Surface Enhanced Flake Graphite and its Utility as a Functional Extender for Molybdenum Disulfide

Albert V. Tamashausky
Director of Technical Services

Asbury Graphite Mills, Inc
PO Box 144
Asbury, NJ 08802

Abstract: The performance of surface enhanced natural flake graphite (SEFG) was studied to determine its utility as a functional extender for molybdenum disulfide in PAO grease. The SEFG was compared to conventional flake graphite and high surface area synthetic graphite in the same application. Friction and wear performance were evaluated using ASTM D2266 and D2596. Graphite and molybdenum disulfide concentrations were varied at 0%, 2.5%, and 5% for each component. Total solid lubricant phase was maintained at 5% except in the neat grease. The data showed that grease with added solid lubricant out performed neat grease in all cases. Surface enhanced flake graphite outperformed conventional flake graphite and high surface area synthetic graphite. The trend in the data collected indicated that surface enhanced flake graphite can be substituted up to 50 weight percent for molybdenum disulfide without degradation of grease performance.

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Introduction: Graphite and molybdenum disulfide (molybdenite) are naturally occurring minerals that are used as solid lubricants in a significant number of grease products. Both substances crystallize in the hexagonal system and have lubricity mechanisms that rely on formation of very thin, strong, and flexible material layers that form as a result of perfect cleavage parallel to the {0001} basal pinacoid.

In graphite, carbon atoms are found in interlocking 6 member rings that form two dimensional "**graphene**" layers. These layers are stacked parallel to the "c" crystallographic axis to form the graphite crystal. Intra layer strength is strong, but inter-layer bonding is weak. Weak interlayer bonds result in perfect basal cleavage and excellent film formation.

Molybdenum disulfide has a layered crystal structure made up of a layer of Mo atoms sandwiched between two layers of sulfur atoms. Intra-layer bonding is strong. Inter-layer bonding is between adjacent layer sulfur atoms and is weak. This results in perfect basal cleavage parallel to sulfur planes with corresponding excellent film forming properties.

Graphite and MoS_2 are used in many applications where their specific properties require that either one or the other be used due to intrinsic physical or chemical limitations. For example:

1. Graphite has limited lubricity, in high vacuum, anhydrous, or in some inert atmospheres. However, MoS_2 is not limited by atmospheric pressure or inert environments and is the solid lubricant of choice under these conditions.

2. MoS_2undergoes irreversible physical and/or chemical changes at temperatures approaching 400 °C. These changes include oxidation to molybdenum trioxide, MoO_3, in an oxidizing atmosphere, or sublimation under reducing conditions. At 450 C the lubricity of graphite is only slightly reduced but complete restoration of lubrication is restored upon cooling. Also, graphite does not begin to oxidize significantly until the temperature is increased to above 500 ºC.

3. Graphite's lubricity is not affected negatively by high moisture content. The lubrication mechanism in graphite is linked to surface functionalities, some of which are adsorbed water. Graphite works well as a solid lubricant in water and moist environments. The long term lubrication performance of molybdenum disulfide is degraded in high moisture environments due to oxidation (1).

As pure materials, graphite and molybdenum disulfide are very useful and effective solid lubricant additives although both substances do have their own intrinsic limitations. This is especially true when these minerals are utilized in their pure, dry powdered form as they are in "dry friction" applications. However, when used to boost the performance of conventional oil or grease products the physical limitations (i.e. temperature or atmospheric restrictions) may not be as significant an issue since the stability of the oil or grease carrier is typically the limiting performance factor.

One attribute which has a great deal of influence on the utilization of a solid phase lubricant additive is the price of that additive. In this regard there is a significant difference between the efficiency of a solid lubricant package that contains only molybdenum disulfide compared to one that contains graphite in some proportion. In this case the term "efficiency" is defined as the "price + performance" of the additive package.

In the last two years the availability of molybdenum disulfide has dropped appreciably with a corresponding price increase. The cost for lubrication grade molybdenum disulfide powder has increased between 200-300% over this time period. In contrast, graphite price and supply has remained relatively stable over the last 5 years. While molybdenum disulfide is geologically uncommon, graphite is geologically quite plentiful. With molybdenum disulfide availability down, and the price elevated, the incentive to evaluate graphite based functional extenders for MoS_2 is high.

The use of graphite as an adjunct to MoS_2 in grease and oil products is not a new or unique idea. The ability of mixtures of graphite and molybdenum disulfide to work "synergistically" in lubricating oil and grease products is well known. However, most formulations that contain these two solid lubricants rely on various grades of molybdenum disulfide powder mixed with conventional amorphous, flake, or synthetic graphite powders. In this study a relatively new form of graphite powder described as "surface enhanced flake graphite" is evaluated as a functional extender to molybdenum disulfide in clay filled PAO grease.

Materials Evaluated in this Study: Four solid lubricant additives were evaluated in this study: conventional natural flake graphite, enhanced-surface natural flake graphite, ultra-high surface area synthetic graphite, and molybdenum disulfide. Detailed physical, chemical, and mineralogical descriptions of graphite and molybdenum disulfide are available in the literature so only a brief review of these substances will be provided below.

Ultra High Surface Area Synthetic Graphite: Synthetic graphite, also known as artificial graphite, is manufactured graphite that is made by the high temperature heat treatment of certain forms of carbon. The macroscopic morphology of synthetic graphite is generally granular or needle-like. However, fine-grinding results in the formation of flaky particles of which all graphite is based. Commercial material is available in purities from 95-99%. Ultra high surface area synthetic graphite, used in this study, is proprietary de-agglomerated, dry-processed graphite that has surface areas in the range of 120-200 m^2/gram.

