RECLAMATION
Managing Water in the West

Technical Memorandum No. MERL-2011-37

Investigation of Molybdenum Disulfide and Tungsten Disulfide as Additives to Coatings for Foul Release Systems

**Materials Engineering and Research Laboratory,
Technical Service Center**

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The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Denver, Colorado

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Introduction

Reclamation is involved in research to identify and evaluate various coatings based on the ability to deter attachment of zebra and quagga mussels on submerged equipment. Molybdenum disulfide, tungsten disulfide, and graphite are the leading solid film lubricants on the market today. One of the conceptual ideas was to determine the feasibility of using one or more of these materials as a coating material or additive in a coating system to enhance foul release performance. Reclamation is interested in this compound because of its very low coefficient of friction values, and its success in other industrial applications. However, no research has been conducted with regards to its effectiveness in preventing mussel attachment. This review investigates the current uses, physical properties, and safety considerations, as well as the practicality of incorporating these materials into a foul release coating.

Current Uses

Molybdenum Disulfide, tungsten disulfide, and graphite are currently being used in industrial, manufacturing, mining, marine, agriculture, and automotive applications to reduce friction and wear.[1] During the Vietnam War, a product called Dri-Slide was used as a weapons lubricant to allow smoother passage of ammunition through gun barrels.[2] This resulted in less bullet deformation and better ballistic accuracy. It has also been used in CV and universal joints, as well as two stroke motorcycle engines. Bicycle suspension systems and many other transportation applications, including cars and motorcycles, rely heavily on these materials in various forms for dry lubrication between moving parts. Molybdenum disulfide is used in coatings to reduce the coefficient of friction.

Bureau of Reclamation Application

Zebra and Quagga mussels are a non-native invasive aquatic species originating in Asia. In 1989 they were found in Lake Erie. More recently, in January 2007, Quagga mussels were discovered in Lake Mead on the Colorado River.[3] These two species pose a significant risk to Reclamation infrastructure. The main threats lie in the mussel's capability to decrease reliable performance at Reclamation facilities. Zebra and Quagga mussels can attach to pumps, intake systems, penstocks, trash racks, screens, and small diameter pipes. This can cause increased head loss and flow blockage, leading to a significant decrease in equipment performance.

Foul-release coatings are one solution being sought to mitigate the potential effects of an infestation. Foul-release coatings function well in preventing mussel attachment as seen in previous studies.[4,5] The silicone foul release coatings work on two basic principles, low surface energy to prevent the mussel adhesive from bonding well, and low elastic modulus to create a peeling fracture between the mussel byssus and substrate. Even though the silicone foul release coatings work, they lack the durability to withstand abrasion and gouging. So far, Reclamation has evaluated many durable foul release coatings with limited success, as the mussels attach to these coatings eventually.[5]

The concept of making a durable foul release coating using molybdenum disulfide, tungsten disulfide, or graphite is to prevent mussel attachment by allowing the weakly bonded atomic layers to peel off the surface with the mussel byssus thereby creating a coating in which a small amount of material is expended incrementally each time a mussel is released. The layers of solid lubricant would require a shear force created by water flow in order for the mussels to shear off the surface. It is assumed that the mussels can and will attach, and that this product probably will not work in a static water environment.

However, with enough shear force the mussels will slough off the surface. If a binder is required, the coating binder would have to slowly erode to expose fresh lubricant to the surface.

Properties

Molybdenum disulfide (MoS_2) is a naturally mined inorganic material that occurs as the mineral Molybdenite. This crystalline solid is extracted from Henderson mine in Clear Creek County approximately 50 miles west of Denver, Colorado. [6] Molybdenum disulfide has many unique properties, which makes it one of the most popular solid film lubricants on the market today. Figure 1 shows the crystal structure of Molybdenum disulfide.[2] Molybdenum disulfide has a lamellar structure material much like graphite and tungsten disulfide. Lamellar structured materials are ones containing layers which alternate between different atoms. Its structure can be thought of as a series of layered sheets, with a molybdenum layer sandwiched between two sulfur layers. These sheets are more commonly referred to as basal planes, set up as a hexagonal crystalline structure. Each basal plane has a central atom surrounded by six others.

