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Rock Island Arsenal Laboratory

TECHNICAL REPORT

WEAR AND CORROSION TENDENCIES OF MOLYBDENUM DISULFIDE CONTAINING GREASES

By

S. Fred Calhoun

Department of the Army Project No. 593-21-060

Ordnance Management Structure Code No. 5010.11.801

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Rock Island Arsenal
Rock Island, Illinois

ABSTRACT

The tendency of molybdenum disulfide to increase the wear of greases is shown by results of laboratory tests made at Rock Island Arsenal. The extreme pressure properties of greases were increased by the addition of the molybdenum disulfide. Both statements are supported by the literature.

Molybdenum disulfide was shown to promote rusting of ferrous metals when added to grease. Literature references show that it also promotes corrosion of other metals.

Laboratory data and photographs are used to support the conclusions which were made.

RECOMMENDATIONS

It is recommended that molybdenum disulfide not be used in greases designed for automotive and artillery use by the Armed Forces. If an extreme pressure grease is needed, it is recommended that extreme pressure agents other than molybdenum disulfide be specified.

CONCLUSIONS

Molybdenum disulfide, when incorporated into a grease, is detrimental to the wear preventive properties of the grease. This was true for all types of greases tested or referred to in the literature. The compound does contribute to the extreme pressure properties of most greases when used under conditions of high pressure and temperature. It is probable that the extreme pressure properties of molybdenum disulfide became apparent under conditions approaching boundary lubrication when the grease or oil is forced from between the rubbing surfaces by the pressure exerted. It is doubtful if such conditions are prevalent for any appreciable time during normal automotive or artillery use.

Molybdenum disulfide, when incorporated into greases, increases the corrosive tendencies of the grease. This was true for all greases investigated by this Laboratory. This is caused by the formation of corrosive products through hydrolysis and by galvanic action between the molybdenum disulfide and metals. Extreme conditions of moisture accelerate this corrosive action which has been observed with many metals. Certain additives incorporated into the molybdenum disulfide grease will reduce or even eliminate the corrosion.

In view of the above mentioned tendencies, it is doubtful if the extra cost of molybdenum disulfide greases can be justified. A good grease is able to meet all the extreme pressure needs of normal automotive and artillery use without being fortified with molybdenum disulfide. If extreme pressure conditions exist, there are many compounds which will enable a grease to meet them and at the same time not reduce its ability to protect against rust and corrosion.

The quality of the MoS_2 is an important factor in its ultimate performance. When it is to be added to greases, careful and strict control of its purity, particle size, and pH is imperative.

WEAR AND CORROSION TENDENCIES OF MOLYBDENUM DISULFIDE CONTAINING GREASES

CONTENTS

WEAR AND CORROSION TENDENCIES OF
MOLYBDENUM DISULFIDE CONTAINING GREASES

OBJECT

To study the effects of the addition of molybdenum disulfide upon the wear, extreme pressure properties, and corrosion resistance of greases.

INTRODUCTION

The recent trend to extended lubrication periods in automobiles, and the insistance of the manufacturers that only their specification greases be used, has created a problem for the Armed Forces. For the past several years, greases meeting Specification MIL-G-10924 have been in general use by all branches of the Armed Services for lubrication of automotive and artillery equipment. Such greases have been generally satisfactory and have greatly reduced logistic problems. If the Armed Services are to use the manufacturers specified greases, a minimum of six different greases would have to be stocked in order to lubricate the various makes of automobiles found in the services. Since different grease fittings are used for each grease, a separate grease gun equipped with a special fitting is practically necessary for each type of grease. The immensity of the supply problem is thus apparent.

Another factor in the problem is the increasing tendency to specify greases containing molybdenum disulfide for use in the automobiles.. This is no doubt largely due to the vigorous manner in which the suppliers of MoS_2 have pushed their product. They have carried out a research and advertising program designed to show their product in its best light. The relatively meager literature on work done by unbiased researchers does not substantiate the findings of the producers. Work done at this Laboratory also indicates that MoS_2 falls somewhat short of the claims made for it.

Some of the properties stressed in the advertising and other sales promotional literature is the ability of MoS_2 to prevent galling and seizure, and to reduce friction and wear when added to greases or other lubricants. Kullman[(1)] used a specially purified MoS_2 in a lithium base grease and obtained the following results. Under high pressure (heavy duty) conditions the MoS_2 apparently plates out on the metal surface and provides "safety" lubrication for short intervals during which the grease may fail to function. At low operating loads, the same effect could not be obtained either by prolonged running times or by increasing the operating temperatures.

A Russian team[2], in determining the coefficients of friction, durability of the film, and antiseize properties of MoS_2, concluded that as a lubricant it was "not as effective as some literature data would indicate".

Halter and associates[3] made a study of MoS_2 sliding on MoS_2 in a nitrogen atmosphere containing various amounts of water vapor and certain hydrocarbon gas vapors. In tests with water vapor they observed an increase in coefficient of friction as the humidity increased. In dry nitrogen the coefficient of friction was 0.115. In an atmosphere containing 8-16 mm partial pressure of water vapor it rose to 0.21. It rose to a maximum of 0.24 at 20 mm partial pressure of water vapor. They also report that when the partial pressure of water vapor exceeded 10 mm, hydrogen sulfide was detected in the test chamber exit gas.