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. Flake graphite has a flaky morphology regardless of particle size. Commercial material is available in purities from 80-99%. The flake graphite used in this study was a nominal 99% carbon flake.

Surface Enhanced Flake Graphite: SEFG is manufactured from conventional natural flake graphite feedstock. This product is made by a proprietary process and is not the same as the product known as “polarized graphite” as reported by Holinski. Surface enhanced flake graphite has approximately twice the BET surface area of conventional flake of the same size. SEFG with a BET surface of 20m2/gram will increase the viscosity of naphthenic oil more than graphite having a BET surface area above 150m2/gram (2).

Molybdenum disulfide: MoS_2 or molybdenite is a naturally occurring mineral. Molybdenum disulfide is formed in high temperature vein deposits, in some granite, and in pegmatites and aplites. MoS_2 has a flaky morphology regardless of particle size. MoS_2 is an intrinsic lubricant.

Five different solid lubricant products were evaluated in this study, grade 3777, 3775, 230U, 4827, and ITAMoly 98. Grades 3777 and 3775 are surface-enhanced flake graphite products ground from the same feedstock. 230U is nominal 99 carbon natural flake graphite. 4827 is ultra-high surface area synthetic graphite, and ITAMoly 98 is a 98% molybdenum disulfide lubricant-grade powder.

The nominal physical and chemical properties of each the solid lubricant products used in this study are presented in the Table 1.

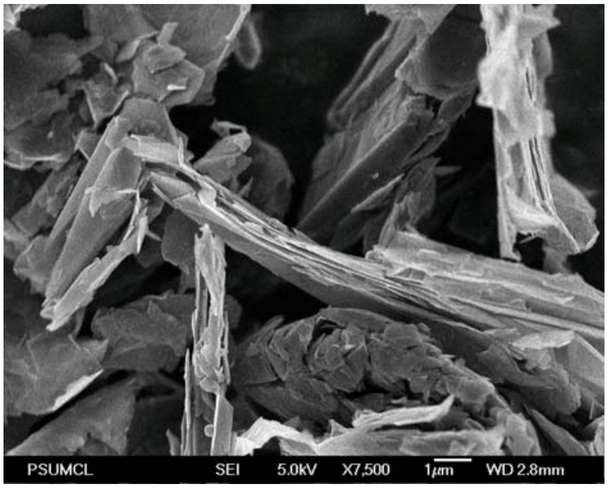
Table 1: Analysis of graphite and molybdenum disulfide samples

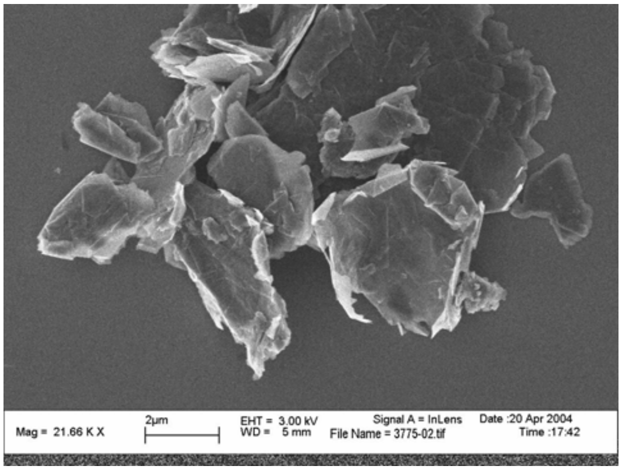
Grade	Type	Purity	Nominal particle size	Nominal surface area
3775	SEFG	98	8 micrometer	24m^2/gram
3777	SEFG	99	19 micrometer	23m^2/gram
230U	Conventional flake graphite	99	19 micrometer	8m^2/gram
4827	Ultra-high surface area synthetic	98	2.5 micrometer	200 m^2/gram
ItaMoly 98	Molybdenum disulfide	98	16 micrometer	1m^2/gram

SEFG- Surface enhanced flake graphite. Property testing of all powders was performed at Asbury Graphite Mills, Asbury, New Jersey. All sizing was performed using laser diffraction techniques. “Nominal” refers to the 50th percentile of the distribution.

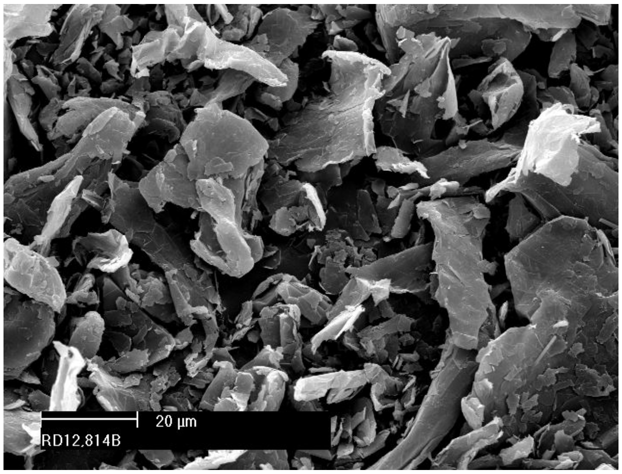
Morphological Character: Both graphite and molybdenum disulfide crystallize in the hexagonal crystallographic system and have virtually identical morphology. In fact, except for the higher density of molybdenum disulfide the two substances are difficult to distinguish visually or tactilely when in powdered form. To provide the reader with a better understanding of the morphology of graphite and molybdenum disulfide the following scanning electron micrographs of the materials evaluated in this study are included.

