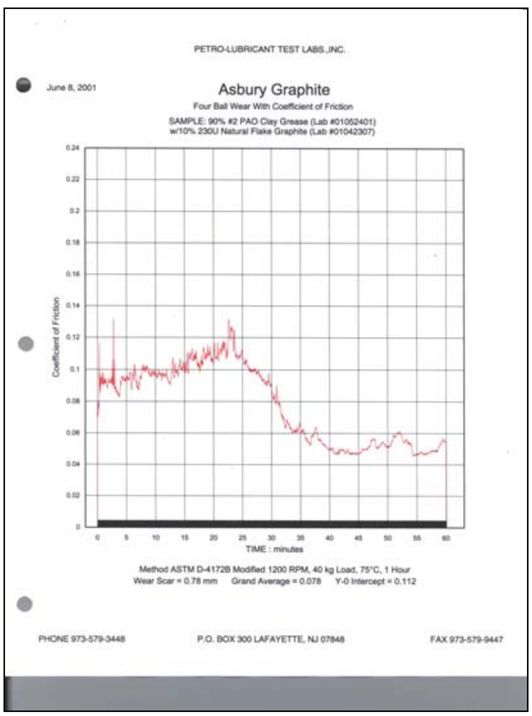
Coefficient of Friction vs. Time Plots, and Micrographs for the 10% Blends

