

MOLYBDENUM DISULFIDE IN LUBRICANT APPLICATIONS – A REVIEW

Yakov Epshteyn and Thomas J. Risdon

Climax Molybdenum

A Freeport-McMoRan Company

Phoenix, Arizona, USA

Presented at the 12 Lubricating Grease Conference

NLGI-India Chapter

28-30 January 2010

Hotel Cedade de Goa

Goa, India

MOLYBDENUM DISULFIDE IN LUBRICANT APPLICATIONS – A REVIEW

Yakov Epshteyn* and Thomas J. Risdon**

**Climax Molybdenum
A Freeport-McMoRan Company**

Abstract

Molybdenum disulfide is one of the best known solid lubricants, and although it originally gained popularity in aerospace and military applications, it is now commonly found in a variety of lubrication applications. It is widely used in greases and specialized grease-like products known as pastes, in fluid lubricants such as automotive and industrial gear oils, in solid film lubricants including but not limited to burnished (rubbed-on) films, sputtered coatings, resin bonded and impingement coatings.

This paper reviews the properties of MoS₂ including physical and chemical properties, electrical properties, effects of temperature and oxidation as well as application areas such as greases, fluid lubricants, and solid film (dry) lubricants where molybdenum disulfide is widely implemented.

* Chief Engineer, Lubrication-Climax Molybdenum

** Consulting Engineer, Solid Lubricant Solutions, Dexter, MI

Properties of molybdenum disulfide

Molybdenum disulfide is a dark gray to black powder (the color depending on its particle size). The most important, basic physical properties are listed in the table below and some of the additional physical properties given in Reference 1.

▪ Density	4.9
▪ Color	blue gray to black
▪ Molecular weight	160.08
▪ Crystal form	Hexagonal, rhombohedral
▪ Electrical Conductivity	Low but variable
▪ Vacuum Lubrication	Excellent
▪ Radiation Stability	Good
▪ Magnetic properties	Diamagnetic
▪ Dissociation temp.	1370°C (non-oxidizing environment)
▪ Melting Point	1700°C (under pressure)
▪ Sublimation temp.	1050°C in high vacuum

Molybdenum disulfide exists in two crystalline forms, hexagonal and rhombohedral. The hexagonal form is by far the most common and being the only type found in commercial ores. Also, the hexagonal form has been found in synthetic MoS₂. The rhombohedral was first identified in a synthetic material ² and subsequently found in several natural sources³.

The hexagonal form is characterized by MoS₂ layers in which the Mo atoms have trigonal prismatic coordination of six sulfur atoms, with two molecules per unit cell. The crystal structure consists of "sandwiches" in which one planar hexagonal layer of molybdenum atoms is interspersed between two layers of sulfur atoms.

Molybdenum disulfide is classified as a transition metal dichalcogenide (TMD) which includes the disulfides, diselenides and ditellurides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. These compounds exist in various crystalline forms but only the Mo and W compounds form the MoS₂ hexagonal type crystal structure⁴.

Thus the excellent lubricant properties of MoS₂ are attributable to the large spacing (and weak Van der Waals bonding) between S-Mo-S sandwich layers. Differences in lubricating behavior among the TMD compounds are attributable to the distribution of electrons on the constituent atoms. In MoS₂, there are six non-bonding electrons which can completely fill a band which physically confines the electrons within the crystal structure⁵. This creates a net positive charge on the surface of the S-Mo-S sandwich layers which promotes easy shear

through electrostatic repulsion. Therefore, as it is generally accepted, the low friction observed with MoS₂ could be explained in part to the large spacing between S-Mo-S layers, and in part to the favorable distribution of electrons on the constituent atoms.

The use of MoS₂ is most useful in the boundary lubrication regime where metal to metal contact exists, in contrast to the hydrodynamic regime where a sufficiently thick fluid film exists to prevent asperity contact and where virtually no wear takes place. Factors that contribute to the existence of boundary lubrication include high operating temperatures, low sliding speeds, stop/start or oscillatory motion and shock loading.

Generally molybdenum disulfide in its naturally occurring hexagonal form is chemically very inert. It is insoluble in both oil and water. Molybdenum disulfide is unreactive with most acids; however it is not resistant to attack of hot concentrated sulfuric and nitric acids. Also, molybdenum disulfide dissolves in strong oxidizing agents such as aqua regia.