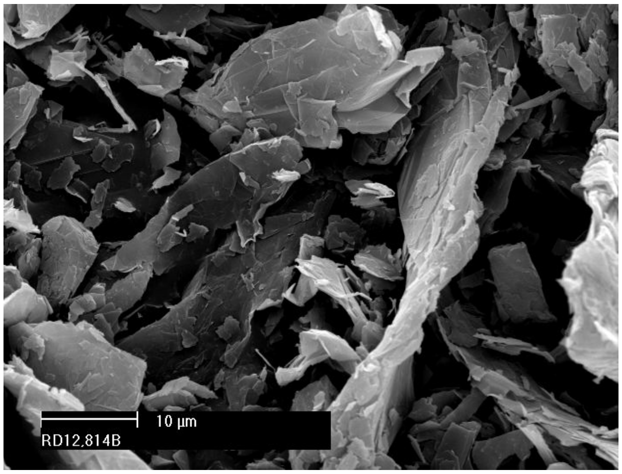
3775- 8um Surface Enhanced Flake Graphite:



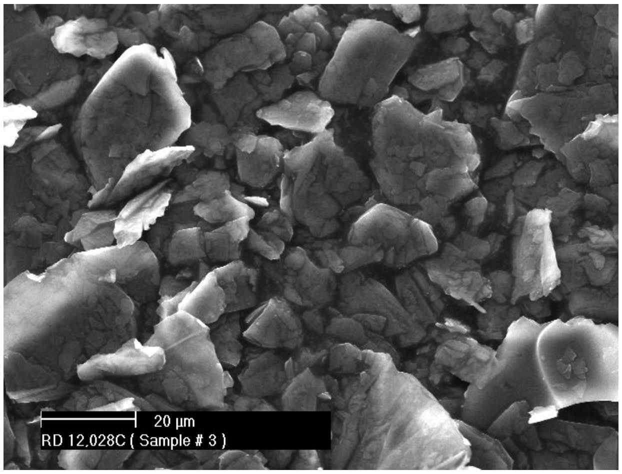


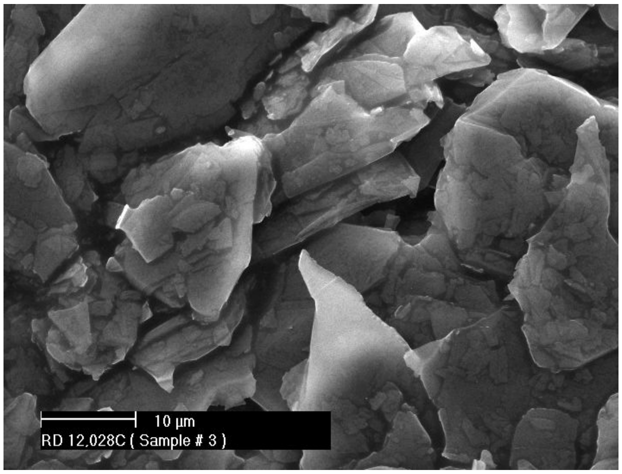
3777- 20um Surface Enhanced Flake Graphite:



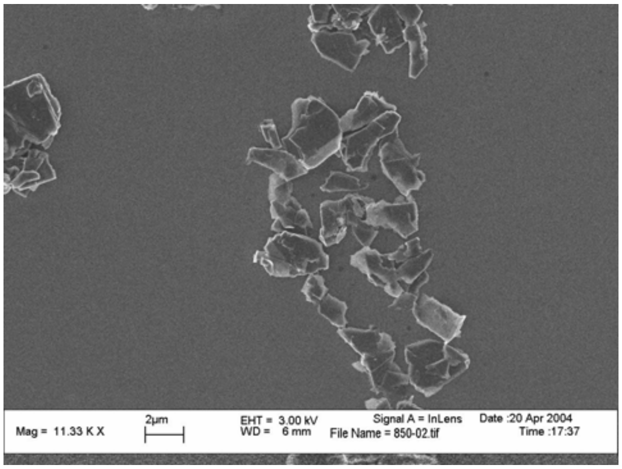


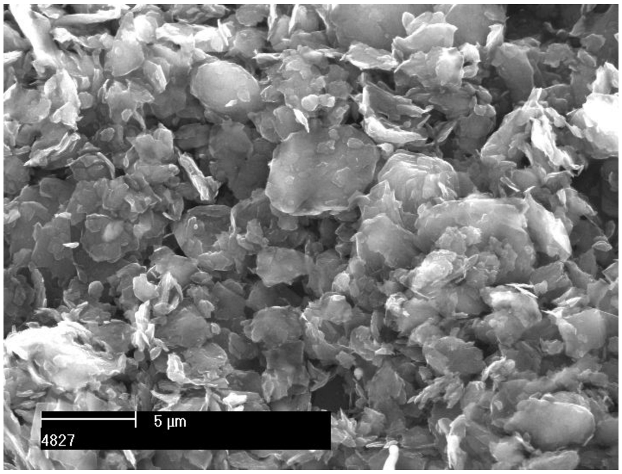
230U- 20um Conventional Flake Graphite:



