SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE. (U)

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SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE

James P. King and Yayesh Asmerom

Pennwelt Corporation
Central Research and Development
King of Prussia, PA 19406

July 1982

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Solid Lubricants for Improved Wear Resistance

James P. King and Yayesh Asmerom

Pennwalt Corporation
900 First Avenue
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Department of the Navy
Office of Naval Research
Arlington, VA 22217

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Antimony thioantimonate
Antiwear additives
Extreme pressure additives
Metal sulfides
Oxythiomolybdates

Detailed studies including synthesis, characterization and evaluation of antimony thioantimonate, SbSbS₄, were carried out. As a solid lubricant additive in various greases, this material exhibited superior extreme pressure and antiwear properties as demonstrated by the Four-Ball weld points and load-wear indexes.
on both AISI-52100 and AISI-440C steels. Moreover, impressive abrasive wear resistance properties were imparted by low concentrations of SbSbS$_4$ in greases deliberately contaminated with hard abrasive particles. This additive appeared to be compatible with all the base greases investigated including a silicone grease in which very few additives show good response.

The lubricant properties of a number of cerium and zinc thio- and oxythiomolybdates were also investigated. The cerium complexes, as additives in a lithium grease, showed excellent antiwear properties on both chrome tool and stainless steel. However, their non-stoichiometric composition and tendency to form hydrates caused complications during synthesis and evaluation of properties. The zinc complexes were found to be even more promising as antiwear additives, especially for high temperature use on stainless steel.
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Appendix II. "Effect of Antimony Thioantimonate in Greases on Abrasive Wear", manuscript presented at the Symposium on Innovation for Maintenance Technology Improvements, NBS, April 21-23, 1981
SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE

A. OBJECTIVE

This program was for development of superior extreme pressure, antiwear, thermally stable lubricants and lubricant additives for use in both conventional and corrosion resistant metal surfaces. It was the objective of this task to extend the useful life of Navy lubricated bearings, seals, splines, aircraft arresting cables, and sliding metallic surfaces. Lubricants for corrosion resistant metals are particularly desirable because the use of these metals in corrosive environments is often precluded by the lack of lubricants suitable under these conditions.

B. INTRODUCTION

The approach investigated in this program was a follow-up to an earlier study carried out at Pennwalt's laboratories with partial support by the U. S. Navy and where a number of complex metal chalcogenides had been examined for their performance as extreme pressure and antiwear additives in greases, solid film lubricants, and fluids. As extreme pressure and antiwear additives, these complex chalcogenides had been found superior to simple sulfides, including MoS$_2$. One composition, arsenic thioantimonate was a particularly outstanding solid lubricant and, therefore, became the subject of much characterization and evaluation. When the safety of all inorganic arsenic compounds came under question, further development of arsenic thioantimonate was terminated. However, under that program other promising leads had been uncovered and which were then selected for additional studies in a subsequent effort whose results are summarized in this report. Of particular interest was antimony thioantimonate (SbSbS$_4$) which received special attention in this study. Other promising materials described
in this report include cerium and zinc oxythiomolybdates. While SbSbS$_4$ was found to be an outstanding extreme pressure lubricant additive with unique antiabrasive properties, the oxythiomolybdates were noteworthy for their antiwear characteristics and high thermal stability.

C. ANTIMONY THIOANTIMONATE - SbSbS$_4$

1. General

Laboratory synthesis and performance data on SbSbS$_4$ are described in detail in the attached copies of publications (Appendix I and II). The preparative method reported in Appendix I represents an improved reaction route with greater simplicity, reproducibility, product priority, and higher yield compared with the original method. Commercial production of SbSbS$_4$ should be possible without a major process development effort. A cost estimate for the production of several million pounds of SbSbS$_4$ has shown that this product can be made available at a price comparable to, and possible lower than, that of molybdenum disulfide, MoS$_2$.

2. Field Tests

Field tests with greases containing SbSbS$_4$ are being carried out by the Marine Corps at Camp Lejeune, NC, on high mobility vehicles. Another series of field tests is expected to start shortly at a Marine Corps base in California.

Test results to date from Camp Lejeune (after about one year of use in heavy duty vehicles) indicate that grease with SbSbS$_4$ as an additive is greatly superior to the standard GAA grease used by the military.
3. **Aircraft Arresting Cables**

The Naval Air Engineering Center, Lakehurst, NJ, is evaluating greases containing SbSbS$_4$ on arresting cables used on aircraft carriers. Major improvements including longer cable lives and less slippery decks are sought. This application study is sponsored by NAEC (contract N68335-81-C-5280); however, the ONR program provides the necessary basic technical underpinning.

4. **Toxicology**

Because greases containing SbSbS$_4$ have advanced to the field test stage, we have obtained acute oral and dermal toxicity data on this compound which indicate that it is nontoxic. All animals survived at an oral dose of 5 g/kg (rats) and a dermal dose of 2 g/kg (rabbits), were normal clinically, and gained weight throughout this study. Skin and eye irritation tests also indicate that the compound is substantially benign. Arrangements have been made with the Naval Medical Research & Development Command for a 90-day subchronic dermal study which is expected to be completed by early 1983.

D. **CERIUM OXYTHIOMOLYBDATES**

1. **General**

Numerous attempts to prepare cerium thiomolybdate, Ce$_2$(MoS$_4$)$_3$, gave products with elemental analysis corresponding to cerium oxythiomolybdate complexes, Ce$_2$(MoO$_x$S$_4$)$_3$·$x$H$_2$O, where $x$ = 1-3. These complexes were evaluated for lubricant properties in a lithium base grease and found to exhibit good antiwear properties on both chrome tool and stainless steels. These results prompted our further study of the synthesis, character-
ization, and evaluation of cerium oxythiomolybdate complexes. A number of reactions were carried out using three different routes but in all cases the reaction products were found to be non-stoichiometric. It was not clear whether this non-stoichiometry reflected the particular nature of complex sulfides involving cerium and molybdenum or was due to lack of suitable reaction conditions. The three reaction routes, the resulting compositions, and their performance as lubricant additives are summarized below.

2. Reaction of ammonium molybdate with hydrogen sulfide

\[
\begin{align*}
(NH_4)_6Mo_7O_{24} \cdot 4H_2O + nH_2S & \rightarrow (NH_4)_2MoO_xS_{4-x} + \text{by-products} \\
3(NH_4)MoO_xS_{4-x} + 2CeCl_3 \cdot 7H_2O & \rightarrow Ce_2(MoO_xS_{4-x})_3 \cdot nH_2O + \text{by-products}
\end{align*}
\]

Analysis of the cerium complex reaction products showed variable ratios of sulfur to cerium depending on the particular experiment. A large supply of cerium complex, prepared by the above reaction sequence for detailed evaluation and characterization, approximated \(Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O\) by elemental analysis. The material was found to be amorphous by X-ray diffraction.