Molybdenum disulfide is converted directly to molybdenum metal under heating in hydrogen gas via intermediate compound Mo₂S₃, and to MoO₃ via a highly exothermic oxidation reaction in air at 500-600 °C . Reaction of natural MoS₂ and chlorine gas in absence of air at elevated temperature generates molybdenum pentachloride.

The oxidation characteristics of lubricant grade natural MoS₂ have been studied by several researchers. The thermal oxidation rate of MoS₂ in air studied by x-ray diffraction showed that below 300 °C, the rate is very slow and difficult to measure accurately, and that below 388 °C, MoS₂ oxidized at a slower rate than WS₂⁶. The oxidation behavior of MoS₂ in dry air has also been studied by thermogravimetric analysis⁷. It was determined that 10%, 50% and 90% MoO₃ was formed at temperatures of 435 C, 466 C and 516 °C respectively.

Besides temperature and humidity, the MoS₂ particle size can significantly affect the rate of oxidation. Smaller particles of MoS₂ have much higher rate of oxidation compared to larger particles due to the fact that edge sites of the particles oxidize at a much higher rate versus the basal plane area of a particle, and also, finely divided particles have a higher specific ratio of the edge to basal plane.

The oxidation behavior of molybdenum disulfide has considerable practical importance for the following reasons:

- oxidation of MoS₂ can cause corrosion in certain cases
- oxidation of MoS₂ can determine the life of bonded or burnished MoS₂ films

- products of MoS₂ oxidation can cause an increase of friction
- oxidation of MoS₂ can cause problems with gelling capabilities in some greases
- oxidation of MoS₂ can lower maximum temperature for usage of MoS₂
- oxidation process determines shelf life of MoS₂

At the same time it would be incorrect to over estimate the contribution of molybdenum disulfide oxidation to its lubrication capabilities because the typical, stable product of molybdenum disulfide oxidation is MoO₃ which is not abrasive⁸. Therefore, even after considerable degree of oxidation, molybdenum disulfide can still deliver an acceptable level of lubrication performance.

The electrical properties behaviors of MoS₂ are of significant practical importance particularly for implementation in electrical brushes and spacecraft. Most conductivity measurements have been conducted on either large single crystals or compacts of MoS₂. According to Lansdown's observation⁸ there is no clear agreement about electrical conductivity of MoS₂. However, the general view is that molybdenum disulfide could be classified as a "p" type semiconductor⁹.

There is a strong correlation between MoS₂ conductivity and temperature. Despite the fact that absolute values of resistivity or conductivity could be different it is well established that with increasing temperature MoS₂ demonstrates a gradual decrease in resistivity and increase in conductivity.

The conductivity also is a function of the direction of the current flow in relation to the crystal structure especially at the higher temperature. Electrical conductivity at room temperature for several single crystals ranged from 0.16 to 5.12 Ω⁻¹ cm⁻¹ along the cleavage plane and from 1.02 x 10⁻⁴ to 5.89 x 10⁻⁴ Ω⁻¹ cm⁻¹ parallel to it¹⁰. At the same time it was demonstrated¹¹ that at 19 °C the resistance is the same regardless of the direction of the current flow in relation to the crystal structure.

There are also varieties of parameters that potentially can correlate with MoS₂ resistivity. However parameters such as the applied current potential, pressure and light appears to be much less significant compared to temperature and level of impurities (contaminants) of MoS₂.

Greases

Greases containing molybdenum disulfide are implemented in a wide variety of applications in nearly all markets where greases are used and in virtually all types of grease thickener systems, including bentonite clay, lithium, lithium 12-hydroxystearate, lithium complex, aluminum complex and polyurea. It has also been cited as a useful additive in titanium complex greases, that in themselves have inherently high load carrying capability, to obtain even better performance¹².

In general greases contain 1 to 2% of MoS₂ with critical parameters being surface roughness, load and speed. For the relatively rough metal surface the large MoS₂ particles size is desirable because large particles fill the deep valleys and facilitate the establishment of a smoother finish. For a smoother finish mid and small particles will provide better load-carrying ability at a given MoS₂ concentration. At the same time very small particles can potentially generate some corrosion issues due to the higher acid numbers. In general, mid size particles with median particle size ~ 6 μm (corresponding to Climax Technical Fine Grade) is the most commonly used MoS₂ particle size in greases.