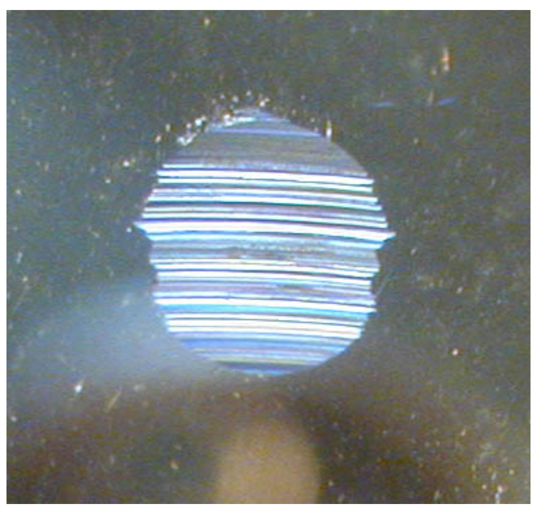
Grade 146, 10%





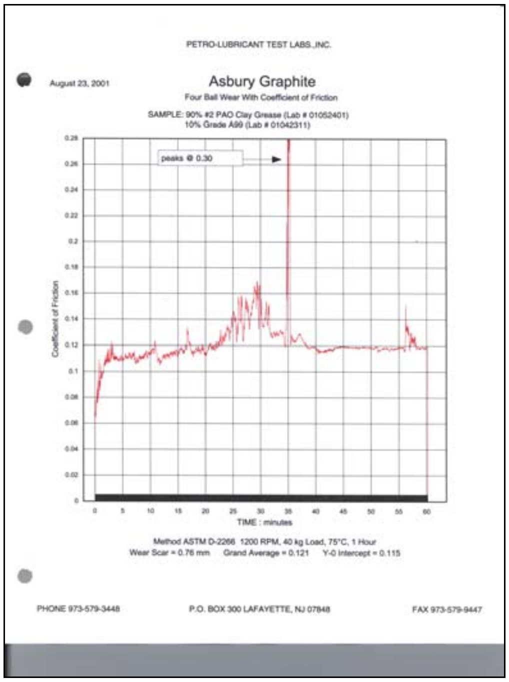
Grade 230U, 10%

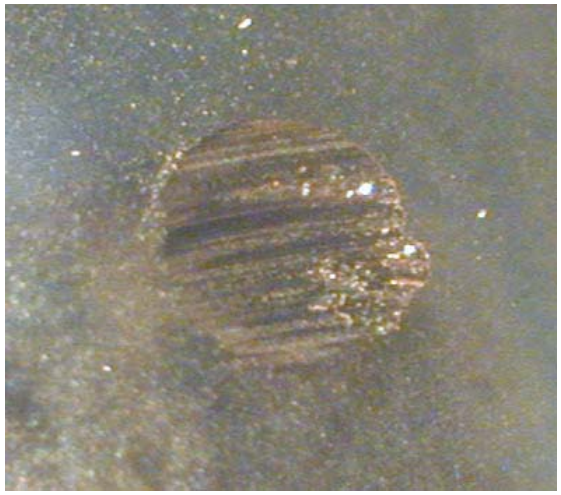




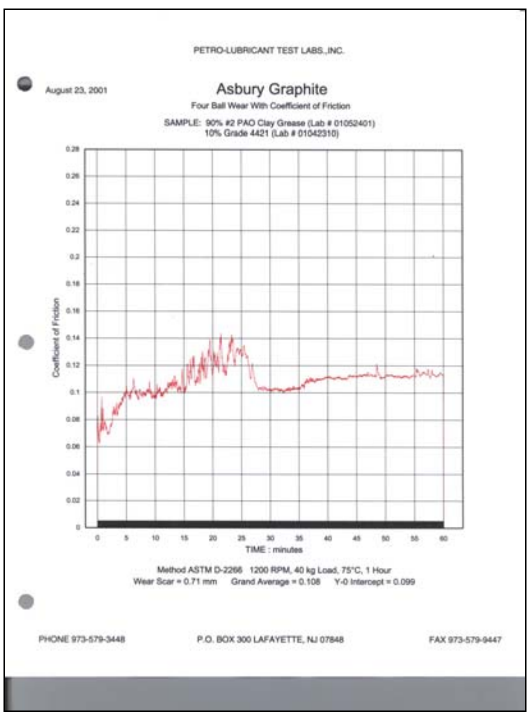
Coefficient of Friction vs. Time Plots, and Micrographs for the 10% Blends