Tables I through IV summarize the performance data of \(Ce(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O\) as a lubricant additive at various concentrations primarily in a lithium grease. For reference purposes, the lubricating properties of greases containing 5\% MoS\(_2\) are also listed. On chrome tool steel 52100 the weld point of the base grease containing 5\% cerium complex is comparable to that of the grease containing MoS\(_2\); however, the load wear index and wear prevention characteristics of the grease containing the cerium complex are definitely superior (Table I). On stainless steel 440-C the grease containing 5\% cerium
complex again shows superior antiwear characteristics and comparable extreme pressure properties to those of molybdenum disulfide.

A lithium grease containing a mixture of 1% SbSbS$_4$ and 1% Ce$_2$(MoO$_{1.2}$S$_{2.8}$)$_3$·6H$_2$O was also evaluated. The objective of this experiment was to see whether such a combination could impart both extreme pressure and antiwear properties to the base grease at a low level of additive concentration. The results are recorded in Tables I, II, and III and show that this combination at a total concentration level of 2% greatly improves the EP and antiwear properties of base grease.

The concentration effect (0.1 to 5%) of the cerium complex in a lithium grease on the wear prevention characteristics is shown in Table IV. The scar diameters on chrome tool steel are quite small and do not show much concentration dependence as indicated by very little change in the wear scar diameters of the greases containing 0.5 to 5% of the cerium complex. In the case of stainless steel, there is a definite trend of increasing wear scar diameters with decreasing concentration of the cerium complex.

The cerium complex was also evaluated in an aluminum complex grease. The Shell Four-Ball weld points and load wear indices of this grease containing 5% MoS$_2$ and 5% Ce$_2$(MoO$_{1.2}$S$_{2.8}$)$_3$·6H$_2$O are recorded in Table I. It appears that the cerium complex shows slightly superior EP performance to MoS$_2$. 

-5-
3. Reaction of Sodium Molybdate with Sodium Sulfide

\[ \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 3\text{Na}_2\text{S} \rightarrow \text{Na}_2\text{MoO}_x\text{S}_y \cdot 2\text{H}_2\text{O} + \text{by-products} \]

\[ 3\text{Na}_2\text{MoO}_x\text{S}_y \cdot 4-x + 2\text{CeCl}_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Ce(MoO}_x\text{S}_y \cdot 4-x \text{)}_3 \cdot n\text{H}_2\text{O} + \text{by-products} \]

Because of difficulties encountered in controlling the flow of hydrogen sulfide in the reaction with ammonium molybdate, sodium molybdate was treated with sodium sulfide to produce a solution of sodium oxythiomolybdate. The sodium oxythiomolybdate solution was then treated with a cerium trichloride solution at different pH ranges. None of the product analyses correspond to the expected cerium to molybdenum ratio. No additional work on this reaction was carried out.

4. Reaction of Sodium Molybdate with Cesium Acetate

\[ \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + \text{CsOAc} \rightarrow \text{Cs}_2\text{MoO}_3 \cdot n\text{H}_2\text{O} + \text{by-products} \]

\[ 3\text{Cs}_2\text{MoO}_3 + 2\text{CeCl}_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Ce}_2\text{(MoO}_3\text{)}_3 \cdot n\text{H}_2\text{O} + \text{by-products} \]

The synthesis of cesium oxythiomolybdate, \( \text{Cs}_2\text{MoO}_3 \), was carried out as reported in the literature by reaction of cesium acetate with sodium molybdate followed by passing hydrogen sulfide through the reaction mixture at pH 10.

Attempts were then made to prepare \( \text{Ce}_2\text{(MoO}_3\text{)}_3 \cdot n\text{H}_2\text{O} \) starting from \( \text{Cs}_2\text{MoO}_3 \). In our first attempt, an aqueous solution of \( \text{CeCl}_3 \cdot 7\text{H}_2\text{O} \) was added to an aqueous solution of \( \text{Cs}_2\text{MoO}_3 \) in 2:3 molar ratio at room temperature. A light brown solid was isolated (about 50% yield) whose analysis \( \text{Ce:Mo:S} = 2:2:5:7 \) did not correspond to the expected composition, \( \text{Ce}_2\text{(MoO}_3\text{)}_3 \cdot n\text{H}_2\text{O} \). However, its extreme pressure and antiwear properties in a lithium grease are superior to those of the sample obtained from ammonium oxythiomolybdate (Figure I).
5. Thermogravimetric Analysis of $\text{Cs}_2\text{MoOS}_3$ and Selected Samples of Cerium Oxythiomolybdate Complexes

a. Cesium Oxythiomolybdate - $\text{Cs}_2\text{MoOS}_3$

Thermogravimetric analysis of cesium oxythiomolybdate was carried out both in air and nitrogen at a heating rate of 5°C/minute. This product was selected for thermal study because it has a well defined composition and, therefore, it can provide information on the expected thermal stability of complexes containing the $\text{MoOS}_3^{-2}$ anion. As shown in Figure II, the material is remarkably stable both in air and nitrogen. With the exception of a slight weight loss of about 2% at 280°C followed by gradual weight gain of up to 4% around 410°C in air, there is no change until 600°C. Under nitrogen, there is essentially no change in weight up to 600°C; a very slight deflection showing less than 2% weight loss between 300 and 500°C may be attributed to the presence of impurities.

b. Cerium Oxythiomolybdate Complexes Prepared by Different Methods

Two samples of cerium oxythiomolybdate complexes prepared from ammonium oxythiomolybdate and cesium oxythiomolybdate, respectively, were selected for thermal study in air. The TGA curves are shown in Figure III. The initial weight loss up to 300°C for both samples may be attributed to water and this appears to be consistent with the elemental analysis. The two samples show different modes of decomposition with increasing temperatures. The complex prepared from $\text{Cs}_2\text{MoOS}_3$ shows weight gain from 400 to 600°C whereas the complex prepared from ammonium
oxythiomolybdate shows a slight weight gain between 350 and 380°C, followed by a weight loss of about 8% from 380 to 450°C. Both complexes appear to be stable up to 400°C in air after dehydration.

E. ZINC THIO- AND OXYTHIOMOLYBDATES

1. General

Synthesis and characterization of three stoichiometric zinc thio- and oxythiomolybdates - ZnMoS₄·3H₂O, ZnMoO₃·3H₂O, and ZnMoO₂S₂·3H₂O - and their corresponding anhydrous compositions, was more successful. The compositions showed considerable promise as antiwear additives especially for high temperature use on stainless steel. For example, ZnMoO₂S₂ was found to be much superior to MoS₂ as an extreme pressure and antiwear additive in lithium grease and was stable in air up to 400°C (750°F).

The following sections describe the synthetic procedures for these compositions. Table V lists the performance data of both hydrated and anhydrous zinc complexes. The thermogravimetric analysis of ZnMoO₂S₂ in air is shown in Figure IV.