Peterson and Johnson[4] studied the coefficients of friction and wear characteristics of 27 crystalline solids. They observed that the lubricative effect of MoS_2 was impaired by moisture. They also stated that the ability of a solid to form an adherent film on a metal was more important than crystal structure in determining lubricating ability. They[5] obtained galling and seizure type failures when they attempted to determine the coefficients of friction of titanium surfaces coated with MoS_2.

Horth and associates[6], in a study of greases for ball joint suspensions, found that the best one was a soft grease made from a low viscosity oil. They found that the addition of MoS_2 to a lithium-calcium soap grease was detrimental both from the standpoint of friction, as observed in steering torque, and wear.

Smith[7], in his paper, lists a large amount of data which in the main indicates MoS_2 to be a good extreme pressure agent and to produce good film life. There are some cases, especially with high viscosity oils and with high soap content, where the MoS_2 was detrimental. He used the Timken and Falex machines in what are primarily boundary and extreme pressure conditions.

Kay[8,9] studied the frictional properties of MoS_2 and made the following observations:

1. The values of the coefficients of friction of MoS_2 films rubbed onto various metals is very dependent upon temperature and humidity.

2. In an investigation of a series of greases using the Navy Gear Wear Tester with various gear combinations, it was observed that for all metal combinations used the greases containing 10% MoS_2 gave greater wear than the base grease itself.

3. In tests made on the Four Ball machine using balls of ball bearing steel it was observed that at the lowest load (20 Kg.) the addition of MoS_2 to a grease resulted in deterioration of performance. With loads of 40 Kg. there was no appreciable difference in performance while at higher loads the presence of MoS_2 results in improved performance.

Another important factor in the use of molybdenum disulfide containing greases is the tendency of the compound to promote rusting or corrosion of various metal surfaces. This was first noticed by this Laboratory during the development of dry lubricants. The problem has been partially solved by surface pretreatments[10,11]. Further improvement in rust preventive properties have been obtained by use of acid acceptors incorporated into the dry lubricant formulation.

The manufacturers of commercial dry lubricant formulations are rather quiet concerning the corrosion preventive properties of their products. Some typical statements taken from the brochures of various companies include, "no acceleration of corrosion of 2024 aluminum alloy anodized as per MIL-A-8625, Type 1"; "noncorrosive to any bearing metal"; and "Resistant to water". In some cases they are more frank about it. A news item concerning one such lubricant[12] states; ". . . does not give corrosion protection". Weisman[13], in speaking before the Air Force-Navy-Industry Conference in San Antonio, Texas in 1956, states bluntly, "In my opinion, dry film lubricants have no rust preventive properties".

Picatinny Arsenal[14] conducted a study to evaluate the use of molybdenum disulfide in munitions parts and came to the following conclusions.

1. Molybdenum disulfide accelerates galvanic corrosion when placed in contact with various metals in moist atmospheres.

2. The quality of the molybdenum disulfide contributes significantly to the extent and rapidity of this deterioration.

3. Molybdenum disulfide will accelerate the deterioration of cadmium at high humidities.

4. The use of existing Specification, MIL-M-7866, does not insure the application of material capable of long term open storage without deleterious effects.

5. Molybdenum disulfide, in the presence of moisture, will act as the cathode to several metals to form a galvanic cell generating potential differences of as much as 0.5 volt. This is sufficient to cause severe and rapid corrosion.

In view of these observations it is evident that MoS_2 would contribute nothing to the rust preventive properties of a grease but might in fact accelerate corrosion.

Erb[15], in a study of antiseize formulations, listed the properties of sixty-one different resin or elastomer based mixtures. His results show that in thirty-nine cases where MoS_2 was included in the formulation all except those containing a corrosion inhibitor allowed the panel to show deep pitting or a badly rusted surface at the conclusion of the 200 hour salt spray test. Addition of a corrosion inhibitor merely reduced the severity of the rust and in no case eliminated it. In the 100 hour humidity cabinet test the only formulations allowing rust to form were, with but two exceptions, those containing MoS_2.

PROCEDURE AND OBSERVATIONS

This Laboratory has on several occasions observed the short comings of molybdenum disulfide as an additive for greases. The following data from Table 5 of a published report[16] is illustrative of the usual observations. The additive #21 is molybdenum disulfide. The Four Ball Wear scars for both the 3% and 5% molybdenum disulfide concentrations are larger than for the base grease except for condition #3. This is a high load, high temperature condition that could well be termed an expreme pressure condition. The Mean Hertz load and welding loads are improved by the MoS_2, but the Falex and Timken results are not significantly bettered. Based on these, and similar results, this Arsenal has concluded that a minimum of 5% MoS_2 must be used to achieve any significant improvement in extreme pressure properties. Table I contains the pertinent data from the referenced report to support the observations made.

TABLE I

SULFUR-CONTAINING ADDITIVES

Additive No.	Additive, %	Four-Ball Wear, mm Conditions No. 1	No. 2	No. 3	Mean Hertz Load	Welding Load, Kg.	Falex Load, Lb.	Timken OK Load, Lb.
0	Base grease	0.469	0.354	0.866	19.0	100	425	2
21	3	0.583	0.485	0.778	28.8	160	Fail	3
	5	0.589	0.383	0.752	31.9	175	850	5

The data in Table II and Table III is taken from an unpublished report of this Arsenal[17]. Table II contains Four Ball Wear test results on three greases. They are: a qualified MIL-G-10924A grease both before and after addition of 5% of microsize MoS_2 and a commercial lithium soap grease which analyzed 3% molybdenum disulfide. Table II contains the wear results under the stated conditions.