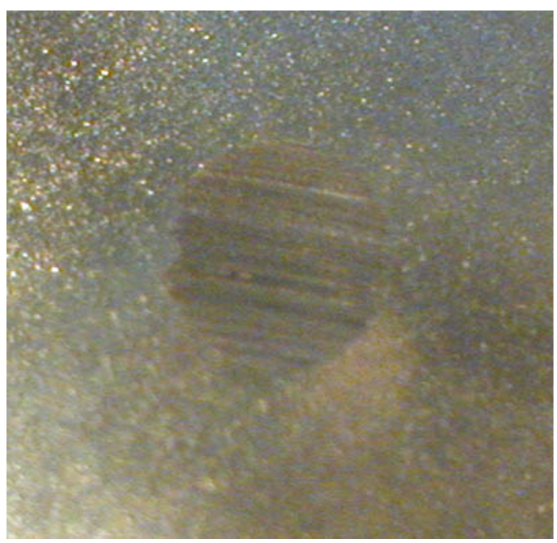
A99, 10%





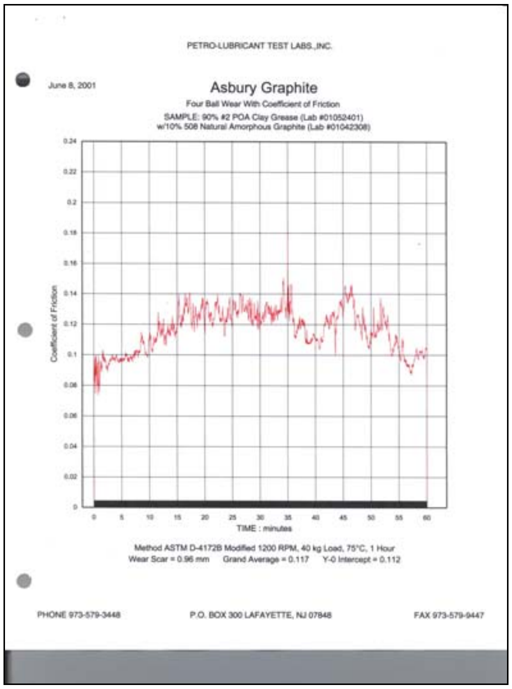
Grade 4421, 10%

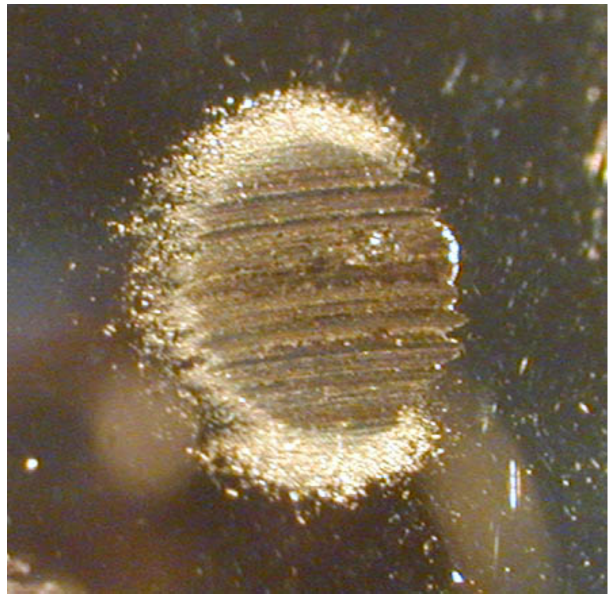




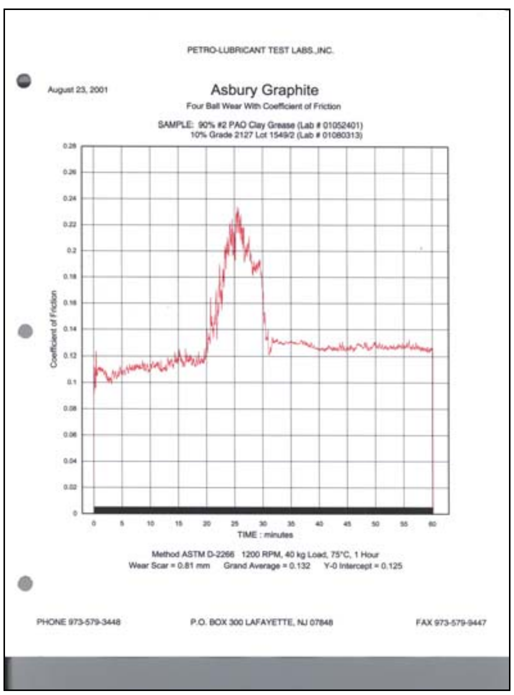
Coefficient of Friction vs. Time Plots, and Micrographs for the 10% Blends

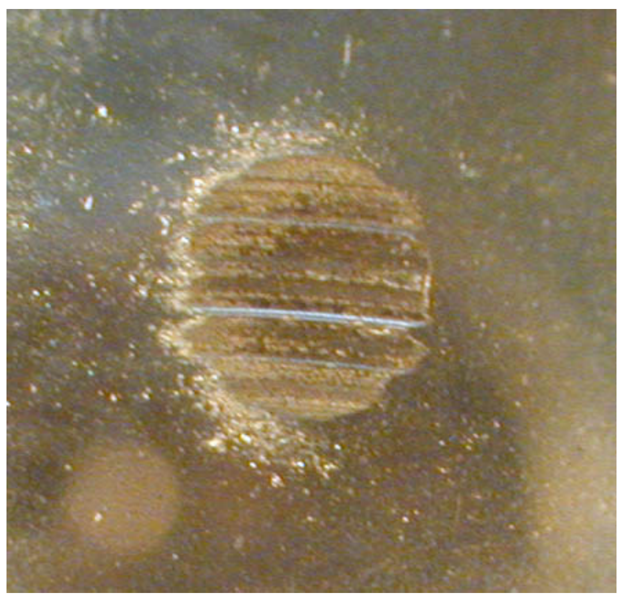
Grade 508,10%





Grade 2127, 10%





20% Blends

The wear scar diameters show the least variation, 0.72-0.88 mm, in the 20% blends, and all wear scars are smaller in diameter than the neat grease. The average wear scar was 0.795mm, the lowest average of the three groups studied. The blend containing #4421, high purity synthetic graphite, had the smallest wear scar (0.72mm) of this group.