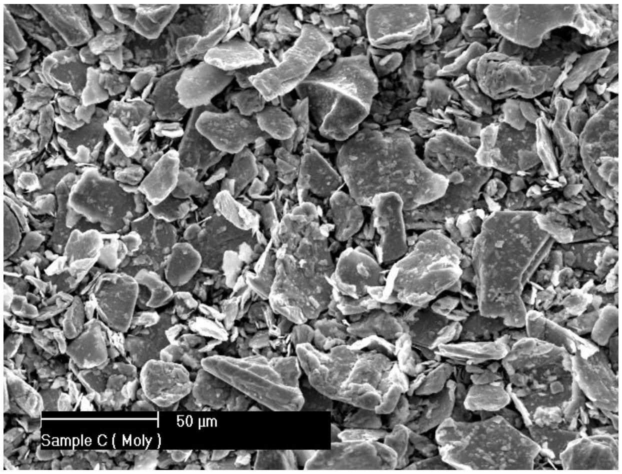


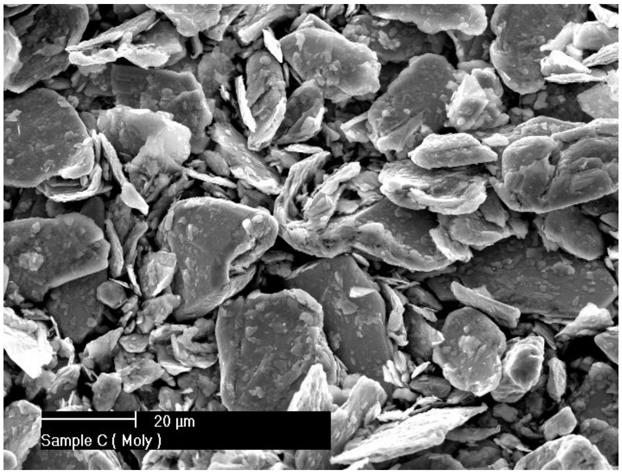
4827-Ultra-High Surface Area Synthetic Graphite:





ItaMoly 98: Molybdenum disulfide:





Experimental Method: In order to determine the efficiency of surface enhanced flake graphite as a functional extender to molybdenum disulfide in grease, mixtures of grease with various proportions of graphite and/or molybdenum disulfide were tested using Four Ball Wear (ASTMD2266), and Load Wear Index (ASTMD2596). Except for testing performed on the neat grease, solid lubricant loading was always 5 weight percent of the lubricant mixture. Mixing proportions were 0% solids/100% grease, 5% graphite/95% grease, 5% MoS_2/95% grease, 2.5%graphite +2.5% MoS_2/95% grease.

Data collected from the Four Ball Wear (D2266) method included average coefficient of friction and wear scar dimension. Data collected from Load Wear Index (D2596) testing included last non-seizure load, last seizure load, weld load, and calculated load wear index. Methods D2266 and D2596 were performed at Petro-Lubricant Testing Laboratories, Lafayette, New Jersey.

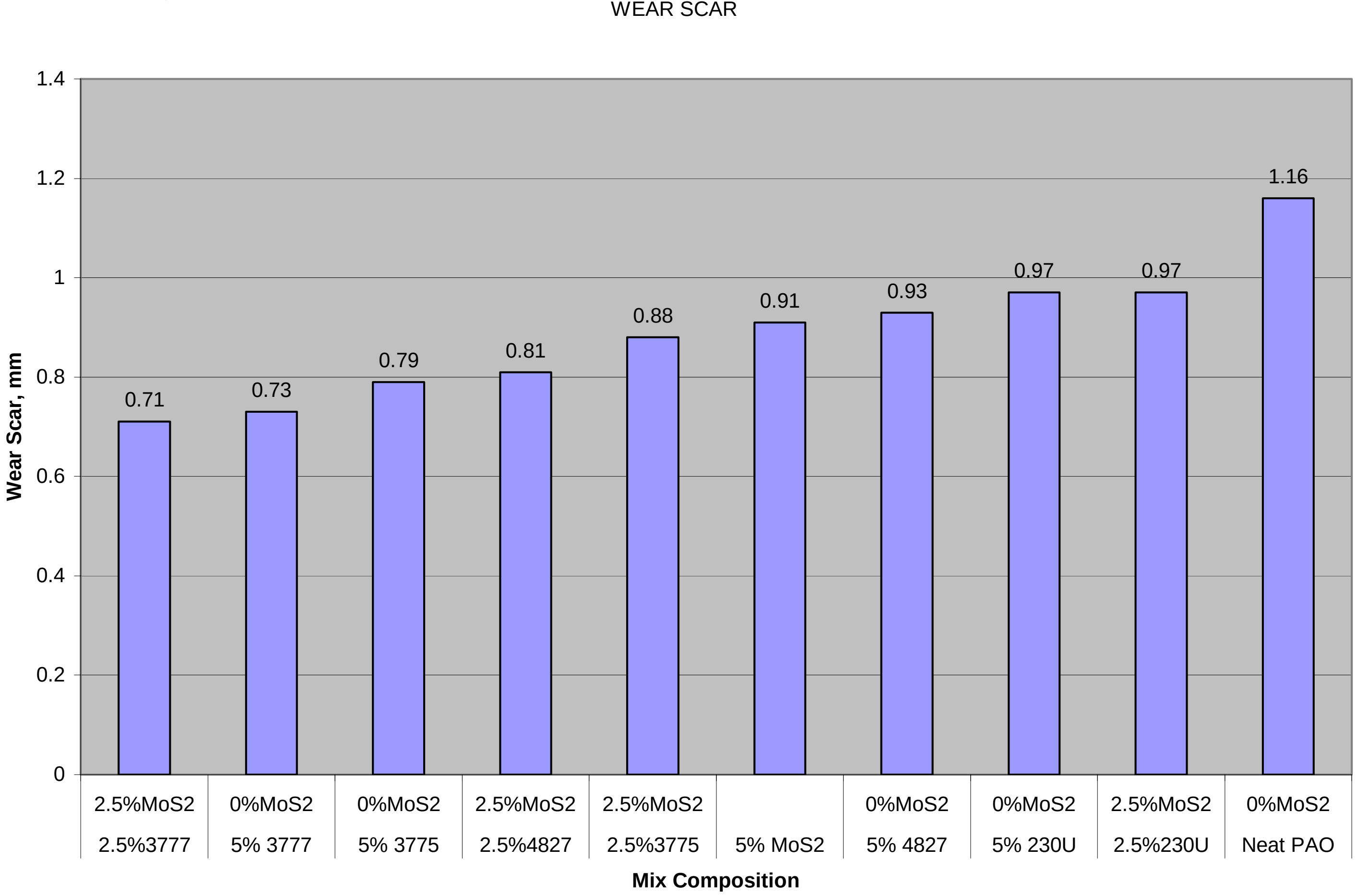
Clay filled polyalphaolefin grease was used as the base lubricant for this study. The grease consisted of Albemarle Durasyn #166 filled with Rheox Baragel 3000, organically treated smectite. The base grease was supplied by Summit Lubricants.