TABLE II

FOUR BALL WEAR RESULTS, SCAR DIAMETER, MM

	Conditions	MIL-G-10924A Grease	MIL-G-10924A + 5% MoS_2	Commercial Lithium Soap Grease - 3% MoS_2
1	28 Kgm, 600 rpm 100°F 60 Min.	0.35	0.35	0.46
2	28 Kgm, 600 rpm 250°F 60 Min.	0.40	0.37	0.56

Table III contains the results of the Four Ball Extreme Pressure tests on the same greases.

TABLE III

FOUR BALL EXTREME PRESSURE RESULTS

	MIL-G-10924A Grease	MIL-G-10924A +5% MoS_2	Commercial Lithium Soap Grease - 3% MoS_2
Mean Hertz Load, Kg.	23.9	48.8	42.5
Welding Load, Kg.	160	315	200
Seizure Range, Kg.	44-68	80-100	100-126

The data in Table II indicates further what seems to be a trend. Molybdenum disulfide usually does not improve the antiwear properties of a grease but in fact quite often worsens it.

Table III confirms the data in Table I that the extreme pressure properties are usually improved by addition of MoS_2. It is also rather indicative that at least 5% of MoS_2 is required to produce significant results.

Table IV contains the results of wear and extreme pressure tests on four commercial specification greases recommended by the manufacturer for lubricating the 1961 and 1962 automobiles with extended lubrication periods.

TABLE IV

WEAR AND EXTREME PRESSURE RESULTS ON GREASES FOR USE ON NEW CARS

Grease	Shell Four Ball Wear at 40 Kg., 1200 RPM, 75°C 60 minutes Scar Diam., MM	Mean Hertz Load, Kg.	Welding Load, Kg.
E.P. Lithium	0.38	30	200
Moly E.P. Lithium	0.39	31.1	200
Barium	0.48	27.9	160
Barium + 10% Moly	0.66	59.0	400

It is readily apparent that the MoS_2 did not improve the extreme pressure lithium grease in either wear or extreme pressure properties. It is quite possible that a grease with built in extreme pressure is not helped by the MoS_2. The addition of 10% MoS_2 to the barium grease was definitely detrimental to its antiwear properties, but enhanced the extreme pressure qualities appreciably.

The corrosive tendencies of molybdenum disulfide containing greases have been observed in this Laboratory in the following described manner.

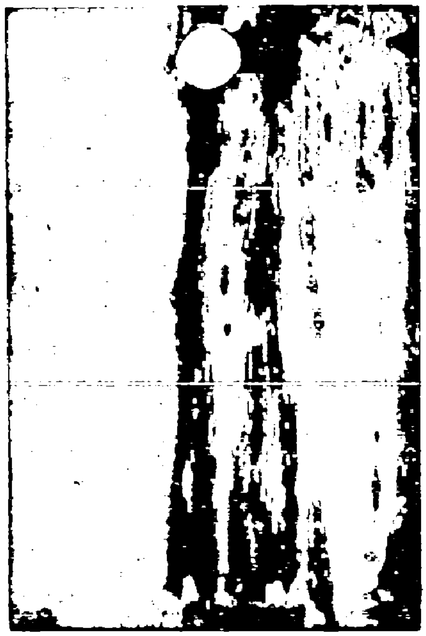
A qualified MIL-G-10924A grease was selected and found to have a neutralization number of 0.78 alkaline. Five percent by weight of dry microfine molybdenum disulfide was then mixed into the grease. One hour after mixing the neutralization number was determined to be 0.59 alkaline. The grease was then stored for eight days at ambient conditions of temperature and humidity. The neutralization number was then found to be 0.39 alkaline. The grease was then placed in a desiccator over water for eight days after which the neutralization number was 0.5 acid. This confirms the findings of Picatinny Arsenal[14], and also reported personally by other investigators, that MoS_2 hydrolyzes in the presence of moisture to form acid products which could be quite corrosive to metals.

To further investigate the corrosive tendencies of MoS_2 in greases, the following tests were performed. Specification MIL-G-10924A contains a requirement that the greases protect a steel panel for 100 hours in a salt spray of specified composition. Two qualified greases were each mixed with 5% MoS_2 and the right hand side of a steel panel coated with the MoS_2 containing grease. The left hand side of each panel was coated with the grease containing no MoS_2. The condition of the panels after 24 hours in the salt spray is shown pictorially in Figure 1A and 1B. In both cases the side coated with the grease containing the MoS_2 had rusted severely while the side coated with the original MIL-G-10924A grease was free of rust.

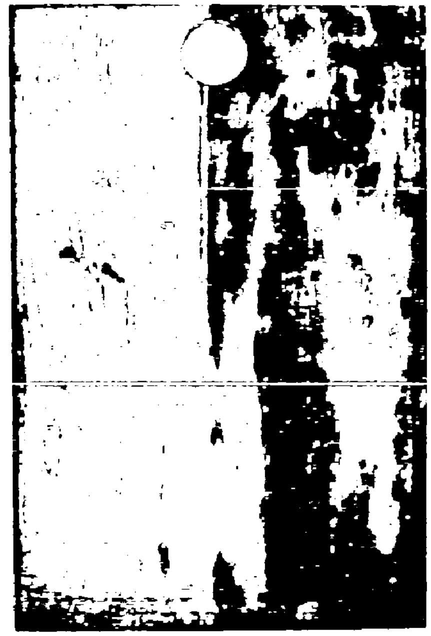
In another test a similar steel panel had MoS_2 powder rubbed onto the right hand side by means of clean tissue paper. The left hand side was left bare. The condition of the panel after only one hour in the salt spray is shown in Figure 1C. The heavier rust on the right hand side is clearly evident.