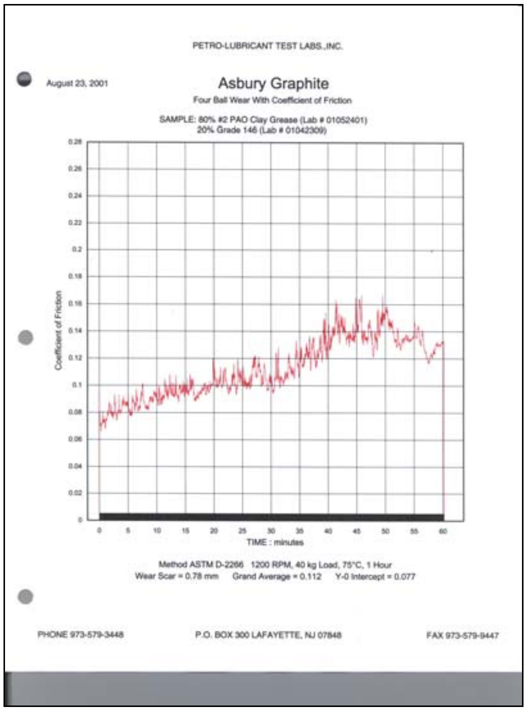
Wear scar micrographs of the 20% blends indicated rougher wear texture, overall, than the other sample groups. All samples, except #4421, showed wear in the high turbulence area adjacent to the scar. The “intensity” of the wear varied, being hardly discernable in the blends containing #A99 and 230U, obvious in the blend containing #146, and extensive in the #508 and #2127 blends. Although wear-groove depth was not measured, it appeared as though grooving was more extensive in this sample group.

The grand average coefficient of friction for the 20% blends varied from 0.112-0.128 and averaged 0.121. The between sample variation in the CoF was the smallest in this test group. Examination of the coefficient of friction vs. time plots for the 20% samples typically indicated a longer “break in” time than the other sample groups. The blends containing #230U, #4421, and #508 showed that the CoF rose nearly continuously, although cyclically, throughout the entire test time. The #146 blend showed some evidence of leveling off toward the end of the one hour test time, and the #A99 and #2127 blends both leveled off approximately 45 minutes into their respective test runs.

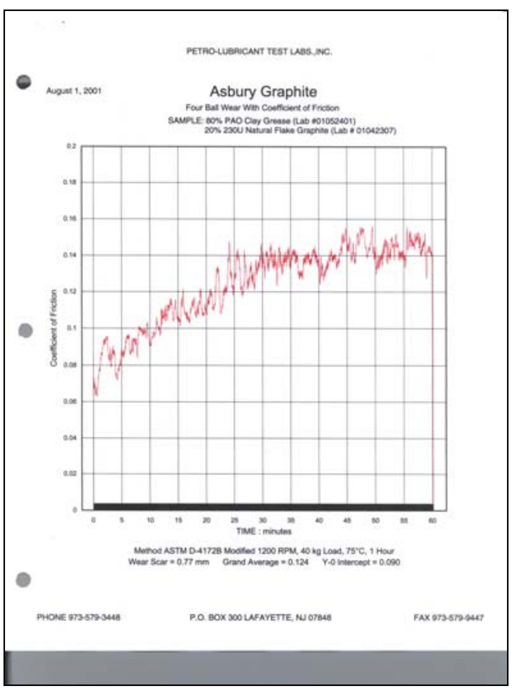
The blend containing 20% #2127 vein graphite was the only sample in this group, which showed stable friction after the initial “break in”. The #A99 sample showed somewhat stable friction after the initial “break in” but only for less than 5 minutes. At 20% concentration, graphite type and purity appears to have little or no effect on the wear properties.