Molybdenum disulfide also contains more than one type of chemical bond. Looking at Figure 1, the horizontal bonds are within the basal planes, and vertical bonds are in between the basal planes. Structurally, molybdenum disulfide functions in a manner intended to keep the basal planes intact, even when faced with a tangential force. Strong covalent bonds within the planes function to serve this purpose. There are two types of vertical bonds: the longer sulfur-sulfur bonds which are 3.08 angstroms long, as well as the shorter sulfur-molybdenum bonds which are 1.54 angstroms long. [7] The longer sulfur-sulfur bonds are connected by weak van der Waals forces and the shorter sulfur-molybdenum bonds are connected by strong covalent bonds. [8] The configuration actually creates a net positive charge on the surface of the layers causing an electrostatic repulsion between the layers. Van der Waals forces are the weakest of all types of chemical bonds. These bond strengths and locations give molybdenum disulfide its lubricating properties by promoting shear deformation along the basal plane between the two sulfur layers. This provides a low coefficient of friction. In static conditions values have been reported at approximately 0.07, while dynamic conditions are as low as 0.03. [9]

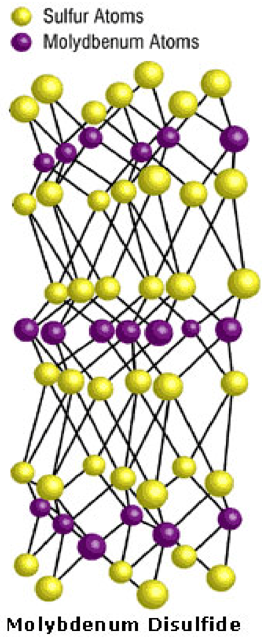

Figure 1: Crystal Structure Molybdenum Disulfide[2]

The lubricating properties are not a result of absorbed films, gases, or liquids.[10] Molybdenum disulfide is considered a sacrificial lubricant and transfers material between the two mating surfaces involved, which is aimed to increase wear resistance. These sacrificial layers, and its lubricating properties, give the coating its low coefficient of friction. Figure 2 shows coefficient of friction values for three selected materials at different contact pressures between mating surfaces coated with solid lubricant.[11] At low pressures all three materials appear to have equivalent coefficient of frictions.

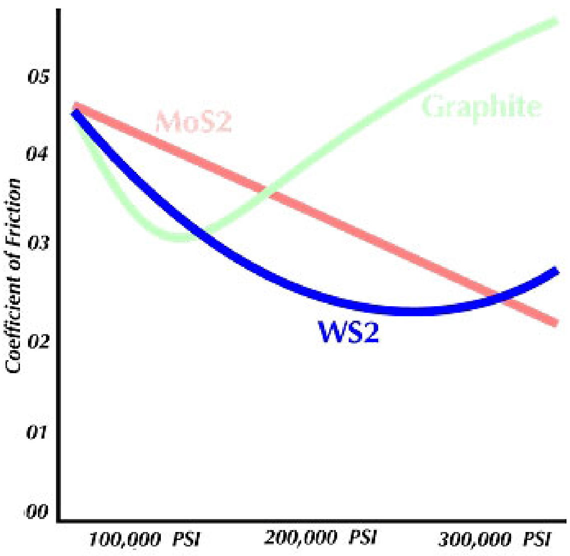

Figure 2: Coefficient's of Friction on selected materials at various pressures.[11]

Graphite and Tungsten Disulfide are also used as dry lubricants and have many similar properties and crystalline lattices to molybdenum disulfide. However, each material reacts differently at various loading pressures. Tungsten disulfide operates best between contact pressures of 125,000 to 300,000 psi, while graphite functions best below 100,000 psi. Molybdenum disulfide has the lowest coefficient of friction at contact extreme pressures above 300,000 psi.

Besides the working pressures, another interesting fact is that graphite relies on an adsorbed vapor or moisture layer to reduce the coefficient of friction.[12] The coefficient of friction actually increases slightly if molybdenum and tungsten disulfide develop a moisture adsorbed layer. Since the application will be in water immersion, graphite may actually work better than the other materials.

Table 1: Physical Properties of Molybdenum Disulfide, Tungsten Disulfide, and Graphite[14, 15]

Name	Molybdenum disulfide	Tungsten disulfide	Graphite
Chemical Formula	MoS_2	WS_2	C_4
Molecular weight	160.08 g/mol	248 g/mol	12 g/mol
Density	5.06 g/ml	7.5 g/ml	2.16 g/ml
Hardness	1-1.5 moh’s	0.5-0.75 moh’s	1.5-2 moh’s
Water solubility	Insoluble	Insoluble	Insoluble
Chemical Durability	Inert	Inert	Inert
Contact angle	60 degrees in H_2O	93 degrees in H_2O	85 degrees in H_2O
Surface Tension	24 dynes/cm	not available	55dynes/cm
Compatibility	Oil, solvents, paint, fuel	Oil, solvents, paint, fuel	Oil, solvents, paint, fuel