Results and Discussion: Four-Ball Wear Testing (ASTM D2266): The average coefficient of friction and wear scar dimensions were generated. The four ball wear data is presented in Table 2, Figure 1, and Figure 2.

Table 2: Wear Scar and Average Coefficient of Friction

Grade/blend	Wt % MoS2	Wear Scar mm	Coefficient of friction X-bar
Neat grease	0	1.16	0.188
5% 3775	0	0.79	0.114
5% 230U	0	0.97	0.129
5% 4827	0	0.93	0.132
5% 3777	0	0.73	0.107
2.5%230U	2.5	0.97	0.129
2.5%3775	2.5	0.88	0.102
2.5%4827	2.5	0.81	0.108
2.5%3777	2.5	0.71	0.101
5% MoS_2	5	0.91	0.102

Figure 1



Wear scar dimensions for mixtures of solid lubricant and grease varied between 0.71mm and 0.97mm. There was a significant reduction in wear scar dimension for grease containing the solid lubricant system compared to the neat grease. The smallest wear scar occurred for a mixture of 2.5% 20um SEFG (3777) and 2.5% MoS_2. The largest wear scars occurred in the neat grease and the mixtures containing conventional 20um flake graphite with and without MoS_2.

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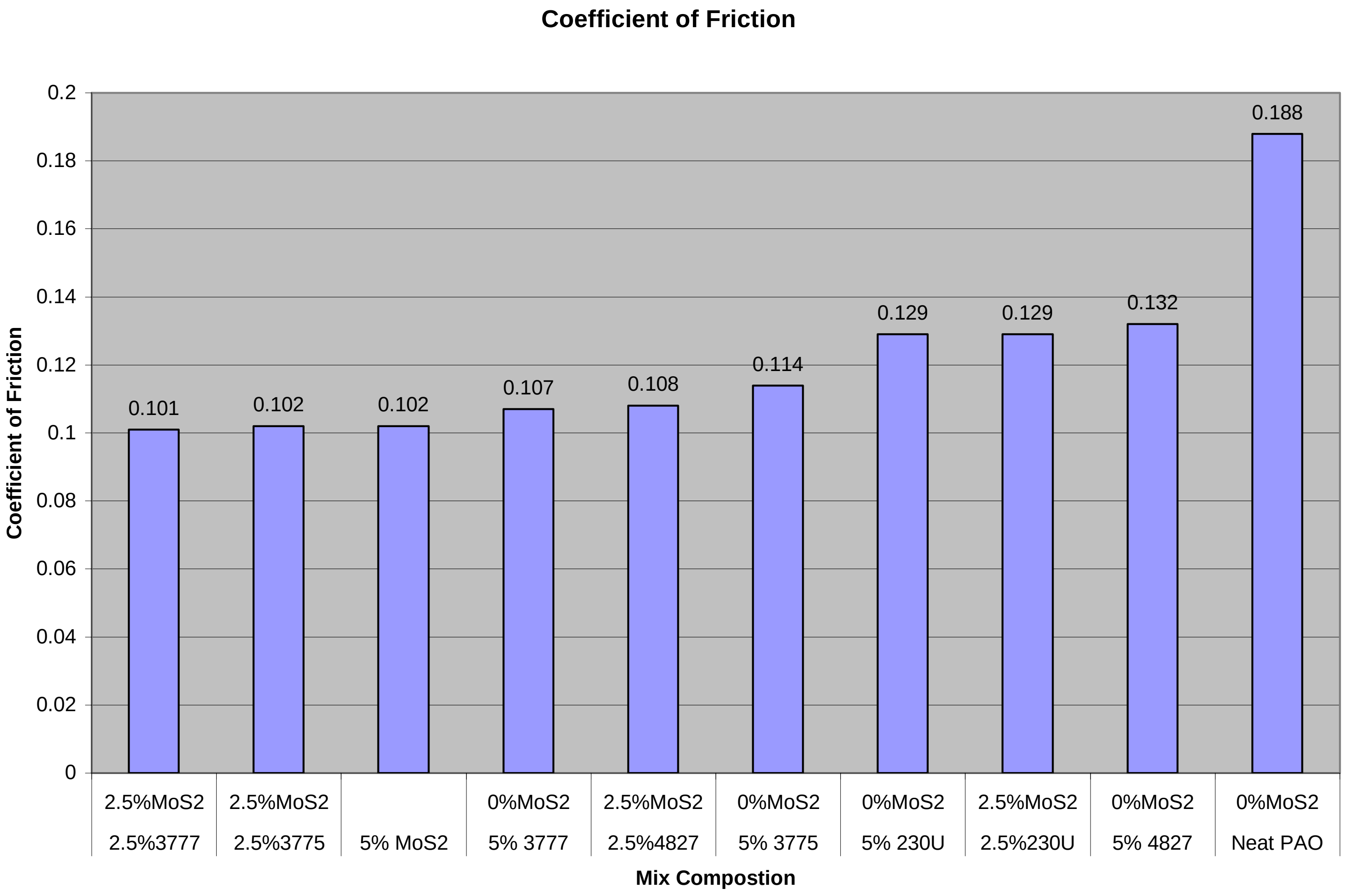
Figure2