Another panel was coated with a commercial MoS_2 grease. The rusted condition of this panel after 24 hours in the salt spray is shown in Figure 1D.

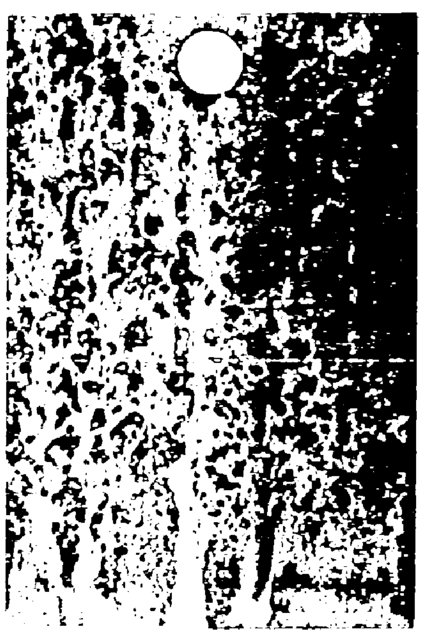
Another rust preventive test which has risen in favor recently and is included in Specification MIL-G-10924B is Federal Standard No. 4012. This test involves coating a bearing with the grease under specified conditions and then keeping it in a moist atmosphere in a sealed jar for fourteen days. A good grease will prevent any rust forming on either



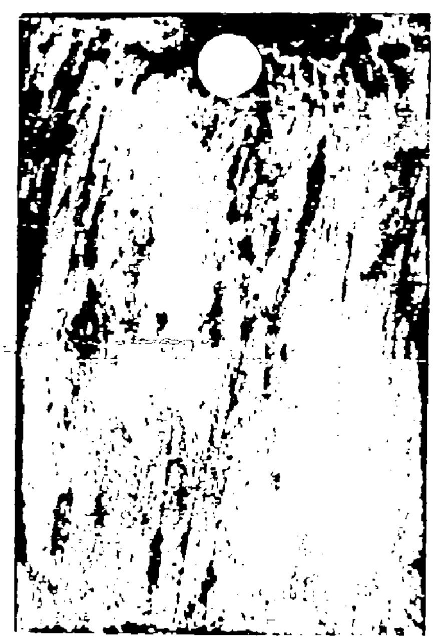
A



B



C



D

CONDITION OF PANELS AFTER SALT SPRAY TEST

FIGURE 1

the race or the rollers of the bearing. Figure 2 shows the results when an acceptable MIL-G-10924B grease was tested without and also with 5% of MoS_2 mixed into it. The rusting due to the MoS_2 is clearly evident.

Figure 3 shows the results obtained when the same test was made on two commercial MoS_2 greases. An acceptable MIL-G-10924B grease is included for contrast. The two MoS_2 greases included in this test displayed an extreme amount of rusting which is evident from the photograph.

The results of the test on two commercial MoS_2 greases are shown in Figure 4. These are products specified by car manufacturers for use in late model cars with the extended lubrication periods.

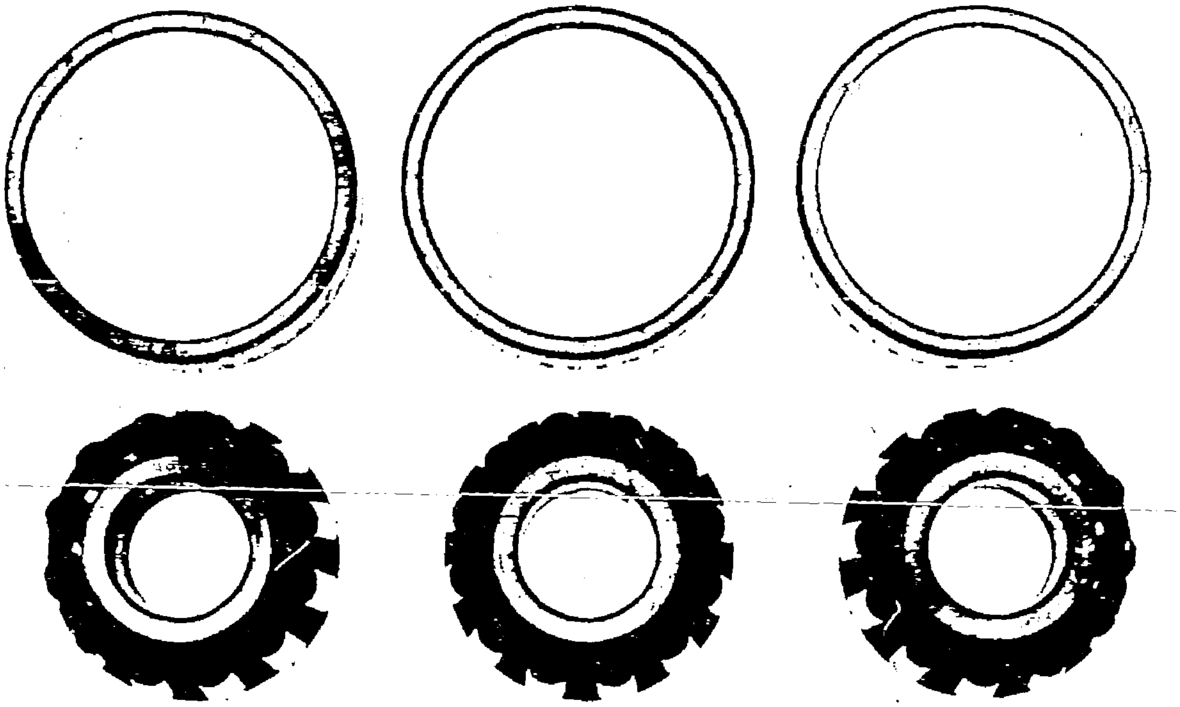
Again we see an amount of rusting which is far beyond that which would be sanctioned by the Military.