Literature reports a molybdenum disulfide contact angle of 60 degrees with water, but has an overall surface tension value of 24 dynes/cm, a relatively low value which is similar to what is found in silicone foul release coatings.[16] Low surface tension is synonymous with surface energy and describes the energy created by broken atomic bonds at the surface. When a bond is created between two surfaces, the free energy is lowered but this energy must be balanced by the interfacial free energy of the substrate-air interface, and the liquid-air interface. The total surface energy of the solid substrate (24 dynes/cm) is the sum of a dispersive component and a polar component. A low contact angle with water would indicate a higher relative contribution from the polar component. This would signify that hydrophobic molecules which tend to be non-polar (dispersive) molecules would maintain a much higher contact angle. Mussel adhesives are hydrophobic, so the mussel adhesive may not adhere well to the surface. This has not been proven or evaluated to date, but it was an interesting observation seen in the literature. Regardless if the mussel adhesive adheres well to the molybdenum disulfide, the dominating mechanism for foul release will be the disbondment of the basal planes under shear forces. The bond strength between basal planes for graphite and molybdenum disulfide is critical for this concept to achieve success. Studies have been done in an effort to obtain data on peeling forces for graphite and molybdenum disulfide. These forces are very weak and it was determined that less than 10 kJ/mol is required to separate graphene sheets.[17]

Hazards and Safety

Reclamation must abide by the clean water act for keeping waters safe for drinking by humans and animals, for use by farmers to water crops, and to insure a safe living environment for native aquatic wildlife. It is important to assess the safety and health risks with molybdenum disulfide if it is put in the water. Graphite is not as big of a concern since it is used for purifying water.

Human and animal testing have been done to evaluate the effects of short term and long term exposure to molybdenum disulfide. Information on human trials is very limited. Significantly more research has gone into animal testing, and will be the focus of this section. Molybdenum can react to form compounds which may or may not be soluble in water. The soluble compounds are considered to be hazardous while the insoluble ones are considered non-toxic and chemically inert. Molybdenum Disulfide is an insoluble compound and is considered to be safe. Molybdenum disulfide doesn't react with moisture unless it is at very high temperatures.[18]

Studies have been conducted on rats, rabbits, and guinea pigs on the effects of acute toxicity to molybdenum disulfide. The acute inhalation hazard is very low, and manufactures are not required to label molybdenum disulfide with the risk phrase harmful by inhalation. Multiple oral toxicity studies were done. In one study, a group of rats received a single oral dose of 2,000 mg per kg of bodyweight. There were no deaths and the only side effects reported were a hunched posture and an ungroomed appearance displayed in all the rats participating in the study.[19,20] Recovery was seen in all rats by day four, satisfactory weight gains were observed, and autopsies on day fifteen revealed no abnormalities. In another study, rats were subjected to a single dose of 6 grams per kilogram of bodyweight.[20] No fatalities were seen, and all rats appeared normal, with no signs of any side effects.[20] Acute dermal toxicity studies revealed that molybdenum disulfide is not required to be labeled with the phrase harmful in contact with skin.[20] After a topical cream was applied of 2,000 mg per kg of bodyweight, there was no systematic response in any of the rats.[20]

Molybdenum Disulfide has also been used in medical devices, food applications, and fertilizers.[21, 22, 23] From these studies, it appears that molybdenum disulfide is a safe compound. Acute and subchronic studies in animals indicate no health hazards. Human studies, though limited, have allowed insight into its toxicity towards humans. In a preliminary assessment and health hazard classification of Molybdenum Disulfide, it was said that with the available information, there is no need for a health hazard classification, due to its negligible solubility and chemical inertness.[24]

Coating Methods

Molybdenum disulfide is a versatile compound that can be applied as a standalone coating to a variety of metals and other substrate materials including glass, plastics, ceramics, and coatings. One of the simpler coating methods is referred to as a burnished film where molybdenum disulfide can actually be physically rubbed onto a substrate. In doing so, a 1 to 5 micrometer thick film is created. Another simple method is using impingement with a high velocity particle-entrained air stream and would be the preferred method of application. A sample of a nut and bolt coated with Tungsten Disulfide using the impingement method was examined at Reclamation's Materials Research Engineering Laboratory (MERL). Figure 3 shows a photograph taken under low magnification (35X). Note that layers of coating are visible on the bolt surface.

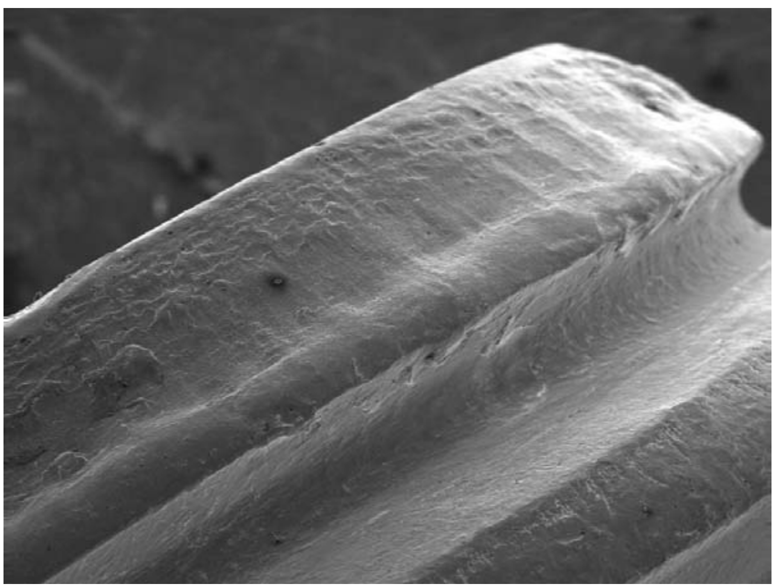

Figure 3: Bolt coated with Tungsten Disulfide at 35X magnification. The bolt was coated using the impingement process.