2. Preparation of ZnMoS₄·3H₂O and ZnMoS₄

\[ ZnCl_2 + (NH_4)_2MoS_4 \xrightarrow{in H_2O} ZnMoS_4·3H₂O + 2NH_4Cl \]

\[ ZnMoS_4·3H₂O \xrightarrow{350°C/2hrs in N} ZnMoS_4 + 3H₂O \]

A sample of 5.0 g (NH₄)₂MoS₄ (prepared as described in the literature⁶) was dissolved in 100 ml distilled water. The resulting solution was slowly added with an aqueous solution of ZnCl₂ (2.6 g in 20 ml distilled water). A black solid formed immediately. The reaction
mixture was then stirred for two hours at room temperature and filtered. The solid product was washed with acetone and dried at 110°C for four hours (5.3 g or 75% yield). X-ray diffraction indicated that this material was amorphous.

Calculated for ZnMoS₄·3H₂O: Zn, 19.0; Mo, 27.9; S, 37.3
Found: Zn, 19.6; Mo, 28.6; S, 37.9

The anhydrous material was prepared as indicated above.

3. Preparation of ZnMoO₂S₂·3H₂O and ZnMoO₂S₄

\[
\text{ZnCl}_2 + (\text{NH}_4)_2\text{MoO}_2\text{S}_2 \xrightarrow{\text{H}_2\text{O}} \text{ZnMoO}_2\text{S}_2 \cdot 3\text{H}_2\text{O} + 2\text{NH}_4\text{Cl}
\]

\[
\text{ZnMoS}_4 \cdot 3\text{H}_2\text{O} \xrightarrow{350^\circ\text{C}/2\text{hrs}} \text{ZnMoO}_2\text{S}_2 + 3\text{H}_2\text{O}
\]

An aqueous solution of ZnCl₂ (5.38 g in 50 ml distilled water) was slowly added to a solution of (NH₄)₂MoO₂S₂ (9.0 g in 100 ml distilled water; the compound was prepared as described in the literature⁶,⁷) resulting in slightly exothermic reaction. A dark brown solid formed immediately. The reaction mixture was stirred for one hour at room temperature and then filtered. The black solid was washed with distilled water and dried at 110°C for three hours (6.6 g or 66% yield). X-ray diffraction indicated that this solid was amorphous.

Calculated for ZnMoO₂S₂·3H₂O: Zn, 21.0; Mo, 30.8; S, 20.6
Found: Zn, 23.9; Mo, 29.8; S, 23.4

The anhydrous material was prepared as indicated above.
4. Preparation of ZnMoO$_3$·3H$_2$O and ZnMoO$_3$

\[
\text{Cs}_2\text{MoO}_3 + \text{ZnCl}_2 \xrightarrow{\text{in H}_2\text{O}} \text{ZnMoO}_3 \cdot 3\text{H}_2\text{O} + 2\text{CsCl}
\]

\[
\text{ZnMoO}_3 \cdot 3\text{H}_2\text{O} \xrightarrow{350^\circ\text{C}/2\text{hrs}} \text{ZnMoO}_3 + 3\text{H}_2\text{O}
\]

A solution of 15.4 g Cs$_2$(MoO$_3$) (prepared as described in the literature) in 100 ml distilled water was treated with a ZnCl$_2$ solution (4.4 g in 30 ml distilled water). The reaction mixture was reflexed for 1.5 hrs. A brown solid deposited. The solid product was isolated by filtration, washed twice with distilled water and dried at 105°C for three hours (10.2 g). X-ray diffraction indicated that this solid was amorphous.

Calculated for Zn(MoO$_3$)·3H$_2$O: Zn, 20.0; Mo, 29.3; S, 29.3

Found: Zn, 23.4; Mo, 30.1; S, 29.2

The anhydrous material was prepared as indicated above.

5. Toxicology

Some toxicology tests were carried out on ZnMoO$_2$S$_2$·3H$_2$O with favorable results, as follows:

Skin irritation test: Non irritating

Eye irritation test: Mildly irritating without washout

Acute dermal LD50 (rabbits) >2g/kg
F. REFERENCES


G. ACKNOWLEDGEMENT

We would like to acknowledge the many scientific contributions of Mr. M. J. Devine who has provided support of the highest professional level at the request of ONR and especially for his attention to requirements of the U. S. Marine Corps for amphibious and desert operations.
Table I. Shell Four-Ball Weld Points and Load Wear Indices$^1$

of Cerium Oxythiomolybdate$^2$ in Lithium and Aluminum Complex Greases on Chrome Tool Steel Balls (AISI-52100)

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Weld Point kg</th>
<th>Scar Diameter Before Weld mm (kg)</th>
<th>Load Wear Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>140</td>
<td>2.64(126)</td>
<td>18.3</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS$_2$</td>
<td>250</td>
<td>2.90(224)</td>
<td>30.4</td>
</tr>
<tr>
<td>Lithium Grease + 5% Cerium Complex</td>
<td>250</td>
<td>2.02(200)</td>
<td>41.4</td>
</tr>
<tr>
<td>Lithium Grease + 1% SbSbS$_4$ + 1% Cerium Complex</td>
<td>400</td>
<td>1.61(315)</td>
<td>59.5</td>
</tr>
<tr>
<td>Aluminum Complex Grease (ACG)</td>
<td>100</td>
<td>2.10(70)</td>
<td>11.8</td>
</tr>
<tr>
<td>ACG + 5% MoS$_2$</td>
<td>190</td>
<td>2.24(160)</td>
<td>35.5</td>
</tr>
<tr>
<td>ACG + 5% Cerium Complex</td>
<td>200</td>
<td>2.10(160)</td>
<td>40.2</td>
</tr>
</tbody>
</table>

1. ASTM-D-2596  
2. Ce$_2$(MoO$_1$2S$_2$.8)$_3$·6H$_2$O
Table II. Shell Four-Ball Weld Point and Load Wear Index\textsuperscript{1} of Cerium Oxythiomolybdate\textsuperscript{2} in Lithium Grease on Stainless Steel Balls (AISI-440C)

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Weld Point</th>
<th>Load Wear Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>80</td>
<td>3.5</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS\textsubscript{2}</td>
<td>100</td>
<td>6.1</td>
</tr>
<tr>
<td>Lithium Grease + 5% Cerium Complex</td>
<td>100</td>
<td>10.4</td>
</tr>
<tr>
<td>Lithium Grease + 1% SbSbS\textsubscript{4} and 1% Cerium Complex</td>
<td>140</td>
<td>11.8</td>
</tr>
</tbody>
</table>

\textsuperscript{1} ASTM-D-2596
\textsuperscript{2} Ce\textsubscript{2}(MoO\textsubscript{1.2}S\textsubscript{2.8})\textsubscript{3} \cdot 6H\textsubscript{2}O
Table III. Shell Four-Ball Wear Prevention Characteristics\(^1\) of Lithium Grease Containing Additives on Chrome Tool Steel Balls (AISI-52100) and Stainless Steel Balls (AISI-440C)

