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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 MoS_2 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.

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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. $1370^{o}C$ (non-oxidizing environment)
- Melting Point $1700^{o}C$ (under pressure)
- Sublimation temp. $1050^{o}C$ 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 MoS_2. The rhombohedral was first identified in a synthetic material [2] and subsequently found in several natural sources[3].

The hexagonal form is characterized by MoS_2 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 MoS_2 hexagonal type crystal structure[4].

Thus the excellent lubricant properties of MoS_2 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 MoS_2, there are six non-bonding electrons which can completely fill a band which physically confines the electrons within the crystal structure[5]. 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 MoS_2 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 MoS_2 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 Mo_2S_3, and to MoO_3 via a highly exothermic oxidation reaction in air at 500-600 ^oC . Reaction of natural MoS_2 and chlorine gas in absence of air at elevated temperature generates molybdenum pentacloride.

The oxidation characteristics of lubricant grade natural MoS_2 have been studied by several researchers. The thermal oxidation rate of MoS_2 in air studied by x-ray diffraction showed that below 300 ^oC, the rate is very slow and difficult to measure accurately, and that below 388 ^oC, MoS_2 oxidized at a slower rate than WS_2[6]. The oxidation behavior of MoS_2 in dry air has also been studied by thermogravimetric analysis[7]. It was determined that 10%, 50% and 90% MoO_3 was formed at temperatures of 435 C, 466 C and 516 ^oC respectively.

Besides temperature and humidity, the MoS_2 particle size can significantly affect the rate of oxidation. Smaller particles of MoS_2 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 MoS_2 can cause corrosion in certain cases
- oxidation of MoS_2 can determine the life of bonded or burnished MoS_2 films

- products of MoS_2 oxidation can cause an increase of friction
- oxidation of MoS_2 can cause problems with gelling capabilities in some greases
- oxidation of MoS_2 can lower maximum temperature for usage of MoS_2
- oxidation process determines shelf life of MoS_2

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 MoO_3 which is not abrasive[8]. Therefore, even after considerable degree of oxidation, molybdenum disulfide can still deliver an acceptable level of lubrication performance.

The electrical properties behaviors of MoS_2 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 MoS_2. According to Lansdown's observation[8] there is no clear agreement about electrical conductivity of MoS_2. However, the general view is that molybdenum disulfide could be classified as a "p" type semiconductor[9].

There is a strong correlation between MoS_2 conductivity and temperature. Despite the fact that absolute values of resistivity or conductivity could be different it is well established that with increasing temperature MoS_2 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 1.02×10^{-4} to 5.89×10^{-4} Ω^{-1} cm^{-1} parallel to it [10]. At the same time it was demonstrated[11] that at 19 ^{o}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 MoS_2 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 MoS_2.

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-hydroxysterate, 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 performance[12].

In general greases contain 1 to 2% of MoS_2 with critical parameters being surface roughness, load and speed. For the relatively rough metal surface the large MoS_2 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-caring ability at a given MoS_2 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 MoS_2 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 MoS_2 and high density polyethylene that has been used since 1961 in steering linkages, ball joints and wheel bearings. MoS_2 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. Fish[13] has detailed the complex and demanding role that greases play in the lubrication of CVJ's, many of which contain MoS_2. Also in the transportation sector, railroad curve-rail greases, either petroleum or soybean oil based, containing MoS_2 and/or other solid lubricants are being used to reduce wheel/rail wear and fuel consumption[14].

In construction, mining and agricultural markets, greases containing MoS_2 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 bearings[15]. 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 MoS_2 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% MoS_2 in a silicone oil is used as a backing plate lubricant in vehicles with disc brakes.

Military applications for MoS_2-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% MoS_2 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% MoS_2 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 MoS_2 could be between 0.1 and 60%, in most of cases of MoS_2 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 MoS_2 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 MoS_2 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 MoS_2 resulted in up to 5% improved efficiency and lower bulk oil temperatures[16].

In automotive hypoid axle tests, conducted under laboratory conditions, a 1% dispersion of MoS_2 in an 80W gear oil, a 1.5% gain in axle efficiency was achieved[17].

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% MoS_2 added gave a consistent 8 C lower operating temperature than the same oil without MoS_2[18].

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 MoS_2 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 MoS_2 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 MoS_2 is directed onto and adheres to the piston surface by entrainment of the powder in a high velocity air stream. The thin MoS_2 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 MoS_2 film is on O-rings to reduce friction between the elastomer and the metal surface with which it is in contact. The MoS_2 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 MoS_2 particle sizes (for example, Climax offers MoS_2 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 MoS_2 is accomplished by bombarding a target material of compacted MoS_2 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 MoS_2 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, MoS_2 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 Ag [8].

Sputtered films of MoS_2 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 MoS_2 films deteriorate due to the exposure of crystal edge sites[19]. 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 MoS_2 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 environment[19].

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 surface[20]. Many different compositions are commercially available with different binder and additives.

A typical formulation is composed of MoS_2, 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 durability[21]. 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 tightening[22].

A variety of MoS_2 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 MoS_2 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 MoS_2 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^{o}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.

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