In an attempt to determine if the corrosive tendencies of MoS_2 could be reduced the following investigation was made. One of the commercial MoS_2 greases was treated by incorporating into it 1% of nonyl phenoxyacetic acid (NPA). This compound has been found to be one of the better antirust agents in another investigation carried out by this Laboratory. The results are shown in Figure 5. It is thus evident that a MoS_2 grease can be treated to prevent rusting. The effects of NPA on other properties of the grease have not been fully determined at this time and the results obtained here are not to be construed as an unqualified recommendation for its use.

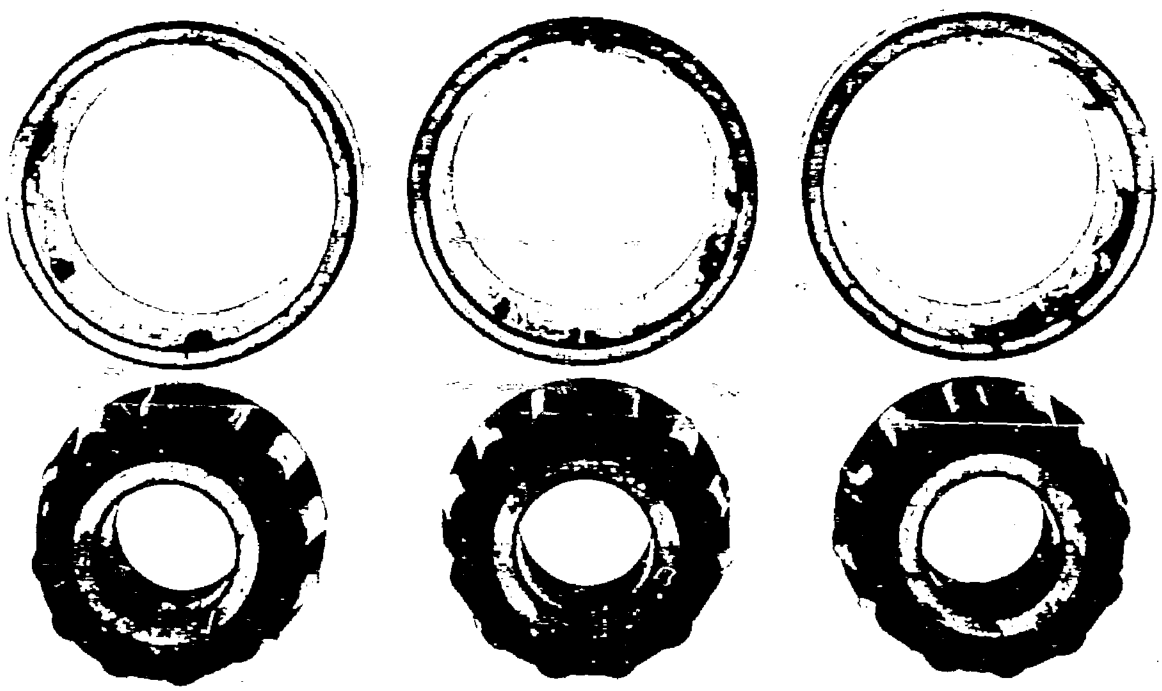
DISCUSSION

A possible explanation of why MoS_2 added to greases is ineffective or harmful as a lubricant is found in the National Engineering Laboratory report(18). They state: "It is known that molybdenum disulfide is effective as a lubricant only if it can be bonded to the surface, and results show that the presence of surface active agents such as oleic acid is detrimental; they form their own mono layer on the surface and repel the molybdenum disulfide." Petroleum oils, and greases made from them, usually contain polar materials, either natural or added, and thus would negate any advantage of the molybdenum disulfide.

Jost(19) mentions three catagories of application of molybdenum disulfide in antifriction bearings. First, where it is harmful, second, where it gave inconclusive or controversial results, and third, where positive evidence showed some benefit. Applications where molybdenum disulfide