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Wear Scar Diameter on 52100 Balls mm</th>
<th>Wear Scar Diameter on 440-C Balls mm</th>
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<tbody>
<tr>
<td>Lithium Grease</td>
<td>0.70</td>
<td>3.96</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS(_2)</td>
<td>0.65</td>
<td>2.34</td>
</tr>
<tr>
<td>Lithium Grease + 5% Cerium Complex(^2)</td>
<td>0.40</td>
<td>1.38</td>
</tr>
<tr>
<td>Lithium Grease + 1% SbSbS(_4) and 1% Cerium Complex(^2)</td>
<td>0.43</td>
<td>0.84</td>
</tr>
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1. ASTM-D-2266 - 1200 rpm, 167°F, 40 kg for one hour
2. Ce\(_2\)(MoO\(_1.2S_2.8\))\(_3\cdot6H_2O\)
Table IV. Effect of Concentration of $\text{Ce}_2(\text{MoO}_1.2\text{S}_2.8)_{3.6}$ in Lithium Grease on Wear Scar Diameters

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<thead>
<tr>
<th>Grease Composition</th>
<th>Wear Scar Diameter on 52100 Steel Balls (mm)</th>
<th>Wear Scar Diameter on S.S. 440C Balls (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>0.70</td>
<td>3.96</td>
</tr>
<tr>
<td>Lithium Grease + 0.1% Cerium Complex</td>
<td>0.59</td>
<td>2.64</td>
</tr>
<tr>
<td>Lithium Grease + 0.5% Cerium Complex</td>
<td>0.39</td>
<td>2.47</td>
</tr>
<tr>
<td>Lithium Grease + 1% Cerium Complex</td>
<td>0.40</td>
<td>2.26</td>
</tr>
<tr>
<td>Lithium Grease + 3% Cerium Complex</td>
<td>0.40</td>
<td>1.84</td>
</tr>
<tr>
<td>Lithium Grease + 5% Cerium Complex</td>
<td>0.41</td>
<td>1.38</td>
</tr>
</tbody>
</table>

1. ASTM-D-2266 - 1200 rpm, 167°F, 40 kg for one hour
Figure I. Wear Scar Diameter vs. Load
(52100 Steel Balls; 25°C, 1800 rpm, 10 sec.)

I. Lithium Grease

II. Lithium Grease + 5% \( \text{Ce}_2(\text{MoO}_x\text{S}_{4-x})_3\cdot n\text{H}_2\text{O} \) prepared from ammonium oxythiomolybdate

III. Lithium Grease + 5% \( \text{Ce}_2(\text{MoO}_x\text{S}_{4-x})_3\cdot n\text{H}_2\text{O} \) prepared from cerium oxythiomolybdate
Figure III. Thermogravimetric Analysis in Air of Cerium Oxythiomybdate Complexes Prepared by Two Different Methods

I = Prepared from Cs$_2$MoOS$_3$
II = Prepared from (NH$_4$)$_2$MoO$_x$S$_4$$_x$
Table V. Lubricant Properties of Thio- and Oxythiomolybdate Complexes

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Weld Pt. kg</th>
<th>LWI</th>
<th>Wear Scar Diameter, MM&lt;br&gt;Before Dehydration</th>
<th>After Dehydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease (L.G.)</td>
<td>140</td>
<td>18.3</td>
<td>0.70</td>
<td>3.96</td>
</tr>
<tr>
<td>L.G. + 5% MoS₂</td>
<td>250</td>
<td>80.4</td>
<td>0.65</td>
<td>2.34</td>
</tr>
<tr>
<td>L.G. + 5% ZnMoS₄·3H₂O</td>
<td>250</td>
<td>37.4</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>L.G. + 5% ZnMoO₃·3H₂O</td>
<td>315</td>
<td>52.0</td>
<td>0.44</td>
<td>0.53</td>
</tr>
<tr>
<td>L.G. + 5% ZnMoO₂S₂·3H₂O</td>
<td>315</td>
<td>60.6</td>
<td>0.40</td>
<td>0.84</td>
</tr>
</tbody>
</table>

a. 1200 rpm, 167°F, and 40 kg for 1 h.
b. The zinc complexes were dehydrated under N² at 350°C for two hours.
Figure IV. Thermogravimetric Analysis of ZnMoO$_2$S$_2$ in Air
Investigation of Extreme-Pressure and Antiwear Properties of Antimony Thioantimonate

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Pennwalt Corporation
King of Prussia, Pennsylvania 19406

INTRODUCTION

Continuing advances in technology require the development of lubricant systems capable of meeting the challenge presented by increasing speed, high loads, and extremes of temperature. Lubricants may also be required to function in high vacuum or corrosive environments and to exhibit broad response to various metals and alloys. There is a need for effective solid lubricants in aircraft, ship, mining, and oil drilling equipment, and space vehicle parts to lower friction, prevent contact surfaces from welding and reduce energy requirements. The solid lubricants commonly used for these purposes are graphite and molybdenum disulfide. The use of graphite as solid lubricant has certain drawbacks in some applications because of limitations such as galvanic corrosion, necessary presence of water vapor or hydride formation in order to be effective and unsatisfactory performance in vacuum. Molybdenum disulfide is in short supply. There are few solid lubricants available today that can function properly under high load. It is, therefore, essential that effective replacements for these materials be found and made available.

A number of complex metal chalcanohedrites previously synthesized were examined (11, 12, 13, 14) for their performance as extreme-pressure and antiwear additives in greases, solid-helix lubricants and fluids. As extreme-pressure and antiwear additives, these complex chalcogenides were superior to simple sulfides, including MoS2. One composition, arsenic thioantimonate—which was well characterized and evaluated (21)—was found to be an outstanding solid lubricant. When the safety of all montanic arsenic compounds came under question, development of arsenic thioantimonate was terminated.

A study was then undertaken to determine the potential of antimony thioantimonate, SbSbS, as a solid-lubricant additive. This report covers investigation of the lubricating properties of SbSbS in various greases. Of particular interest is the development of a lubricant effective for use with chrome tool and stainless steels.

Experimental

Preparation of Antimony Thioantimonate

Antimony thioantimonate was prepared from aqueous solutions by a precipitation procedure similar to that used to prepare arsenic thioantimonate (21). An alkaline solution of SbO was added to an aqueous solution of sodium thioantimonate (NaSbS3H·O). The resulting solution was filtered to remove a small amount of NaSbO·H·, and the filtrate was slowly neutralized with phosphoric acid solution under nitrogen atmosphere. (Hydrochloric or sulfuric acid could also be used.) A precipitate was formed, filtered, washed several times with distilled water, alcohol, acetone, and carbon tetrachloride, and dried in vacuum at 75°C to constant weight. Sodium thioantimonate solution was prepared by redissolving a mixture of sodium sulfide, sulfur, and antimony trisulfide (13:1:6.1 molar ratio) in an aqueous medium under a nitrogen atmosphere. After most of the sulfur had disappeared, the reaction product was filtered to remove the excess sulfur, and the filtrate was combined with an alkaline solution of antimony oxide. The overall reaction may be represented as follows:

\[ \text{SbO} + 2\text{KOH} + 2\text{Na}_2\text{SbS}_3 + \text{SH}_3 \rightarrow \]

\[ 2\text{K}_2\text{SbS}_3 + 2\text{K}^+ + 6\text{Na}^+ + 5\text{H}_2\text{O} \]
The ammonium triantiohal of 95-percent purity and the molybdenum disulfide was of technical grade.