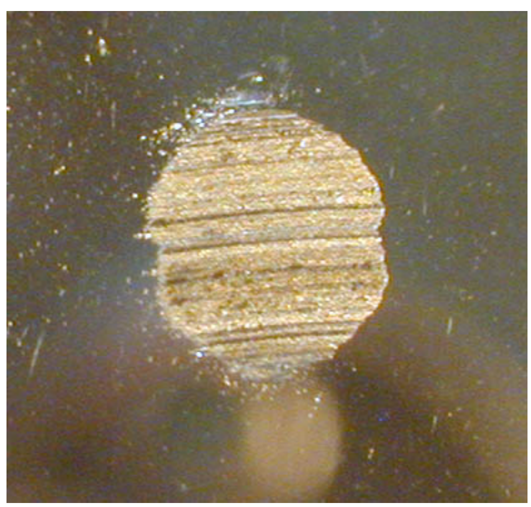
Coefficient of Friction vs. Time Plots, and Micrographs for the 20% Blends

Grade 146, 20%



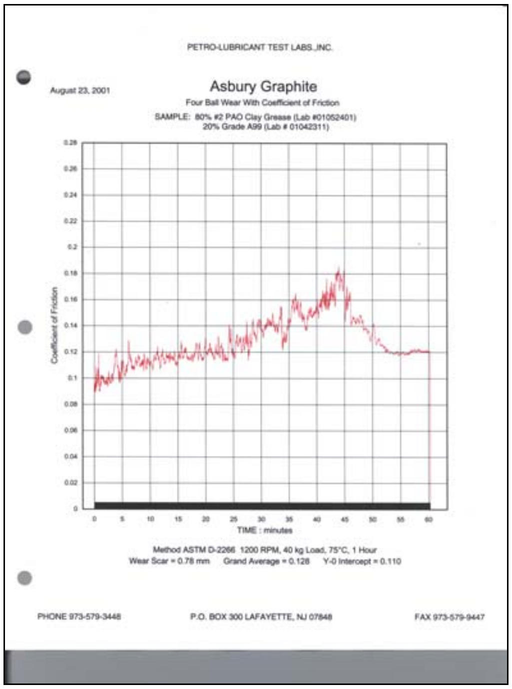
Grade 230U, 20%

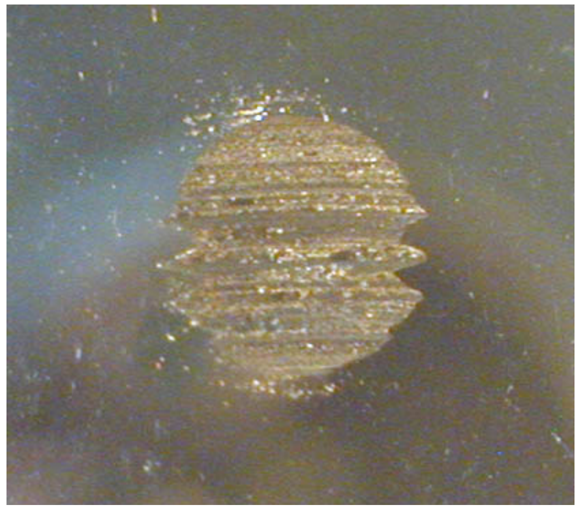




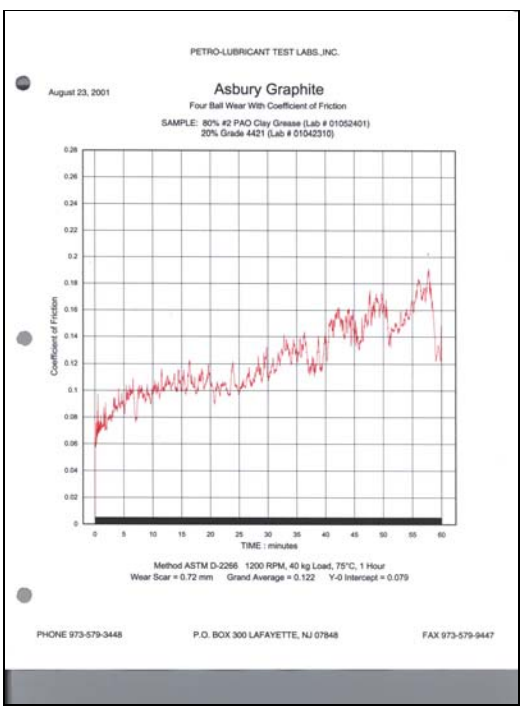
Coefficient of Friction vs. Time Plots, and Micrographs for the 20% Blends