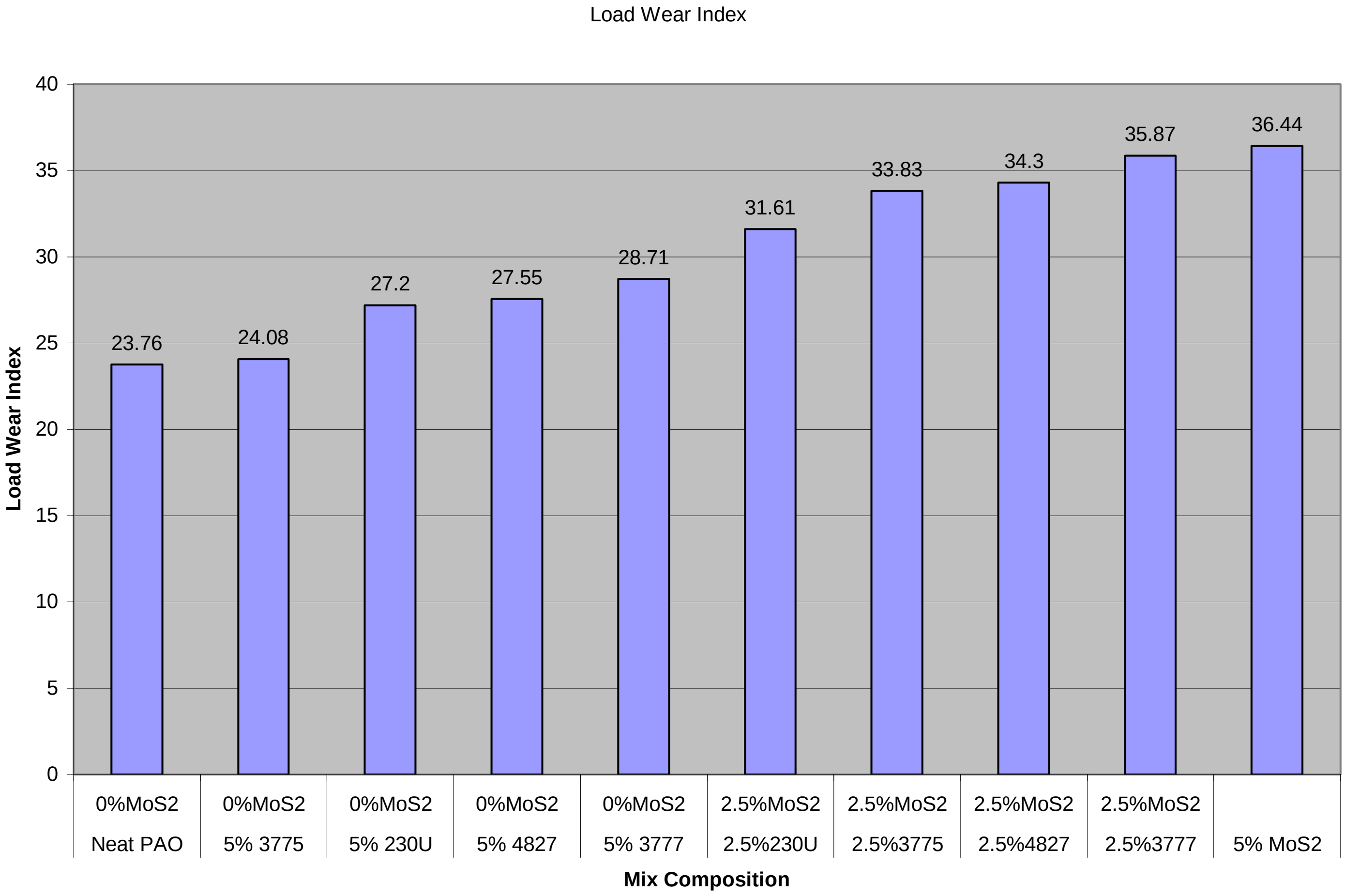
Average coefficient of friction varied between 0.101 and 0.188. The highest value, as expected, occurred for the neat grease. The lowest value occurred for a mixture of 2.5%SEFG and 2.5% MoS_2. There was virtually no difference in the average coefficient of friction between the sample containing 5% MoS_2 and samples containing 2.5% 8um SEFG and 2.5% MoS_2, and 2.5% 20um SEFG and MoS_2. The highest values of coefficient of friction (mixture) occurred in samples containing conventional flake graphite with and without MoS_2, and ultra-high surface area synthetic graphite. Overall there was little difference between the coefficient of friction of all samples that contained solid lubricant.

Load Wear Index (ASTM D2596): Values of last non-seizure load, last seizure load, and weld load were generated. Table 3 presents these values along with load wear index.

Table 3: Load Wear Index

Grade/blend	MoS_2	Load Wear Index	Last non-seizure load, Kg	Last seizure load, Kg	Weld Load, Kg
Neat grease	0	23.76	50	100	126
5% 3775	0	24.08	50	126	160
5% 230U	0	27.2	50	160	200
5% 4827	0	27.55	63	126	160
5% 3777	0	28.71	63	160	200
2.5%230U	2.5	31.61	63	160	200
2.5%3775	2.5	33.83	63	200	250
2.5%4827	2.5	34.3	63	160	200
2.5%3777	2.5	35.87	80	160	200
5% MoS2	5	36.44	100	160	200