Selection of Base Greases

Four base greases representing a broad spectrum of the industrial greases used today were selected for use in evaluating antimony thioantimonate. Test samples were prepared by mixing appropriate amounts of additive and grease expressed in wt percent on a three-roll mill for 3–5 passes. Details of the base greases are given in Table 1.

Test Methods

Four Ball 1.25 cm

The extreme-pressure and antwear properties of the greases were determined on Shell Four Ball EP, and Wear Testers. These testers provide for sliding steel vs steel (M-52100 vs M-52100 and M-100C vs M-100C) with spherical specimens. Weld points and load wear indexes were determined in a series of runs at 1500 rpm, 50 g, conducted at various loads, and scar diameters were measured after each run in accordance with ASTM D 2266. Wear prevention characteristics were determined by measuring scar diameters of test specimens after each run at 1200 rpm, 10 kg, 167 F for one hour. This test is described in ASTM D 2266.

Falex Machine

The load-carrying capabilities of certain selected grease samples were measured on a Falex machine using ASTM-C 3435 steel pins and ASTM-C 1137 A-blocks. The testing procedure is similar to ASTM D 2266.

Oxidation Test

Antioxidant properties of some greases were determined in an oxidation bomb under pure oxygen at 210 ± 2 F for 100 hr. Relative antioxidant ability was rated by measuring the drop in oxygen pressure after 100 hr. This test is described in ASTM D 912.

Copper Corrosion

A copper strip was allowed to remain in contact with the lubricating grease containing the complex sulfide for a period of 24 hr at a specified temperature. After the exposure was completed, the surface of the copper specimen was examined for discoloration, etching, pitting, or other signs of corrosion. This procedure is similar to the method outlined in 5.09.2.0 of FIMS No. 7914.

Characterization of Antimony Thioantimonate

Antimony thioantimonate is a reddish-brown solid insoluble in most organic solvents and mineral acids. It is soluble in alkali and is amorphous by X-ray diffraction. A typical sample analyzed 65.5 percent Sb and 34.5 percent Sb55, 55 percent and 41.5 percent Sb. The density determined at 25 C is 3.55 g/cm³. The thermal stability of SbSbS has been investigated by thermogravimetric analysis. When SbSbS is heated in air at 911 F, there is approximately 8 percent weight loss between 380 F and 700 F, and the rate of weight loss does not become rapid with increasing temperature until 810 F is exceeded. At 1150 F, 90 percent of the compound remained under these dynamic heating conditions. Antimony thioantimonate is a potential candidate for moderate-to-high-temperature solid-lubricant applications. A TGA curve is presented in Figure 1. To further verify the composition and characterize the material, it was heated in a nitrogen atmosphere. It was found to melt at about 510 C. After being held at 525 C for 3 hr, the sample had lost 9.1 percent of its original weight, which closely approaches the theoretical weight loss for conversion of SbSbS to SbSb, and the resulting product was identified as crystalline SbSb by X-ray diffraction analysis.

Results and Discussion

Lubricating Properties of SbSbS, on Chrome Tool Steel AISI-C-52100

The properties of antimony thioantimonate as an antiwear and extreme-pressure additive in various greases were evaluated on Shell Four Ball EP and Wear Testers using both chrome tool and stainless-steel balls. For reference purposes, the lubricating properties of 5-percent molten-

![Fig. 1.—Thermogravimetric analysis of SbSbS, in air](image-url)
denium disulfide in the same base greases were also determined. The weld points and load wear indexes of chrome tool steel balls (AISI-52100) were determined for base greases, base greases containing 5 percent ammonium thioammoniate, and base greases containing 5 percent MoS₂. The results are recorded in Table 2 along with the scar diameters before weld. At 5 percent concentration, ammonium thioammoniate (SbSbS) has an antitrust and FP properties superior to those of molybdenum disulfide. In fact, even the 1 percent SbSbS grease outperformed the 5 percent MoS₂ grease. A graphical comparison of the data obtained in a lithium grease is presented in Fig. 2.

The wear prevention characteristics of the four base greases, and the same greases containing either 5 percent SbSbS or 5 percent MoS₂ were determined on a Four-Ball wear tester at 40 kg, 1000 rpm for one hour. The results for 52100 steel vs 52100 steel and 18-8 stainless steel vs 18-8 stainless steel are recorded in Table 3. The wear prevention characteristics of chrome steel balls (AISI-52100) showed a slight improvement for the greases containing SbSbS and MoS₂ over the corresponding base greases in most cases. There is no significant difference in antitrust properties at 40 kg load between SbSbS and MoS₂ in all four greases.

The effect of ammonium thioammoniate concentration on the lubricating properties of a lithium grease was investigated. The weld points and load wear indexes of a lithium grease containing 0.5 to 5.0 percent ammonium thioammoniate were determined. For comparison, the weld point and load wear indexes of the same base grease containing 1 to 5 percent MoS₂ were also obtained. The results are listed in Table 1. These results suggest that high performance FP greases can be formulated with considerable lower concentrations of SbSbS than of MoS₂. The results of various properties of lithium grease containing 5 percent SbSbS and 5 percent MoS₂ are recorded in Table 5.

A lithium grease containing different extreme-pressure additives, including both molybdenum and organometallic compounds, was investigated. The load wear indexes of the same base grease containing various additives were determined. The results are presented in Fig. 2. Again, the superior extreme-pressure properties of ammonium thioammoniate were demonstrated.

Preliminary evaluation of the load carrying properties of various base greases containing ammonium thioammoniate (SbSbS) and MoS₂ were carried out on a Falex machine. The results are recorded in Table 4.

**Lubricating Properties of SbSbS, on Stainless-Steel AISI-440C**

In general, corrosion-resistant metals or alloys are diff-
cult to lubricate, especially under high load conditions. In many applications, the use of corrosion-resistant alloys is limited by severe wear problems. The lubricating properties of four different greases containing 5-percent SbSbS, have been evaluated with AISI 440C stainless-steel balls in a Shell Four-Ball EP Tester. For comparison, the lubricating properties of the same greases containing 5-percent molybdenum disulfide have also been determined on AISI 440C. At 5-percent concentration of SbSbS, in four greases, the wear points of stainless-steel balls showed improvements of 100 to 100 percent over the same greases containing 5-percent molybdenum disulfide. Experimental results are given in Table 7. The wear diameters vs. load graphs shown in Fig. 4 and 5 indicate that the greases containing SbSbS exhibit excellent response to stainless steel. Stainless steel is difficult to lubricate, and there are very few additives that can impart good response to silicone greases as confirmed by the results obtained on the silicone grease containing 5-percent MoS₂ (see Fig. 5). It is significant that the extreme-pressure properties of the silicone grease containing 5-percent SbSbS are greatly improved over those of the base grease and the base grease containing 5-percent MoS₂.

