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Session III
Lamellar Solids

Chairman: Mr. MEL LAVIK (Midwest Research Institute, Kansas, Mo.)

Discussion led by: Dr. BRUCE DANIEL

MECHANO-CHEMICAL FACTORS IN MoS₂-FILM LUBRICATION

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SUMMARY

The friction properties and the well reproducible endurance limits of MoS₂-lubricant films, prepared from the dry powder, were studied on rigs. Special consideration was given to: (i) automation of the rubbing-in process, (ii) the control of temperature and atmosphere, (iii) photographic recording of the friction surface.

The influence of *physical* factors was found to be similar to that known already for resin coated MoS₂ films. Life expectancy is dramatically shortened by certain *chemical* factors: (a) instantaneously scoring pairs of metals as substrates, and (b) mechano-chemical reaction with water vapour and with oxygen. In a neutral atmosphere the life of the lubricant film becomes very long.

In a film of metallic lustre and under conditions of dynamic loading, blisters, ultimately of microscopic dimensions, are rapidly formed. Blistering can be enhanced by physical means, *e.g.* addition of amorphous carbon, or by oxidation. Prolonged oxidation leads to embrittlement and finally descaling of the MoS₂ film from the substrate.

INTRODUCTION

The outstanding position of molybdenum disulphide (MoS₂) within the family of solid lubricants is due to the fact that it performs well over wide ranges of temperatures and loads. However, there is still a need for compositions which will function under even more severe conditions. It seemed desirable to learn more about the causes of MoS₂ film failure, and, therefore conventional friction rigs were perfected until highly reproducible data on endurance limits could be obtained.

In the course of this development, a number of factors were noted which impair the life of the lubricant film. Looking back at this experience, we can separate these phenomena into two groups: physical factors and chemical factors. We shall show that the chemical factors are by far the more important, but they differ from ordinary chemical phenomena: the reactions detrimental to the film occur rapidly only under conditions of friction; they are therefore of a mechano-chemical nature.

The breakdown of a lubricant film is a special case of surface fatigue. In any fatigue study it remains unsatisfactory to draw conclusions only from a post-mortem. By adding a cine-film unit to our equipment, it became possible to observe changes on the lubricated surface during the friction process. The formation of blisters has been observed previously by most workers in the field. The principal aim of the present study is to understand the significance of this phenomenon and its interrelation with mechano-chemical processes.

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EQUIPMENT

Our experiments were principally performed with a pin (8 mm diameter) and ring (75 mm diameter)-type friction rig developed originally for a study of mild and severe wear¹. Loads were variable between 1–150 kg and speeds between 5–300 m/min. The friction couple was kept in an almost gas-tight transparent casing, which made complete control of the surrounding atmosphere possible.

Friction was recorded and at a pre-set high friction value, indicating the onset of scoring, the drive was cut off automatically. Wear was also recorded, but no wear at all occurred during the smooth running period discussed below. About 1 mm below the friction surface of the ring the temperature was measured with a pair of thermocouples.

The morphological changes of the lubricated surface of the ring were recorded photographically by stroboscopic illumination. The same surface area could be photographed either after each rotation, or, in other cases, after a pre-set number of rotations.

For some experiments the standard LFW-1, manufactured by the Alpha Molykote Corporation*, was fitted with automatic recorders. Results with this machine at somewhat heavier loads and lower speeds were reasonably similar to those obtained on our friction rig. Experiments at low and moderate loads (up to 5 kg) were made on a pin and disk machine, which could also be used for experiments with glass disks.

The powder was rubbed-in on a specially constructed machine. The prepared surface of the ring was rotated and rubbed with a MoS₂-filled sponge at a load of 5 kg. It was found that this pre-treatment was essential to obtain reproducible results.