Figure3



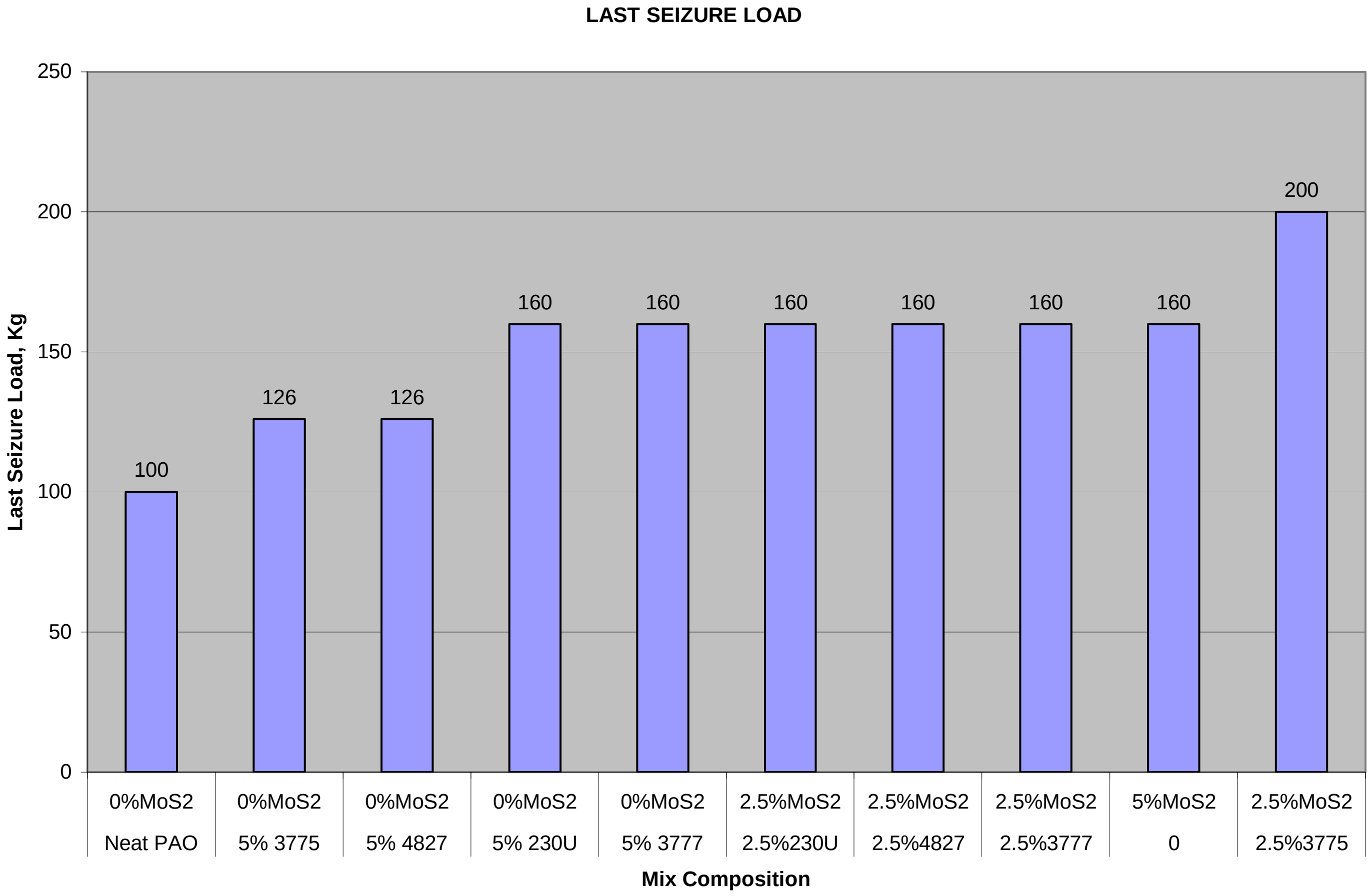
The values of load wear index are plotted on Figure 3. The lowest LWI was observed for the neat grease. The highest LWI occurred in the 5% MoS_2 grease mixture, and the 2.5% 20um SEFG-2.5% MoS_2 blend. The LWI of these 2 samples were virtually identical. The lowest mixture-LWI occurred in the 5% 8um SEFG mixture.

The trend of the LWI data indicates a clear extreme pressure advantage to grease using MoS_2 as part of the solid lubricant package. The data also indicate that substitution of up to 50% of the MoS_2 with 20um surface enhanced flake graphite does not have a negative impact on the LWI.