Molybdenum disulfide grease markets include transportation, construction (on and off road), mining, agricultural and military/aerospace.

In the transportation sector, Ford Motor Company developed a grease (Spec M1C75B) containing MoS₂ and high density polyethylene that has been used since 1961 in steering linkages, ball joints and wheel bearings. MoS₂ grease is also used in the constant velocity joints (CVJ) used in front-wheel drive cars and some rear drive cars that have CVJ's as part of the drivetrain. In CVJ's, as well as many other applications, the grease as a whole passes into the contact zone rather than only the oil component of the grease. Fish¹³ has detailed the complex and demanding role that greases play in the lubrication of CVJ's, many of which contain MoS₂. Also in the transportation sector, railroad curve-rail greases, either petroleum or soybean oil based, containing MoS₂ and/or other solid lubricants are being used to reduce wheel/rail wear and fuel consumption¹⁴.

In construction, mining and agricultural markets, greases containing MoS₂ are used as OEM lubricants by most equipment manufacturers, and also supplied to the aftermarket. Applications include kingpins, ball joints, pivot pins and spherical frame pivot bearings¹⁵. These greases are used to enhance the running-in process of new components as well as protecting load-bearing surfaces operating under arduous conditions.

Grease-like products containing a high percentage (50-70%) of MoS₂ and other solid lubricants are referred to as pastes. These products are typically used as problem solvers for applications such as automotive engine re-builds, new gear sets, and as anti-seize lubricants for threaded connections. A paste containing 50% MoS₂ in a silicone oil is used as a backing plate lubricant in vehicles with disc brakes.

Military applications for MoS₂-containing greases parallel many of those found in non-military markets. For example Mil G-23549 is a general purpose clay thickened grease containing 5% MoS₂ that is used to lubricate Navy catapults on aircraft carriers and also in military automotive vehicles. Mil G-21164 is a lithium complex grease containing 5% MoS₂ in a synthetic base oil recommended for heavily loaded sliding surfaces.

Fluid Lubricants

Molybdenum disulfide can be effectively used to reduce friction and wear in fluid lubricants (oils) under boundary conditions, to provide increased load-carrying capacity and in the event of oil loss may prevent/delay catastrophic seizure. Despite the fact that in dispersions the concentration of MoS₂ could be between 0.1 and 60%, in most of cases of MoS₂ dispersions in oil, the concentration is less than 3%⁸.

If fluid lubricants are highly viscous or can be stirred frequently they may be able to utilize small 1-2 μm MoS₂ particles (Super Fine Grade according to Climax classification). Gears that have a significant amount of sliding contact such as worm gears, helical gears and hypoid gears are responsive to the presence of MoS₂ in the gear lubricant. A laboratory study of worm gear lubricants in an actual worm gear speed reducer, it was shown that in both a mineral oil based AGMA #8 compounded oil and in a PAO based oil, the addition of a 1% colloidal dispersion of MoS₂ resulted in up to 5% improved efficiency and lower bulk oil temperatures¹⁶.

In automotive hypoid axle tests, conducted under laboratory conditions, a 1% dispersion of MoS₂ in an 80W gear oil, a 1.5% gain in axle efficiency was achieved¹⁷.

In another series of tests with a tractor-trailer test vehicle having a 52,000 kg gross vehicle weight, a towing dynamometer simulated a loaded vehicle climbing a 10% grade. The fully instrumented test vehicle recorded lubricant temperature in a 90 minute test. The SAE 90 multipurpose lubricant with 1% MoS₂ added gave a consistent 8 C lower operating temperature than the same oil without MoS₂¹⁸.

Solid Film Lubrication

Solid film lubricants are those that can provide lubrication to sliding surfaces without the presence of a fluid film (i.e., a grease or oil film). Solid film coatings/lubricants are materials with inherent lubricating properties, and which are firmly bonded to the surface of a substrate by some method.