STANDARD TEST CONDITIONS

In order to evaluate the influence of physical and chemical parameters, it was necessary to establish a "standard" condition. Rings were made from a hardened chromium steel (Jessop Alloy C) of Vickers Hardness $H_V = 770 \text{ kg/mm}^2$. Pins were made from "Jessop black label 65" steel of $H_V = 260 \text{ kg/mm}^2$. The rings were wet-blasted with pure quartz sand in water to a roughness of 0.3–0.4 μ c.l.a. As the sieved quartz sand consisted of cuts between certain mesh numbers, the actual surface pattern obtained was very regular. This is important, because isolated peaks will tend to pierce the lubricant layer. Before coating the rings were cleaned with acetone and carefully dried. Pins were ground to 0.05 μ c.l.a. and were used without pre-coating. The powder was rubbed-in mechanically for 30 min at about 50% relative humidity.

The ring was now rotated at a linear speed of 60 m/min and the load, beginning with 2.5 kg, was increased every two minutes with intermediate steps of 6.5, 14.5 and 30.5 kg until the standard load of 62.5 kg was reached after 8 min. Purified air was conditioned to 30% RH at 25°C, and blown into the casing.

The friction record, after running in, was perfectly smooth with an average value of $\mu = 0.07$. Friction became unstable after about 13 hours' continuous running at a load of 62.5 kg, and varied between $\mu = 0.04$ and 0.1. This stick-slip period can last several hours. The experiment was automatically terminated when a friction peak reached $\mu = 0.3$. Experience has shown that the first, smooth phase is reproducible to better than 20% ($13 \pm 1.5 \text{ h}$), whereas the second phase, the stick-slip period,

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differs much more between otherwise identical runs. Comparison with the LFW-1 rig, where stick-slip rarely occurs, indicates that stick-slip depends not only on the properties of the friction film, but also on the construction of the testing rig. Wear occurs only during the second, the stick-slip, phase. All conclusions in this paper are, however, deduced from the length of the first, the *smooth running friction period*.

INFLUENCE OF PHYSICAL FACTORS

In general, the results obtained using dry powders were fairly similar to those reported by PALMER² for resin bonded films.

Surface roughness

SONNTAG³ has shown that, for bonded films, wet (sand)-blasted rough surfaces have a vastly superior life expectancy over polished surfaces. This conclusion is confirmed by our experiments with dry powders. While the standard time for wet-blasted rings covered with MoS₂ was 13 h, rings polished to 0.004 μ c.l.a. and with MoS₂ powder rubbed-in frequently survived only for minutes. Even when seizure occurred later, sometimes after one hour, the friction track during this period was highly irregular. Moreover, the survival of the lubricant film depends in this case on the type of powder and the details of the rubbing-in process⁴.

The c.l.a. value of surface roughness as such, is important, but the actual surface topography is also important. The influence on life expectancy here is less spectacular, but the process of destruction differs in essential details. Fig. 1 (a) shows a sand-blasted surface after rubbing-in, and the same surface after running under heavy load for about 3 km is shown in Fig. 1 (b). It is evident that blisters have been formed. On another part of the same surface descaling has already occurred, and the surface of the supporting metal becomes visible, (Fig. 1 (c)). This proves that blisters form *between* the metal and the coating. The actual thickness of the MoS₂ film can be estimated from this photograph to be about 2 μ . This local damage, however, does not spread; therefore, the ring will survive many more hours of rubbing. The difference between a wet-blasted and turned surface after running-in of the powder becomes evident from Fig. 2. No blisters are visible after the same period of running. They probably are formed, but immediately cause descaling.

Hardness

If the hardness of the steel pin is reduced below 200 kg/mm², or increased above 800 kg/mm², life expectancy is reduced by about 30%. Although measurable, such effects are small compared with the influence of surface roughness.

Load and speed

For a correct comparison between experiments performed at different speeds, the distances travelled, and not the time of survival, must be considered. This distance was about 40 km for our "standard experiment". Speeds were varied between 1.4 m/min and 168 m/min, and loads between 21 kg and 272 kg. (The range of experimental conditions was extended by performing some of these experiments on the LFW-1 machine.) Comparison of numerous results at a similar product of load $\times$ speed suggests that the influence of these factors is comparatively small as most data fall between the limits of 40 ± 10 km. There is, however, some tendency for longer survival

in the combination of high speeds with low loads (important in space engineering). At the other end of this scale, runs were performed at the lowest speed and highest load; they took 5 days, but a distance of only 9 km had been travelled by the pin during that time, when the film broke down. We shall show that the atmosphere is reactive, so it seems logical that a chemical influence becomes more significant over longer periods of exposure.