QUALIFIED MIL-G-10924B GREASE



SAME GREASE PLUS 5% MOLYBDENUM DISULFIDE

RESULTS OF FEDERAL STANDARD 4012 RUST
PREVENTIVE TEST OF GREASES

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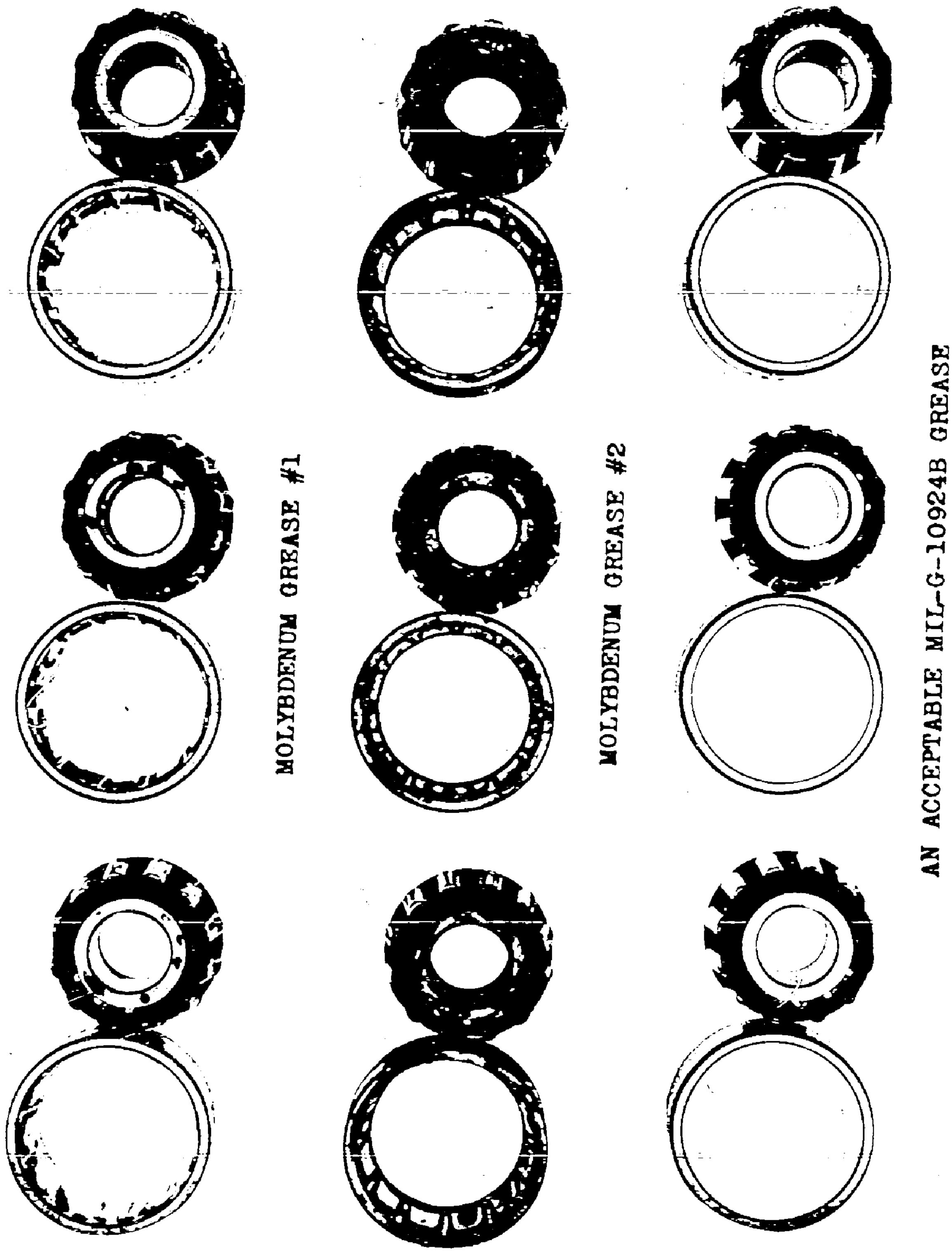
FIGURE 2