The nut spins easily over the bolt even when angular forces are applied during threading. The coating appears to be well adhered to the surface coating and is not easily transferred during casual handling of the piece. Figure 2 shows the end of the coated bolt where a fingernail scratch test was performed. The scratch is visible but the underlying substrate does not appear to be exposed.

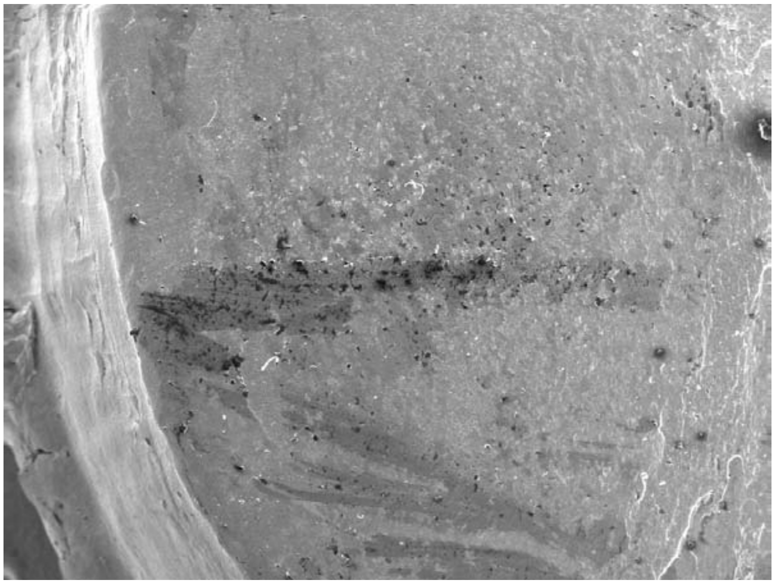

Figure 4: Fingernail scratch visible on the end a bolt coated with WS_2 (35X Magnification)

Physical Vapor Deposition or PVD is another common coating technique used for molybdenum disulfide. However this technique is not practical in coating large infrastructure. Therefore this technique will not be pursued.

Molybdenum disulfide and graphite are easily incorporated into coating binder systems in high volume fractions (loading). These compounds reduce the coefficient of friction in coatings. Commercial coatings that contain molybdenum disulfide or graphite are designed for other applications and the binder systems do not erode or ablate easily. Some typical binder resins include acrylic, phenolic, epoxy, amide-imide, urethane, and polyamide. These products are currently available from a variety of commercial vendors and are marketed to the oil & gas, aerospace, and manufacturing industries as wear resistant coatings designed to increase a product's service life.

Dry lubricants are available in powder form from several Vendors. The morphology of the individual particles is not actually spherical but more platelet-like. A platelet shape will help maximize the surface area at the exposed surface when dispersed into a binder. Particle size ranges from less than 400 nm up to 30 μm. Retail prices for MoS_2 were approximately 30-40 $/lb depending on size and quantity at the time of this study. Graphite prices ranged anywhere from 10-30 $/1b. WS_2 prices were considerably higher at 80-100 $/lb.

Prior art

A patent was found that incorporated molybdenum disulfide or graphite and cuprous oxide into an antifouling coating.[25] The formulations only used 10-20 percent graphite or molybdenum disulfide in the overall cured coating. This shows that other scientists are thinking of similar ideas or concepts. The inventors were able to demonstrate that these coatings successfully deterred attachment of fouling organisms. However, the findings appear to be inconclusive because cuprous oxide, a biocide, was also included as an ingredient in most of the coating systems.

Future Work

Molybdenum disulfide and graphite may offer some potential for foul-release applications. In addition, the health and safety characteristics of molybdenum disulfide do not preclude its use on hydraulic infrastructure.

Plans for next fiscal year will include formulating both graphite and molybdenum disulfide into an erodible binder such as rosin. There will be an impingement type coating application for both graphite and molybdenum disulfide on epoxy coated steel. There will be an application using the burnishing method on epoxy coated steel. These test coatings as well as several commercial products containing graphite and molybdenum disulfide will be incorporated into Reclamation's field study at Parker Dam where other foul release coatings are currently being investigated.

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