Rubbing-in time

Whether the influence of rubbing-in should be listed as "physical" or (also) as "chemical" is not yet certain. By increasing the rubbing-in time from our standard of 30 min to 100 min, the endurance limit is raised by about 3–15 h. On reducing the rubbing-in time to 15 min, the MoS₂ film breaks down 2–3 hours earlier. At an even shorter rubbing-in time, the lubricant film is still less stable and results finally become erratic.

Composition and properties of MoS₂ powders

CANNON⁵ has analyzed specimens of pure natural massive molybdenite; he found only 38.4% sulphur (calculated 40.2%). We have analyzed similar material. After mechanical removal of HCl-soluble impurities, we have found only 37.5% sulphur. It therefore seems unlikely that pure MoS₂ can be obtained from natural sources without intense purification. Several samples of high grade technical powders were analyzed for sulphur by the zinc oxide–nitric acid method⁶ and were found to contain at least 39.0% sulphur. Only traces of other metals and of SiO₂ were present. A particularly interesting point is that the theoretical sulphur content is 40.2%, the balance of about 1% being made up by carbonaceous material, which can be estimated by the conventional method for carbon analysis in steel. This fact is well-known in the trade, but has not yet been mentioned in the scientific literature. The carbon compounds are presumably formed when the raw material is heated in a reducing atmosphere at 850° in order to drive off flotation oils⁷.

MoS₂ powders were heated in a vacuum, and the gases released were analysed chromatographically. Oxygen and nitrogen were driven out first, followed by carbon dioxide above 300°C. Methane was released above 400°, and hydrogen from 450° upwards. We found only traces of carbon monoxide, but CANNON⁵, who analysed gases released between 1000 and 1800°C, found essentially carbon monoxide and some hydrogen. Similar results were obtained on heating thermal carbon blacks. It therefore seems probable that the high-quality powder contains small quantities of "carbon black". Whether this is of practical importance remains to be seen, but in view of the effects obtained with carbons as reported later a possible influence of this impurity should be kept in mind.

Ross^{8,9} has studied the surface oxidation of MoS₂ extensively. It is now known that the surface of the powders contains small quantities of SO₂ and SO₃, which were determined by titration. The amount of these impurities was small in all samples used. Finally, small quantities of molybdenum oxide, if present, were determined by solution in ammonia¹⁰; the content is dependent on the previous history of the sample.

The loss of volatiles from a powder dried at ambient temperature was followed by thermographic analysis. It was less than 0.5% for a powder having a surface area of

Fig. 1. MoS₂ film on a sandblasted steel surface. (a) After mechanical rubbing-in with MoS₂; (b) blister formation after running under a heavy load for 15,000 revolutions; (c) initiation of descaling, also after 15,000 revolutions.

Fig. 2. A MoS₂ film on a turned-steel surface. (a) After mechanical rubbing-in with MoS₂; (b) and (c) descaling after 15,000 revolutions (no blisters are visible).

4 m²/g (B.E.T. method), but it increased to about 2% on heating fine powders with a larger surface area to 800°C.

A synthetic MoS₂ (40.0% S) was prepared¹¹ free from elemental sulphur. However, this sample was only partly crystalline (X-ray analysis). It had similar friction properties to the natural product, but a much shorter life under standard friction conditions. It is known that the crystal structure differs from that of the natural product^{12,13}.

It is sometimes claimed that the oxidation products of MoS₂ are hard and abrasive. Indeed, when the sulphide was heated in a nitrogen atmosphere above 800°C, in a quartz tube, hard particles were formed; they were not further analysed as quartz is attacked by MoS₂ vapour.

SIDGWICK¹⁴ reports a MoO₃ melting to a dark yellow liquid at 795°C. Oxides prepared by us from the sulphide at 500°–650°C by oxidation with dry oxygen were slightly yellow and quite soft. Numerous studies^{15–17} deal with the complex structure of oxides of the general formula (Mo_nO_{3n-x}). It is known that these oxides can form deeply coloured hydrates¹⁸, one of which is the well-known molybdenum blue. No indication was obtained that small quantities of these oxidation products increase the coefficient of friction, or reduce the life of the friction film; this is in good agreement with reports from other laboratories¹⁹.