RESULTS OF FEDERAL STANDARD 4012 RUST PREVENTIVE TEST OF GREASES

FIGURE 3

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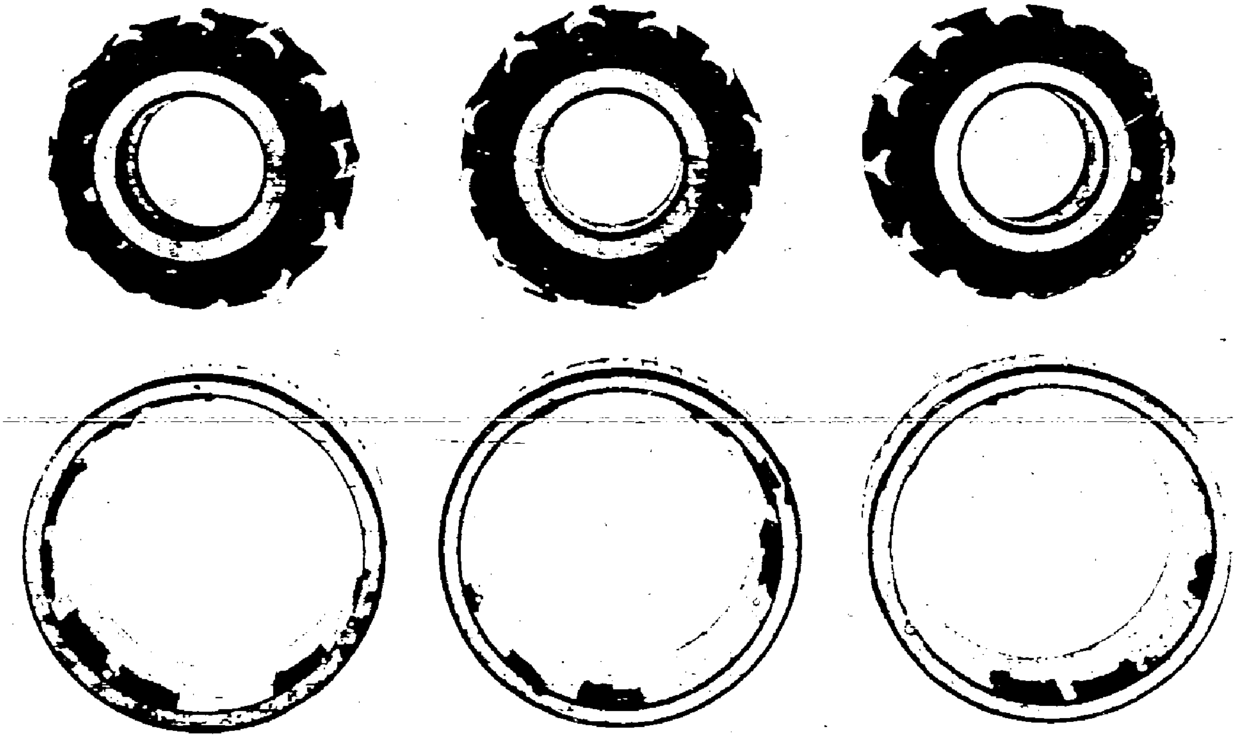
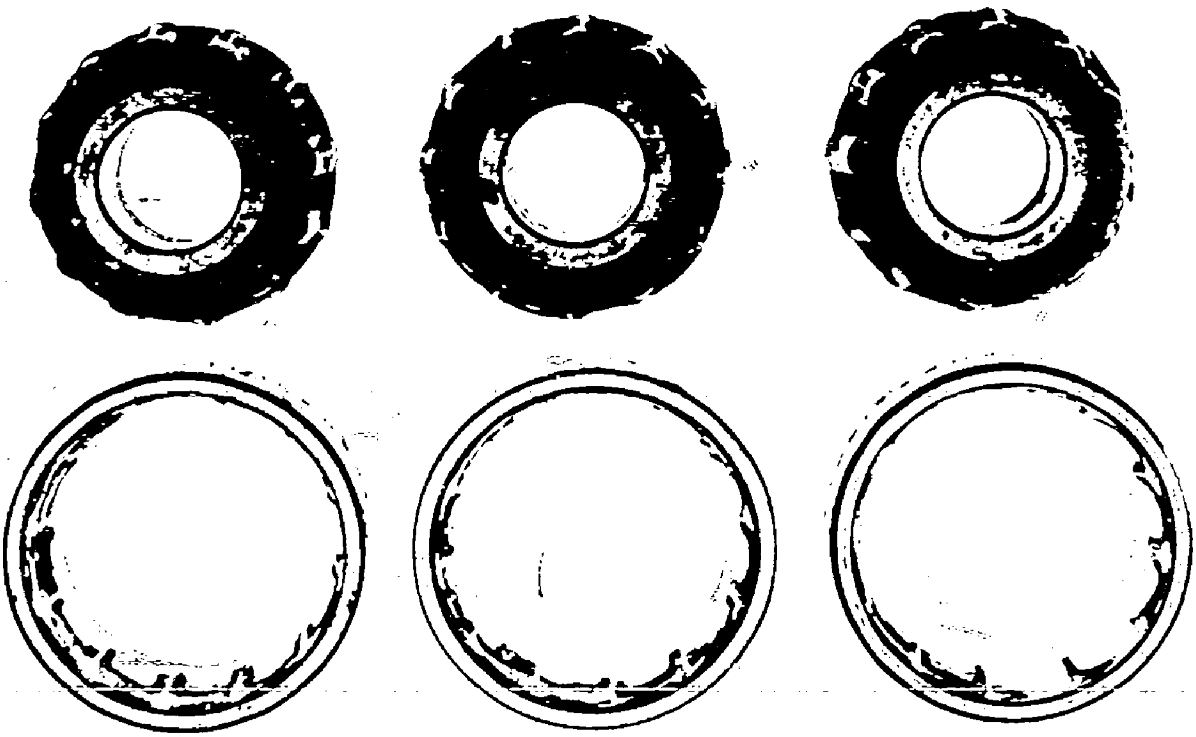