The wear prevention characteristics of 5-percent SbSbS, in three greases—lithium, clay and aluminum complex greases—were determined on a Shell Four-Ball Wear Tester using AISI 440C stainless-steel balls. The wear diameters for the lithium grease and the lithium grease containing 5-percent MoS₂ were 100 and 100 percent larger than for the same base grease containing 5-percent SbSbS. In fact, the wear scar diameter of the lithium grease containing 5-percent SbSbS, on AISI 440C stainless-steel balls was only slightly larger than the wear scar obtained for the same grease on AISI 52100 balls (0.78 vs. 0.63 mm). For 5-percent concentration of MoS₂ in a silicone grease, the wear scar diameter was larger than that for the base grease (2.50 vs. 2.27 mm). However, the presence of 5-percent SbSbS, in the same silicone grease resulted in 100-percent improvement over the base grease (see wear data in Table 4).

Table 8 lists the comparative wear scar diameters of both AISI 52100 and AISI 440C balls obtained for the same base greases under different loads. The differences in performance between MoS₂ and SbSbS, in different greases on both chrome and stainless steel are quite obvious. The results in Table 8 also indicate that the use of MoS₂ on stainless-steel balls is quite limited. The good performance of SbSbS, on various alloys and in a variety of greases has been quite universal. It is interesting to note that lithium grease containing 5-percent SbSbS gives smaller wear scar diameters on AISI 440C stainless-steel balls under a given applied load and a higher weld point than the same grease containing 5-percent MoS₂, on chrome-tool steel.

### Table 3: Shell Four-Ball Wear Prevention Characteristics of Greases Containing MoS₂ and SbSbS

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Wear Scar Diameter, AISI 52100 (mm)</th>
<th>Wear Scar Diameter, AISI 440C (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>0.20</td>
<td>0.34</td>
</tr>
<tr>
<td>Lithium Grease + 5% SbSbS</td>
<td>0.05</td>
<td>0.78</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS₂</td>
<td>0.65</td>
<td>2.34</td>
</tr>
<tr>
<td>Silicone Grease</td>
<td>1.90</td>
<td>2.11</td>
</tr>
<tr>
<td>Silicone Grease + 5% SbSbS</td>
<td>2.11</td>
<td>2.11</td>
</tr>
<tr>
<td>Silicone Grease + 5% MoS₂</td>
<td>2.11</td>
<td>2.11</td>
</tr>
<tr>
<td>Clay Grease</td>
<td>0.65</td>
<td>0.37</td>
</tr>
<tr>
<td>Clay Grease + 5% SbSbS</td>
<td>0.65</td>
<td>0.37</td>
</tr>
<tr>
<td>Clay Grease + 5% MoS₂</td>
<td>0.64</td>
<td>0.37</td>
</tr>
<tr>
<td>Aluminum Complex Grease</td>
<td>0.65</td>
<td>2.27</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% SbSbS</td>
<td>0.65</td>
<td>2.27</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% MoS₂</td>
<td>0.64</td>
<td>2.27</td>
</tr>
</tbody>
</table>

### Table 4: Performance of Lithium Grease Containing Different Concentrations of SbSbS and MoS₂ on Chrome-Tool Steel AISI 52100

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Weld Point (mg)</th>
<th>Load-Wear Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>110</td>
<td>48.3</td>
</tr>
<tr>
<td>Lithium Grease + 0.5% SbSbS</td>
<td>200</td>
<td>25.0</td>
</tr>
<tr>
<td>Lithium Grease + 1% SbSbS</td>
<td>400</td>
<td>43.0</td>
</tr>
<tr>
<td>Lithium Grease + 1% MoS₂</td>
<td>126</td>
<td>17.6</td>
</tr>
<tr>
<td>Lithium Grease + 3% SbSbS</td>
<td>120</td>
<td>57.0</td>
</tr>
<tr>
<td>Lithium Grease + 3% MoS₂</td>
<td>102</td>
<td>26.5</td>
</tr>
<tr>
<td>Lithium Grease + 5% SbSbS</td>
<td>760</td>
<td>98.4</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS₂</td>
<td>250</td>
<td>30.4</td>
</tr>
</tbody>
</table>

CONCLUSION

Antimony thioantimonate incorporated into different greases as a solid additive at low concentration imparts outstanding extreme-pressure properties both on chrome-tool and stainless steels. At lower loads, the wear prevention characteristics on tool steel in various greases are comparable to molybdenum disulfide; however, the wear prevention characteristics of antimony thioantimonate on stainless-steel in different greases showed considerable improvement over molybdenum disulfide. In general, antimony thioantimonate showed excellent response toward both tool and stainless steels in a variety of greases, including a silicone grease with which very few solid lubricants are compatible. Antimony thioantimonate is a candidate solid-lubricant ad-
### Table 5 — Antimony Thioantimonate Performance in Lithium Grease

<table>
<thead>
<tr>
<th>Property</th>
<th>Lithium Grease</th>
<th>Lithium Grease + 5% SbSbS</th>
<th>Lithium Grease + 5% MoS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (ASTM D 217)</td>
<td>253</td>
<td>315</td>
<td>304</td>
</tr>
<tr>
<td>Unworked</td>
<td>285</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>Worked, 60 strokes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drop point (ASTM D 506) F</td>
<td>305</td>
<td>360</td>
<td>470</td>
</tr>
<tr>
<td>Oxidation Stability (ASTM D 921)</td>
<td>10</td>
<td>7</td>
<td>34</td>
</tr>
<tr>
<td>Load in hours, 1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>210 F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lubrication Properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extreme-pressure properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ASTM D 2566)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wear prevention characteristics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ASTM D 2566)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Load, kg, 1000</td>
<td>0.70</td>
<td>0.63</td>
<td>0.65</td>
</tr>
<tr>
<td>Weld point, kg</td>
<td>160</td>
<td>760</td>
<td>250</td>
</tr>
<tr>
<td>Weld prevention characteristics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ASTM D 3253)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weld wear index</td>
<td>1.8</td>
<td>0.80</td>
<td>0.40</td>
</tr>
<tr>
<td>Copper Corrosion</td>
<td>pass</td>
<td>pass</td>
<td>pass</td>
</tr>
</tbody>
</table>

*ASTM D 2566
ASTM D 3253: steel + 1/13 steel blocks
With Cu, dithizone type of additives. The Shell Four Ball weld point of the resultant grease was 0200 kg.