Summing up, we would expect impurities to influence the colloidal properties of suspensions²⁰, as well as the corrosive properties of greases²¹. However, *small* quantities of soft impurities seem to have little influence on the friction properties and on the life expectancy of the film prepared from a high grade dry MoS₂ powder.

INFLUENCE OF CHEMICAL FACTORS

Influence of the substrate

When a titanium rider was rubbed on a glass plate loaded to only 600 g, a friction coefficient of $\mu = 0.6$ was measured. On addition of MoS₂ this value was reduced to about $\mu = 0.1$, which was maintained for several hours in a dry argon atmosphere. The experiment was repeated with a titanium disk and, in other runs, with a molybdenum disk against a titanium pin lubricated with MoS₂. Even at the smallest load possible (50 g), seizure occurred after less than 5 sec. By preparing, first, a well run-in MoS₂ film on molybdenum metal, the time to seizure was increased to about 5 min. It is known²² that certain other solids with layer structure are more efficient with titanium. Rubbing 60/40 brass against MoS₂-covered steel gave an irregular friction track from the very beginning of the experiment which lasted only a short time. Obviously, such scoring pairs of metals, which have a very short dwell period, cannot be parted effectively by an MoS₂ film for any considerable length of time.

Influence of moisture

HALTNER AND OLIVIER²³ have shown that H₂S is formed from MoS₂ and water vapour under conditions of friction; we were able to confirm these results. Tests were performed on the pin and disk machine in dry argon, nitrogen, and air at loads ranging from 0.6 kg to 5.0 kg. By cooling the turn-table on which the disk was mounted, the average surface temperature of the disk did not exceed 25°C.

In a dry atmosphere the MoS₂ film was not destroyed after many hours and no H₂S was developed (odour!). Runs were repeated in argon and nitrogen, with a relative humidity of 90% and at 25°C. H₂S was immediately formed in large quantities,

and the friction coefficient increased until it reached a value of 0.8, after which it gradually dropped again to a value of about 0.15. During this period (several hours) the colour of the lubricant layer changed from grey to deep black, and gradually the film began to bleach until it became cream-coloured. Obviously, the sulphide was transformed *via* hydrates to oxides. It is important to notice that this oxidation of MoS_2 takes place under conditions when even the "calculated"* flash temperatures are quite moderate, *i.e.* about 80°C . It is a mechano-chemical reaction, typical of the freshly-formed friction surface.

In air, only traces of H_2S were found analytically, but again a large increase in friction coefficient was observed. The reaction product was essentially yellow solid sulphur. No continuous film was formed and the powder finally turned brown. As no iron was found in the rubbed-off brown powder (X-ray analysis), it is concluded that only MoS_2 was oxidized.

In view of these well-known, vigorous reactions with high concentration of water vapour^{24,25}, it was to be expected that even small amounts might reduce the endurance limit of the friction system. Quite unexpected, however, was the experience that small quantities of water vapour in air are *beneficial* and increase the length of the smooth-running period, as well as the total life of the film. Results obtained with the pin and ring machine at standard load and speed are summarized in Fig. 3.

Fig. 3. Influence of humidity on the friction coefficient and life expectancy of a MoS_2 film on steel. Load, 62.5 kg; linear speed, 60 m/min. The humidity of the surrounding atmosphere (lower scale) is higher than that of the surface of the ring (upper scale), because the latter is warm (left-hand scale). The friction coefficient (right-hand scale) increases with humidity and is higher in the beginning (μ_i) than near termination (μ_e) of the run. The period of constant friction (left-hand scale) depends on the humidity of the atmosphere.

* The model proposed by J. F. ARCHARD (*Wear*, 2 (1959) 438) was used; we intend to deal with details in the future.