10% MOLY BARIUM



MOLY E. P. LITHIUM

RESULTS OF FEDERAL STANDARD 4012 TEST ON AUTOMOTIVE GREASES

FIGURE 4

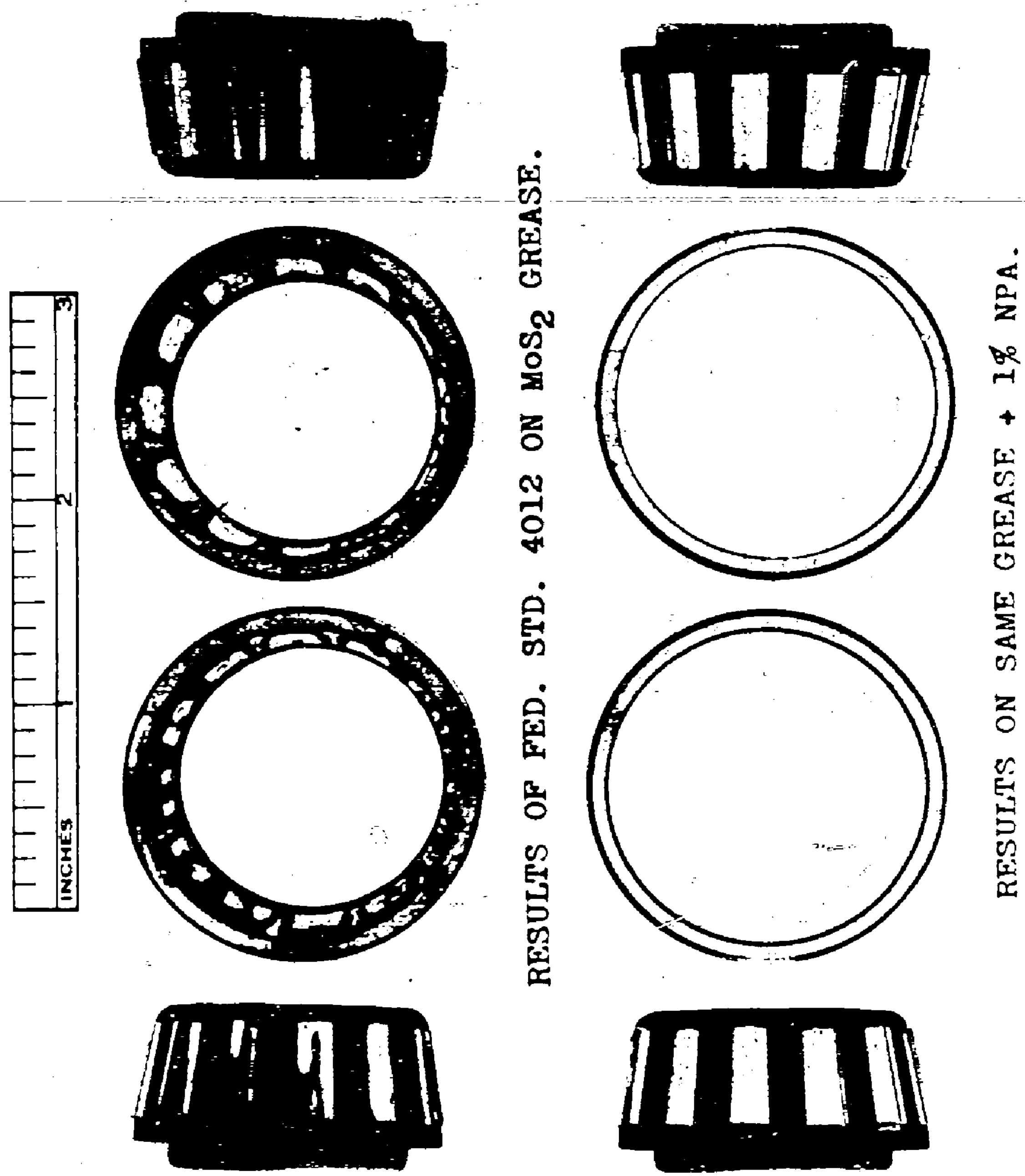


FIGURE 5

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is harmful were usually those where too great an amount of solid matter was introduced into the bearing. In general, the addition of more than 10% of molybdenum disulfide to a grease may lead to operating difficulties.

Applications where the use of molybdenum disulfide is inconclusive include instances where antifriction bearings are operating under conditions where temperature and pressure are not severe and where a first class lubricant is used. The general maxim, that, wherever conventional oils and greases can be used, molybdenum disulfide should not be considered, is true for ball and roller bearings as well as the sleeve type. The author further states that to use any molybdenum disulfide without strict control of its purity, particle size, pH value, carrier or bonding medium and operating conditions is to invite failure.

Molybdenum disulfide is of value where conditions are so severe that seizure and galling are eminent. Under these conditions a grease or an oil would be squeezed from between the contacting surfaces. The presence of MoS_2 thus prevents metal to metal contact and provides lubrication during the critical period. It should be pointed out at this point that there are several polar type compounds which have exhibited extreme pressure properties equal to or superior to MoS_2 and which are noncorrosive or to some extent corrosion preventive.

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Commanding General U.S. Army Weapons Command Rock Island Arsenal Rock Island, Illinois ATTN: AMSWE-RD for release to	3
Canadian Army Staff, Washington 2450 Massachusetts Avenue, N. W. Washington 8, D. C. ATTN: GSO-1, A & R Section	
Prevention of Deterioration Center National Academy of Science National Research Council 2101 Constitution Avenue Washington 25, D. C.	1
Commanding General White Sands Missile Range, New Mexico ATTN: ORDBS-OM- Electro-Mechanical Labs	1
ORDBS-OM- Systems Test Division	1
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Office of Technical Services Stock 1200 South Eads Street Arlington, Virginia	200

AD Accession No. ____
Rock Island Arsenal Laboratory, Rock Island, Illinois
WEAR AND CORROSION TENDENCIES OF MOLYBDENUM DISULFIDE CONTAINING GREASES
by S. Fred Calhoun

RIA Lab. Rep. 62-2752, 15 Aug 62, 21 pages, incl. illus. tables, (DA Project No. 593-21-060, OMS Code No. 5010.11.801)
Unclassified report.

The tendency of molybdenum disulfide to increase the wear of greases is shown by results of laboratory tests made at Rock Island Arsenal. The extreme pressure properties of greases were increased by the addition of the molybdenum disulfide. Both statements are supported by the literature.

Molybdenum disulfide was shown to promote rusting of ferrous metals when added to grease. Literature references show that it also promotes corrosion of other metals.

Laboratory data and photographs are used to support the conclusions which were made.

UNCLASSIFIED

1. Lubricant Additive
2. Greases
3. Molybdenum Disulfide
4. Corrosion
5. Antiwear
6. Extreme Pressure

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