### Table 6 — Falex Load-Carrying Properties* of Greases

<table>
<thead>
<tr>
<th>Grease + Additive</th>
<th>Failure Load (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>300</td>
</tr>
<tr>
<td>Lithium Grease + 5% SbSbS</td>
<td>1850</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS₂</td>
<td>2250</td>
</tr>
<tr>
<td>Silicone Grease</td>
<td>300</td>
</tr>
<tr>
<td>Silicone Grease + 5% SbSbS</td>
<td>300</td>
</tr>
<tr>
<td>Silicone Grease + 5% MoS₂</td>
<td>300</td>
</tr>
<tr>
<td>Clay Grease</td>
<td>2050</td>
</tr>
<tr>
<td>Clay Grease + 5% SbSbS</td>
<td>2850</td>
</tr>
<tr>
<td>Clay Grease + 5% MoS₂</td>
<td>3200</td>
</tr>
<tr>
<td>Aluminum Complex Grease</td>
<td>1000</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% MoS₂</td>
<td>1700</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% SbSbS</td>
<td>2100</td>
</tr>
</tbody>
</table>

*ASTM D 3235

### Table 7 — Lubricating Properties of Various Greases Containing SbSbS and MoS₂ with Stainless-Steel Balls (ASTM 440C)

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Steel Four Ball Weld Point (kg)</th>
<th>Load-Wear Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>80</td>
<td>3.50</td>
</tr>
<tr>
<td>Lithium Grease + 5% SbSbS</td>
<td>450</td>
<td>48.4</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS₂</td>
<td>100</td>
<td>6.14</td>
</tr>
<tr>
<td>Silicone Grease</td>
<td>80</td>
<td>2.9</td>
</tr>
<tr>
<td>Silicone Grease + 5% SbSbS</td>
<td>100</td>
<td>28.8</td>
</tr>
<tr>
<td>Silicone Grease + 5% MoS₂</td>
<td>80</td>
<td>3.28</td>
</tr>
<tr>
<td>Clay Grease</td>
<td>100</td>
<td>5.04</td>
</tr>
<tr>
<td>Clay Grease + 5% SbSbS</td>
<td>250</td>
<td>19.2</td>
</tr>
<tr>
<td>Clay Grease + 5% MoS₂</td>
<td>80</td>
<td>7.04</td>
</tr>
<tr>
<td>Aluminum Complex Grease</td>
<td>100</td>
<td>2.14</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% SbSbS</td>
<td>250</td>
<td>18.3</td>
</tr>
<tr>
<td>Aluminum Complex Grease + 5% MoS₂</td>
<td>100</td>
<td>3.98</td>
</tr>
</tbody>
</table>

Fig. 3—Load wear indexes of various solid additives in lithium grease (AISI-C-52100 steel balls).
Fig. 4—Scar diameter vs load: AISI-440-C stainless-steel balls, 25°C.

Fig. 5—Scar diameter vs load: AISI-440-C stainless-steel balls, 25°C.

1800 rpm. 10 s.

| TABLE 8—COMPARISON OF SLIDE-FOUR BALL WEAR RESULTS OF Si3N4 AND MoS2 ON CHROME STEEL AND STAINLESS STEEL BALLS |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| GREASE AND ADDITIVE | TEST BALL COMPOSITION | WEAR SCAR DIAMETER IN MILLIMETERS FOR 1800 RPM RUNS AT THE FOLLOWING | APPLIED LOADS IN KILOGRAMS |
| | | 10 | 20 | 50 | 100 | 125 | 150 | 200 | 250 | 300 | 400 | 500 | 600 | 750 | 900 |
| Lithium Grease - 3% MoS2 | 52100 | 0.30 | 0.36 | 0.45 | 0.53 | 1.00 | 1.48 | 1.74 | 2.78 weld |
| | 140 | 0.30 | 0.36 | 0.45 | 0.53 | 1.00 | 1.48 | 1.74 | 2.78 weld |
| Lithium Grease - 3% Si3N4 | 52100 | 0.50 | 0.50 | 0.50 | 0.50 | 1.00 | 1.48 | 1.74 | 2.78 weld |
| | 140 | 0.50 | 0.50 | 0.50 | 0.50 | 1.00 | 1.48 | 1.74 | 2.78 weld |
| Clay Grease - 5% MoS2 | 52100 | 0.85 | 0.77 | 0.68 | 0.53 | 0.85 | 2.04 weld |
| | 140 | 0.85 | 0.77 | 0.68 | 0.53 | 0.85 | 2.04 weld |
| Clay Grease - 5% Si3N4 | 52100 | 1.81 | 1.78 | 2.10 | 2.28 weld |
| | 140 | 1.81 | 1.78 | 2.10 | 2.28 weld |
| Silicone Grease - 3% MoS2 | 52100 | 0.71 | 0.72 | 0.71 | 0.72 | 1.23 | 1.46 weld |
| | 140 | 0.71 | 0.72 | 0.71 | 0.72 | 1.23 | 1.46 weld |
| Silicone Grease - 3% Si3N4 | 52100 | 1.59 | 1.60 | 1.59 | 1.60 | 1.47 | 1.66 weld |
| | 140 | 1.59 | 1.60 | 1.59 | 1.60 | 1.47 | 1.66 weld |
| Aluminum Complex Grease - 3% MoS2 | 52100 | 1.93 | 1.93 | 1.93 | 1.93 | 2.22 weld |
| | 140 | 1.93 | 1.93 | 1.93 | 1.93 | 2.22 weld |
| Aluminum Complex Grease - 3% Si3N4 | 52100 | 3.28 | 3.28 | 3.28 | 3.28 | 2.92 weld |
| | 140 | 3.28 | 3.28 | 3.28 | 3.28 | 2.92 weld |

*Chrome steel AISI 52100

ACKNOWLEDGMENTS

This work has been supported by the Office of Naval Research. The authors are grateful for the guidance and advises provided by Hal Martin of the Office of Naval Research on various aspects of this program. They also acknowledge the generous assistance of Paul Lubbs of Keystone Lubricant Division, Pennwalt Corporation.

REFERENCES

(1) Deane, W. H., and Sohlen, R. W.
DISCUSSION

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Philadelphia, Pennsylvania 19140

The authors should be commended for doing an excellent piece of work in the field of complex metal chalcogenides. This is to be expected since they have been doing extensive work in this field for many years. It is particularly interesting to note the results with stainless steel and silicone greases since each, in its own way, has inherent lubricating problems.

Have the authors run or are they contemplating running any tests with antimony thioantimonate to ascertain its value in resin-bonded solid film lubricants?

DISCUSSION

A. A. CONTE, JR. (Member, ASLE)
U.S. Naval Air Development Center
Warminster, Pennsylvania 18974

The potential of complex chalcogenides such as ShSbS4 as improved solid lubricant materials especially for hard-to-lubricate metals has been well documented [authors' references and (B1)] and this paper with its wealth of data continues to demonstrate this potential.

A property common to complex chalcogenides is that they are amorphous solids. This property is in contradiction to what has been generally considered to be a necessary but not sufficient requirement of a good solid lubricant, namely a layer-lattice structure. Would the authors care to comment on this observation? Is there any evidence that the thioantimonate anion is really present, that is, Sb in the +5 oxidation state and the Sh cation in the +3 oxidation state, or is it possible that a co-precipitation took place in which sulfur was intercalated into the structure of ShSbS4?

In the preparation of complex chalcogenides such as FeMoS4, the resultant product is really a mixture of FeS2 and MoS2 but in an intimately mixed state due to co-precipitation. Physically mixing FeS2 and MoS2 however, would not provide the same beneficial results. Finally, how reproducible are these results from batch-to-batch preparations and what is the anticipated cost of ShSbS4 relative to MoS2?