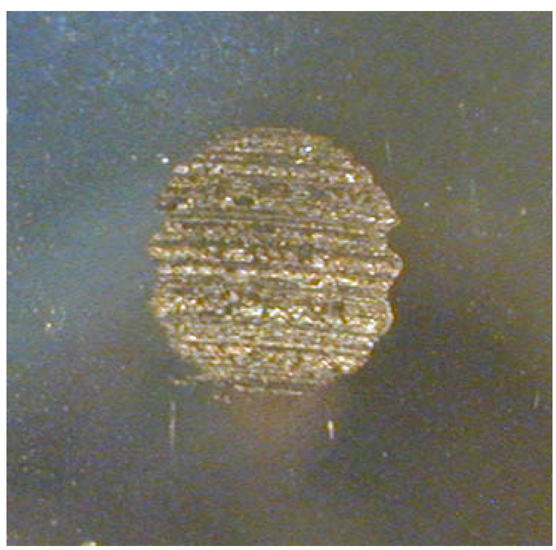
Grade A99, 20%





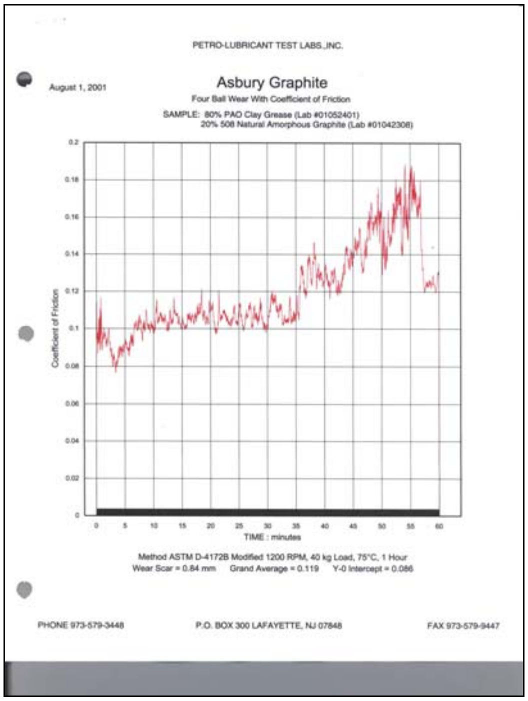
Grade 4421, 20%



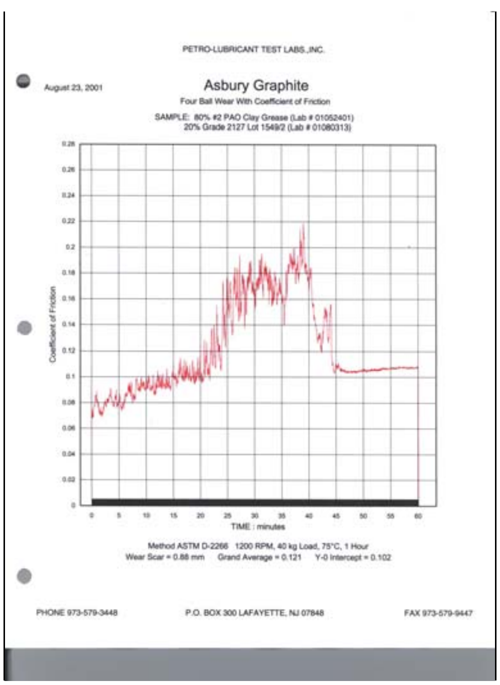


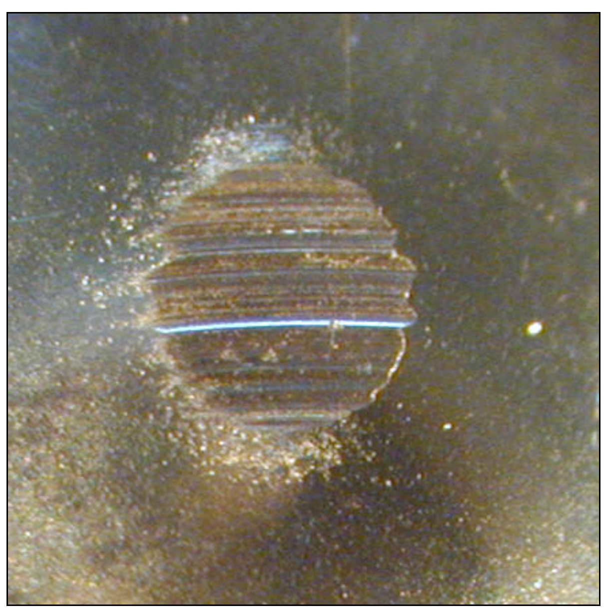
Coefficient of Friction vs. Time Plots, and Micrographs for the 10% Blends

Grade 508, 20%



Grade 2127, 20%





Results and Discussion: Part 2

ASTM D 2596: Measurement of Extreme-Pressure Properties of Lubricating Grease: The same grease base used in Part 1 of this study was used in Part 2 for extreme pressure evaluation. Graphite was again added at 5, 10, and 20 weight percent and samples were evaluated as outlined in ASTM D2596. The neat grease was also tested to provide a reference point. The raw data, weld load, and Load Wear Index are presented below in Table 2, and in Figures 3 and 4.

Table 2: ASTM D 2596: LWI and Raw Data

Mixture	Carbon %	LWI	Last Non-Seizure Scar		Last Seizure Scar		Weld Load
		Kgf	Kgf	mm	Kgf	mm	Kg
Neat		24.92	32	0.28	100	2.29	126
5%230U	99.36	25.75	40	0.3	126	2.29	160
10%230U	99.36	30.04	50	0.36	160	2.18	200
20%230U	99.36	38.86	50	0.36	200	2.07	250
5%146	96.94						
10%146	96.94	27.78	40	0.31	160	3.28	200
20%146	96.94						
5%4421	99.96						
10%4421	99.96	31.65	50	0.34	160	2.21	200
20%4421	99.96						
5%A99	99.57						
10%A99	99.57	31.46	50	0.35	160	2.24	200
20%A99	99.57						
5%508	85.56	26.71	50	0.35	126	3.11	160
10%508	85.56	30.36	50	0.35	160	2.22	200
20%508	85.56	44.37	80	0.4	200	2.15	250
5%2127	97.3						
10%2127	97.3	30.25	50	0.36	160	2.3	200
20%2127	97.3						