Figure 4

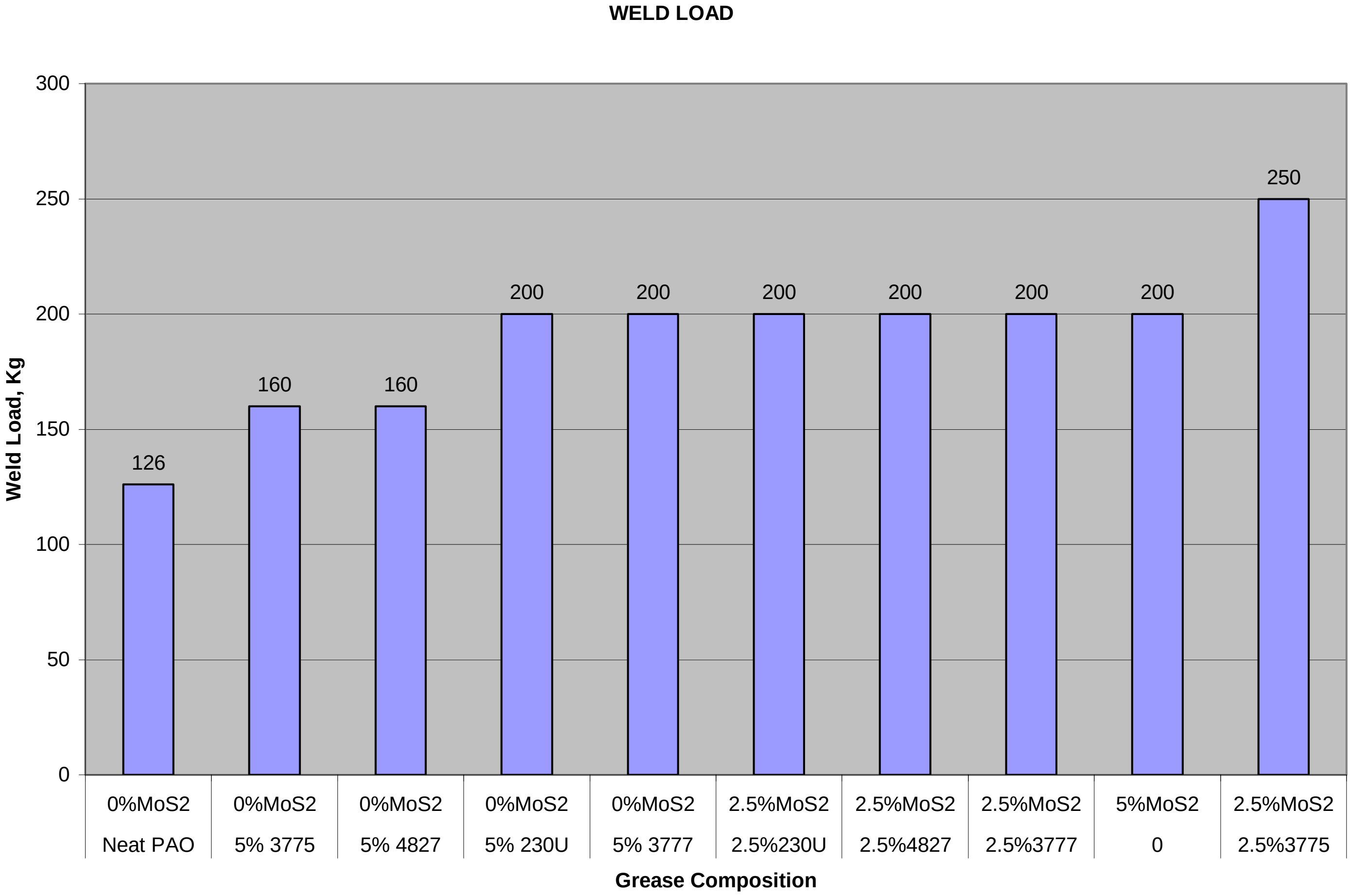
The values of last non-seizure load are plotted in Figure 4. The highest LNSL value of 100kg occurred with the 5% MoS_2 grease. The 2.5% 20um SEFG/2.5% MoS_2 blend had the second highest LNSL value of 80kg. The lowest LNSL values occurred in the neat grease and grease samples containing only graphite in the formulation.

Figure 5



The values of last seizure load are plotted in Figure 5. The highest value of LSL occurred in the blend of 3775 8um SEFG and MoS_2. The lowest last seizure load values occurred in the neat grease, the grease/3775 blend, and grease/4827 blend. The other sample blends showed no negative effect on LSL as a result of diluting MoS_2 with graphite.

Figure 6



The weld load values are plotted in Figure 6. The data indicate that substitution of up to 50% of the MoS_2 with any of the graphite tested does not negatively impact the weld load. The lowest weld load occurred with the neat grease sample, while the highest value was reached with a blend of 2.5% 3775 8um SEFG and 2.5% MoS_2.

Conclusions: Preliminary testing was performed to determine the ability of surface enhanced flake graphite to partially replace molybdenum disulfide in grease. Although the test methods utilized are known to be imprecise, both methods are generally accepted as a means to determine performance trends. For both test regimes used in this study, ASTM D2266 and ASTM D2596, partial substitution of surface enhanced flake graphite in place of molybdenum disulfide in PAO grease did not negatively affect the grease performance. The data also indicated that SEFG improved grease performance to a greater extent than did conventional flake graphite or ultra-high surface area synthetic graphite.

Regardless of the variation inherent to these test methods the data clearly indicates that addition of a solid lubricant system significantly improves the performance of PAO grease. Consideration of all the data also indicate that surface enhanced flake graphite may be used to partially replace molybdenum disulfide in this grease system without sacrificing performance. Application of “cost + performance” to the definition of product efficiency provides impetus to further investigation of this material. Although surface enhanced flake graphite is not expected to replace molybdenum disulfide it may provide grease manufactures with a solid lubricant phase that can be used in conjunction with MoS_2 without sacrificing performance.

In addition to augmentation of MoS_2 grease products, surface enhanced flake graphite may prove to be a solid phase additive that shows improved performance over conventional graphite fillers in lubrication systems.

For additional information, please contact Asbury Graphite at 908-537-2155 or visit our website www.asbury.com

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References:

(1) Friction, Lubrication, and Wear Technology, ASM Handbook, volume 18, ASM International, 1992.
(2) Report# 14211, The Effect of Various Graphite Materials on the Viscosity of Naphthenic Oil, Asbury Graphite Mills Technical Services Department, internal document RD#14211, August 2005.

Mineral Reference Manual, Nickel and Nichols, Van Nostrand Reinhold, New York, 1991
Dana's Textbook of Mineralogy, 4th edition, W.E. Ford, John Wiley and Sons, New York, 1932.
Manual of Mineralogy, Klein and Hurlbut, John Wiley and Sons, New York, 1977.
Handbook of Chemistry and Physics, 63rd Edition, CRC Press
Handbook of Carbon, Graphite, Diamond and Fullerenes, Hugh Pierson, Noyes Publishing, 1993

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