Humidity was increased from 0 % relative humidity for specially-dried air from cylinders until the saturation point of the supplied air was almost reached. However, from the measured temperature of the ring (from 40–50°C) the humidity at the friction surface was calculated to be much lower (from 0 %–21 % relative humidity). The initial coefficient of friction is increased from 0.06 for dry air to about 0.12 for 7% moisture at the surface of the ring (a corresponding increase in temperature occurs).

The smooth running period is increased *discontinuously* when 7% relative humidity is reached from approximately 6 h to approximately 13 h; the latter period is for normal endurance under standard test conditions.

A further increase in moisture has little influence until, at high humidity, the continuous film is rapidly destroyed. It is remarkable that at 0% relative humidity the MoS₂ film has its brightest "metallic" lustre, coupled with rapid formation of many large blisters.

Influence of oxygen

Substitution of dry oxygen for dry air led to the expected, enhanced oxidation of the film, and the lifetime was reduced to about 3 h. This is half the value for dry air. Preliminary experiments in "pure" argon did not indicate a large beneficial effect, due to contamination with oxygen. However, careful removal of oxygen gave quite a different result. In argon containing about 0.05% oxygen (analyzed mass spectrometrically), the endurance limit was raised to above 150 h. Table 1 illustrates the decisive role played by oxygen in limiting the life expectancy of a dry MoS₂ lubricating film. The coefficient of friction in argon (with 0.01% oxygen) is finally reduced to $\mu = 0.02$, *i.e.* to half the value observed in air. This significant observation is in good agreement with the results reported by HALTNER at this Conference²⁶.

TABLE I

INFLUENCE OF OXYGEN ON ENDURANCE LIMIT OF MoS₂ FILM (DETERMINED ON A PIN AND RING MACHINE)

Standard conditions: load, 62.5 kg; linear speed 60m/min; dry atmosphere.
At least three runs were performed in each atmosphere.

Gas	Time to onset of stick-slip (h)
Oxygen	2–4
Air	6–9
Argon containing 0.05% oxygen	>150

FORMATION AND DESTRUCTION OF BLISTERS

Formation of blisters

The formation of blisters was studied on the electron microscope level at low loads (5 kg) and high speeds (100 m/min). In dry or moderately moist air a few blisters (of 0.3 μ diameter) were formed rapidly (Fig. 4). The number and size increased continuously, and, after some time, the largest blisters (3 μ) came within the range of

microscopic observation. The electron microscope picture reproduced (Fig. 5) shows that these comparatively large blisters are built up from a multitude of small voids clustered together. Observed at a magnification of 12,000, the diameter of such "proto" blisters is estimated to be 400 Å. At high humidity, the lubricant film looks like putty, and blister formation becomes negligible. The mechanically weak film is destroyed by the formation of crumbs, which are readily rubbed-off.

Fig. 4. Electron microscope replica of MoS₂ film on steel run in air at 13% relative humidity under a 5 kg load with a linear speed of 100 m/min after 100 revolutions. Replica technique: plastic layer – chemical removal of MoS₂ – carbon deposition – tungsten oxide shadowed.

Fig. 5. The same as Fig. 4 after 100,000 revolutions. (a) Overall view; (b) electron microscope enlargement of detail.

Influence of oxidation on blistering

Cine-films taken at high loads show that blisters of an average size of 0.2 mm and a maximum size of 0.5 mm are formed after some time. In oxygen such blisters are formed after about 15 min. Blister formation in air occurs after a slightly longer time, and in argon containing 0.05% oxygen blister formation occurs after approximately

1 h. In the presence of oxygen, the surface rapidly acquires a metallic lustre, and this condition seems to promote blistering. The phenomenon is distinctly dynamic. The blisters in a certain area are pressed back during the following rotation, and new blisters appear and disappear continuously although the surface remains intact.

Fig. 6. Frames of cine-film of friction surface using MoS₂ on steel under a load of 62.5 kg and at a linear speed of 60 m/min, run in air at 25% relative humidity at 25°C. Exposure after one revolution between frames. (a) Typical of the beginning of blistering during the first hour; (b) typical of most of the life of the lubricant film; (c) typical of the situation shortly before onset of the stick-slip period after 13 h.