Burnished Films

One of the properties of MoS₂ is that it can be physically rubbed on most metal substrates establishing a lubricant film about 1 to 5µm in thickness (for the longest life, the optimum thickness is 3-5 µm). The burnished coating is frequently used as a lubricant in applications such as metal forming dies, threaded parts, sleeve bearings, liquid oxygen valves and electrical contacts in relays and switches. In these applications, the MoS₂ burnished coating can be produced from loose powder, dispersions, wire-brushing or even "sandblasted" onto the metal surface to form a thin adherent film. A "sandblasting" (or impingement) process is used by a major automobile manufacturer to apply a film on engine pistons. The MoS₂ is directed onto and adheres to the piston surface by entrainment of the powder in a high velocity air stream. The thin MoS₂ coating promotes the running in process and reduces friction between the piston skirt and the cylinder wall, thus reducing fuel consumption.

Another example of the use of a burnished MoS₂ film is on O-rings to reduce friction between the elastomer and the metal surface with which it is in contact. The MoS₂ in this case is applied to the O-ring by barrel tumbling where hundreds of pieces can be coated at one time.

Burnishing can be accomplished by hand rubbing using a variety of MoS₂ particle sizes (for example, Climax offers MoS₂ in three distinct grades which differ primarily by average particle size). However, on a commercial scale, burnishing is usually accomplished with medium particles size 30 μm (Technical grade according to Climax classification) by barrel tumbling using burnishing aids such as glass beads or crushed walnut shells.

Overall, if the burnished films are fully and properly consolidated, they are capable to provide high load-carrying capacity, very low friction and wear rate. Also, it is one of the best techniques for lubrication bearings with very small clearances in air.

Sputtered Coatings

Sputtered coating of MoS₂ is accomplished by bombarding a target material of compacted MoS₂ with a charged gas (e.g., Argon) which releases atoms in the target that coat the nearby substrate. The process takes place in a magnetron vacuum chamber under low pressure, producing extremely adherent coatings of MoS₂ that are typically less than 1 μm thick which is much thinner, more adherent and shows greater endurance compare to other types of solid lubricant coatings. Also, MoS₂ sputtering can be performed on a wide variety of substrate materials such as Mo, Fe, Ni, Co, W, Ta, Al, plastics, glass, ceramics and oxidized surfaces (before the sputtering process) of Cu and Ag⁸.

Sputtered films of MoS₂ are primarily used in vacuum environments such as deep space where very low friction coefficients and low wear are achieved. Good lubrication performance can also be achieved in dry air, but in humid air, the tribological properties of sputtered MoS₂ films deteriorate due to the exposure of crystal edge sites¹⁹. Another significant disadvantage of sputtering technique is that a sputtered film production requires specialized equipment and it is also quite difficult to coat complicated part geometries. Specific applications where sputtered MoS₂ is widely implemented include the most critical aerospace applications such as spacecraft and satellite moving mechanical assemblies, solar array drives, antenna control systems, de-spin mechanisms, as well as similar mechanisms on earth that operate in a vacuum or inert environment¹⁹.

Resin-Bonded Coatings

Resin-bonded lubricant coatings are perhaps the most common product for achieving a dry, self-lubricating film on metal surfaces. A resin-bonded lubricant coating has been defined as a solid lubricant dispersed in a continuous matrix of a binder (inorganic or organic) and attached to a surface²⁰. Many different compositions are commercially available with different binder and additives.

A typical formulation is composed of MoS₂, which could be up to 80%, and/or other lubricating solids, additives, a binder (organic or inorganic) and a carrier liquid. Organic resins may include acrylic, phenolic, epoxy, amide-imide, urethane and polyimide. Newer organic resins include polybenzimidazole, and polybenzothiozole. Many newer formulations contain water-borne resins that are more environmentally friendly (lower VOCs) rather than solvent based resins. Some products require a heat curing cycle, while others are ready to use after drying at room temperature. Bonded lubricant coatings can be applied by several methods used in applying paint-like coatings. These include conventional spraying, electrostatic spraying, roll-coating, and dip-coating/centrifuging. Coating thickness and uniformity is critical to optimum performance; typical thickness ranges from 8 μm to 18 μm.

Some resin-bonded coatings are oil compatible, and are able to provide friction and wear reduction under boundary lubrication conditions. One example is an automotive piston skirt coating which improves fuel economy and extends engine durability²¹. Another application for bonded lubricant coatings is fasteners. In threaded connections, the uniform coefficient of friction provided by the bonded coating minimizes the possibility of exceeding the yield strength of the bolt due to erratic friction during tightening²².

A variety of MoS₂ particle sizes may be used for bonded coating applications depending on the specific formulation. For instance, if the product is in aerosol form, the smallest available particles may be required to guard against spray tip clogging.