Figure 3: Weld Load

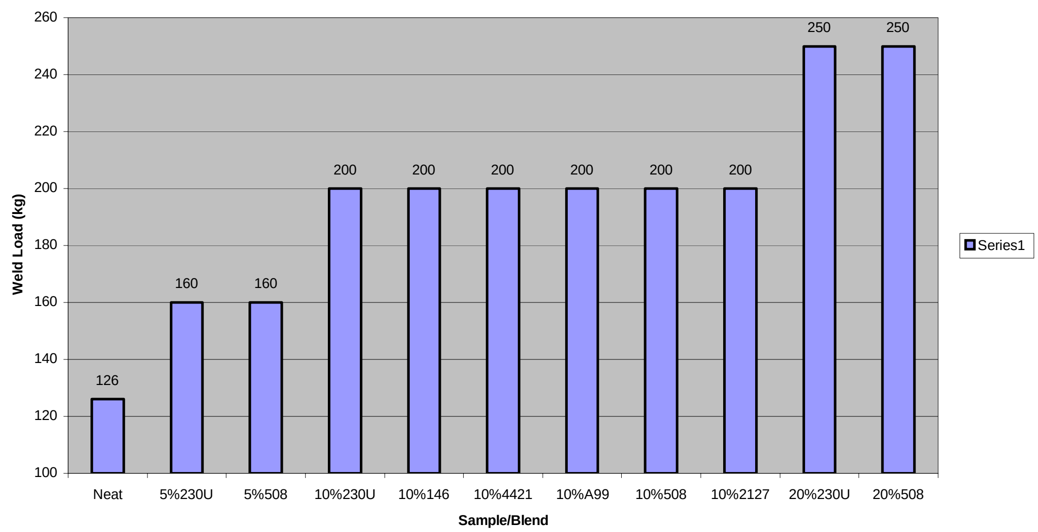
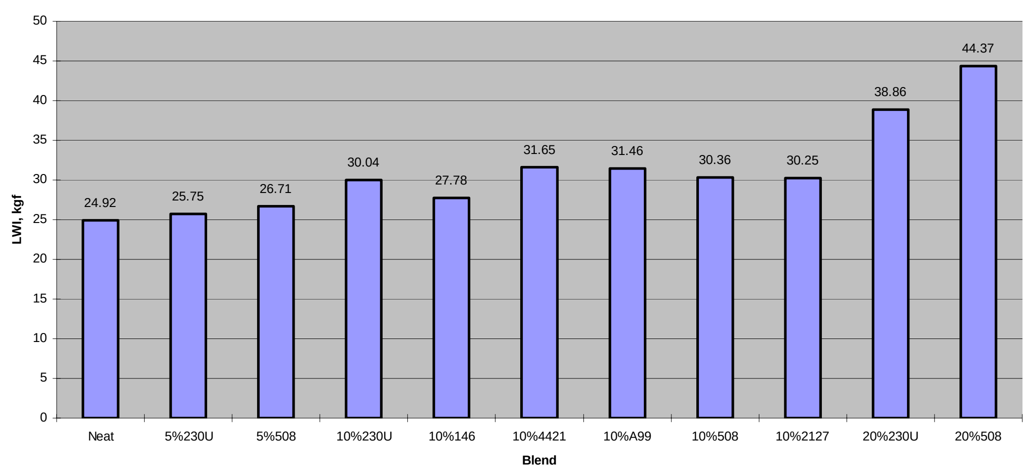


Figure 4: Load Wear Index of Blends



Performance in the conventional four ball wear test (ASTM 2266) showed significant correlation to the type and perhaps purity level of the graphite used. Load Wear Index testing indicated that graphite type and purity have no effect on performance, while graphite concentration had a significant bearing on performance.

The LWI and weld load of the neat grease was 24.9 and 126 kg, respectively. All blends containing graphite showed an increase in both LWI and weld load above the neat grease. However, at 5% graphite concentration the increase in LWI was only slight as indicated in Figure 4. At higher levels of concentration the LWI rises correspondingly. Note that at 10% graphite, there is little difference between the LWI of the six blends tested. At 20% graphite concentration there is only an approximately 5-point difference in LWI between the #230U, 99% carbon flake graphite, and #508 amorphous graphite. The higher value of the blend containing amorphous graphite is somewhat counterintuitive since 230U is expected to provide better filming and less abrasion due to its morphology and purity.

The lack of correlation between graphite type and purity, and LWI is also verified in the weld load and last seizure load data presented in Table 2 and Figure 3. The individual vales of both parameters are identical for all graphite samples at their respective concentrations.

Based on testing performed using ASTM 2596, load wear index, the addition of graphite does provide significant improvement of PAO grease performance under extreme pressure conditions. However, grease performance has been shown to be a function of graphite concentration not graphite type or purity. Under the boundary lubricating conditions prevalent under extreme pressure, subtle differences in macroscopic particle morphology and ash content of different graphite materials, appears to have no bearing on performance.

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