Blisters are extremely brittle, and implode to form a fine powder. This brittleness is probably enhanced by oxidation. The size of blisters formed decreases gradually, and descaling commences where many of these small blisters occur during the final phase. It is surmised that, in the absence of oxygen, no descaling would take place. Figure 6 gives an impression of these changes observed using a cine-camera.

Influence of carbon on blistering

Natural graphite powder forms lubricant films only with difficulty. The run-in period between successive steps of loading must be at least 30 min, and the life of the film is much shorter. Blisters are observed, but on a minute scale. It is well-known in the trade that certain mixtures of MoS_2 and graphite in bonded films have a better life expectancy than pure MoS_2 ²⁷. The correlation of this phenomenon with the dynamic nature of the lubricant film is still being studied.

Fig. 7. 5% (by weight) of a thermal carbon black (P 33) has been added to the MoS_2 powder. Conditions are identical with those used for Fig. 6 (a). Exposure after successive rotations.

Addition of amorphous carbon blacks, even in small quantities, to MoS_2 , greatly reduced the life expectancy of the film. The characteristics of the blistering also changed. On addition of a thermal black (P 33) giant blisters are formed, some of them attaining diameters of 2 mm (Fig. 7). Even these blisters show a distinctly dynamic behaviour; they are pressed back under the passing pin and reappear in a slightly modified shape when pressure is released.

DISCUSSION

An attempt will now be made to separate adhesion, friction and ageing processes of the lubricant film.

Although the run-in film cannot readily be rubbed off, *adhesion* forces do not balance strong shearing forces. This is borne out by the influence of surface roughness and the inability of the film to serve as a parting agent for badly-scoring pairs of metals. It would appear that adhesion is due only to intermolecular forces of a physical nature.

Friction generally decreases with increasing load, presumably as a consequence of better orientation in the plane of shearing²⁸. The lowest coefficient of friction observed in this research occurred in a well run-in MoS₂ layer in argon containing traces of oxygen. This fact suggests that in very pure argon friction forces would still become even smaller.

We surmise that *ageing* of a high grade MoS₂ film is initiated by blocking of slip planes by the inclusion of oxidized areas in the crystalline friction film. This blocking of individual lamellae first gives rise to the observed continuous flat film having a bright metallic lustre. Blisters are readily nucleated in such a dense film. In other words, there are two factors which facilitate sintering of the particles at moderate temperatures: shear compression, and oxidation *in situ* of reactive crystal sites. Quite recently, evidence has been published that annealing of pyrolytic graphite is accelerated by shear compression²⁹.

Both the similarities and the differences between MoS₂ and graphite become evident if the reasoning of MIDGLEY AND TEER is applied^{30,31}. These authors show that the presence or the formation of amorphous material in the surface graphite film triggers blister formation. Similarly, the addition of a thermal black (P 33) accelerates the formation of giant blisters (Fig. 7) in the highly crystalline MoS₂ film. This black has an average particle diameter of 700 Å, and it is completely amorphous. In contrast to graphite, however, the pure MoS₂ film does not show any periodic increase in friction in an inert atmosphere. MIDGLEY AND TEER conclude³⁰ that friction and wear of graphite are interrelated, whereas we observed *no* wear during the smooth running period of MoS₂ films.

It is not yet clear why a small quantity of water vapour should have a beneficial effect on endurance, in spite of increases in friction. High humidity, however, leads to large scale chemical decomposition of MoS₂, and, consequently, to a considerable reduction in life expectancy of the film.

The observed influences of oxygen and water vapour are special cases of mechanically-activated reactions in solids. Numerous examples of similar processes are known³²⁻³⁵. This mechanically-activated oxidation has consequences different from those observed after the addition of small quantities of oxidation products to a high grade MoS₂ powder. Only the *in situ* oxidation at points of elastic strain triggers ultimate destruction.

The photographic evidence of blister formation presented in Figs. 6 and 7 indicates clearly that blisters recur in the same area of the surface. Such voids represent regions of stress concentration leading to physically induced surface fatigue, but they also act as points of enhanced chemical reactivity, leading to chemical decomposition in a reactive atmosphere; their formation, therefore, should be suppressed.

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