Summary

The molybdenum disulfide used in lubricant applications is the purified form of the mineral Molybdenite. The commercial form of lubricant grade of MoS₂ possesses a hexagonal layer lattice crystal structure which gives it low friction and excellent adherence to most metals. As a solid lubricant, the excellent lubricant properties of MoS₂ are attributable to the large

spacing (and weak Van der Waals bonding) between S-Mo-S layers and the favorable distribution of electrons on the constituent atoms. Molybdenum disulfide is thermally stable in vacuum or inert environments, but in air or oxygen it begins to oxidize to MoO_3 at approximately 400°C .

MoS_2 is used as a boundary lubrication additive in virtually all grease thickener types and consistencies where high loads, low speeds, high temperatures and stop-start conditions exist.

The main lubricant sectors in which MoS_2 greases are used are transportation (automotive and rail), industrial, mining construction and agricultural and military/aerospace.

Pastes are a special form of greases that contain $>50\%$ lubricating solids. These products are used as problem solving materials, break-in aids and anti-seize compounds.

In fluid lubricants such as gear oils, MoS_2 dispersions can be effectively used to reduce friction, wear and bulk oil temperature in the boundary lubrication conditions found in worm gears, helical gears and hypoid gears.

Solid film lubricants containing MoS_2 are firmly bonded to sliding surfaces and are able to provide low friction and low wear without the presence of an oil or a grease. These coatings can be applied by several techniques including burnishing, impingement, sputtering and resin-bonding. The most common of these are resin-bonded coatings, which can be applied as thin films using the same processes used for paint application. Some resin-bonded coatings are oil compatible, providing surface protection when the fluid film is too thin.

References

1. Risdon, T.J., "Properties of Molybdenum Disulfide", Climax Molybdenum Company, January 2003
2. Bell, R.E. and Herfert, R.F. Preparation Characterization of a New Crystalline Form of MoS_2 , J.A.C.S., 79, 3351, 1957
3. Chianelli, R.R., Prestridge, E.B., Pecoraro, T.A. and DeNeufville, J.P. Molybdenum disulphide in the poorly Crystalline Rag Structure, Science, 203, 1105, 16 March, 1979
4. W. E. Jamison and S. L. Cosgrove, ASLE Trans., 14, (1971), 62-72
5. W. E. Jamison, ASLE Trans., 15, 4 (1972), 296-305
6. H. E. Sliney, "Proceedings of USAF Aerospace Fluids and Lubricants Conf., April 1963, (350-367). P. M. Ku, ed.
7. M. T. Lavik, T. M. Medved and G. D. Moore, ASLE Trans 11, (1968), 44-55

8. Lansdown A.R. Molybdenum Disulphide Lubrication, Tribology Series, 35, Elsevier, p.380
9. Magie, P.M., A review of the Properties and Potentials of the New Heavy Metal Derivative Solid Lubricants, Lubric. Eng., 22, 262, 1966
10. S. R. Guha Thakurta and A. K. Dutta, J. Phys. Chem. Solids, 44, (1983), 407-416
11. Mellor, J.F. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol.XI, Longmans Green, London, 1931
12. Kumar, A. Nagar, S.C., Mittal, B.D, et. al., "Titanium Complex Grease for Girth Gear Applications", NLGI Spokesman, 63, 6(1999)15-19
13. Fish, G, NLGI Spokesman, 51, 9, (1999), 14-29
14. ABIL Advocate, Vol. 7, No. 1, 2002
15. Nemecek, R. E., Lubrication Engineering, 37,5 (1981), 263-267
16. Pacholke, P.J. and Marshek, K.M., Lubr. Eng. 43, 8, (1987) 623-628
17. Braithwaite, E.R., and Greene, A.B., Wear 46, 2, 1978
18. Gresty, D.A., Kunz, E.J., and Risdon, T.J., SAE Paper 770834
19. Spalvins, T., NASA Technical Memorandum 105292, 1991
20. Peterson, M. B. and Winer, W. O., Wear Control Handbook, ASME, 1980
21. Selector Guide for Automotive Lubricant Applications, Molykote[®], Dow Corning Corp., 2005
22. Bickford, J. H., "Bolt Torque-Getting it Right", Machine Design, June 21, (1990), 67-71