REFERENCES


DISCUSSION

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Wear Sciences
Arnold, Maryland 21012

The authors have presented some very interesting results concerning a new lubricant additive, "antimony sulfide." Their basic conclusion is that it is much better than MoS2 in that it increases the weld load to extremely high values even with difficult-to-lubricate metals such as stainless steel.

Since the authors have used standard test devices, the results more or less speak for themselves. There are, however, a few general questions which can be raised:

1. MoS2 does not yield a particularly high weld load when used in greases. Have the authors compared their results with organic sulfides such as di-phenyl, di-phenyl, or di-octyl?

2. Do the authors intend a direct comparison with MoS2? In other words, are they proposing that they are more or less interchangeable for the same types of application? If so, do they have a comparison of the two compounds dry?

3. Would the authors speculate on the mechanism of lubrication with this compound? Is it a low shear strength material, or is there some sulfur reaction which gives the high weld loads?

AUTHORS' CLOSURE

In reply to a point raised by both Messrs. Conte and Peterson concerning the possible lubrication mechanism of antimony thioantimonate—the fact that this amorphous sulfide is so effective as a lubricant is intriguing to us. Work is in progress both at the National Bureau of Standards and at our companies to investigate different aspects that may shed light on the mechanism.

In response to the questions raised by Mr. Peterson regarding comparison of results of organic disulfides and MoS2 with antimony thioantimonate—the reason that we listed the performance data of MoS2 is solely for reference. The weld points of the same base grease containing an organic disulfide have been determined and the results are given in Table 1. A study using antimony thioantimonate as a dry lubricant has been undertaken by the National Bureau of Standards.

Mr. Conte raised an interesting question regarding a possible structure of antimony thioantimonate which may result from elemental sulfur intercalated into ShSbS4 lattice. Interkalation consists of insertion of a guest species into a host structure with substantial retention of the structural features of the host. Virtually all of the intercalation compounds exhibit X-ray diffraction patterns which are differ-
TABLE D1—WELD POINTS OF LITHIUM GREASE CONTAINING VARIOUS ADDITIVES

<table>
<thead>
<tr>
<th>Additive Description</th>
<th>Weld Point, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Grease</td>
<td>140</td>
</tr>
<tr>
<td>Lithium Grease + 5% MoS₂</td>
<td>250</td>
</tr>
<tr>
<td>Lithium Grease + 5% Dibenzyl Disulfide</td>
<td>180</td>
</tr>
<tr>
<td>Lithium Grease + 5% Diphenyl Disulfide</td>
<td>160</td>
</tr>
<tr>
<td>Lithium Grease + 5% Dioctyl Disulfide</td>
<td>120*</td>
</tr>
<tr>
<td>Lithium Grease + 1% SbSbI₃</td>
<td>400</td>
</tr>
<tr>
<td>Lithium Grease + 5% SbSbI₃</td>
<td>760</td>
</tr>
</tbody>
</table>

*Dioctyl disulfide is a liquid at room temperature and the grease structure was destroyed upon addition of 5% dioctyl disulfide. This may explain that its weld point is lower than the base grease.

...ent from those of the hosts because of expansion of lattices. Since antimony thioantimonate is amorphous, formation of an intercalation structure in this case is doubtful.

Good reproducibility on elemental analysis and performance results has been obtained from different batches of antimony thioantimonate. An estimate cost of antimony thioantimonate will be available upon completion of our current scale-up study.
Abstract: There is a crucial need for effective lubricant additives that are capable of preventing damage that may occur due to contamination of lubricating systems by abrasive particles. This is an essential requirement for lubricants used in equipment and military vehicles that are operated in sandy environments. The effect of antimony thioantimonate (SbSbS₄) in three base greases—MIL-G-10924, MIL-G-24139, and MIL-G-81322—was investigated. The presence of SbSbS₄ in these greases provided considerable improvements in weld point, load wear index, and wear prevention properties with two different alloys. Moreover, impressive wear resistance properties were imparted by low concentrations of SbSbS₄ in these greases deliberately contaminated with hard abrasive particles. The combination of outstanding EP and antiwear characteristics and anti-abrasion properties of antimony thioantimonate makes this material an attractive candidate as a grease additive. Extensive field testing of greases containing this material is recommended.

Key words: Solid lubricant additive; antimony thioantimonate; abrasive wear; extreme pressure and antiwear properties; greases.

INTRODUCTION

Abra...
particles become entrained in the lubricant. Sources of such hard particles include airborne contaminants entering the system during equipment assembly or repair, finely divided wear products from system components, fine debris resulting from oxidation or corrosion, and operation in sandy environments. Accordingly, a critical property of a lubricant material or additive is its ability to prevent or minimize component wear in the presence of hard abrasive particles.

Antimony thioantimonate \(\text{SbSbS}_4\), when incorporated into a number of selected greases as a solid additive at low concentration, imparts outstanding extreme pressure properties on both chrome tool and stainless steels.\(^2\) An initial evaluation of \(\text{SbSbS}_4\) in several military greases was conducted with the objective of selecting one or more of these greases to be formulated with \(\text{SbSbS}_4\) for field evaluation involving sandy environment. To investigate additive response in the presence of abrasives, a grit material having precise composition and known particle size was incorporated into those greases with and without the presence of \(\text{SbSbS}_4\). The extreme pressure and antiwear characteristics of these greases with and without \(\text{SbSbS}_4\) and \(\text{MoS}_2\) as additives were determined and compared.

PREPARATION OF ANTIMONY THIOANTIMONATE \(\text{SbSbS}_4\)

Antimony thioantimonate was prepared by the modified procedures as described in Progress Report No. 7. A large supply of this material was synthesized in preparation for the coming field evaluation.

GREASES

Three fully formulated greases meeting the following military specifications were used as base materials:

- MIL-G-10924 - Grease, Automotive and Artillery (GAA)
- MIL-G-24139 - Grease, Multipurpose Quiet Service
- MIL-G-81322 - Grease, Aircraft General Purpose Wide Temperature Range

GRIT MATERIAL

The grit material used in abrasive study was supplied by the A/C Division of General Motors Corporation, Flint, Michigan. It has an average particle size of 60-80 \(\mu\) and the following composition:
The abrasive wear study was carried out on a Falex machine using AISI-C-3135 steel pins (Rb87-91) and AISI-C-1137 V-blocks (Rc20-24). The testing speed, temperature, and load were 290 rpm, 77°F, and 100 lbs, respectively. The following procedures were employed.

1. Test specimens (pin and V-blocks) were cleaned with xylene followed by acetone and then air dried.
2. Test pin was inserted in pinholder.
3. Grooves of V-blocks were filled with grease sample and struck flush.
4. V-blocks were set in their sockets.
5. Jaw loading assembly was mounted on lever arms.
6. Jaw load was brought to a gauge load of 100 lbs (manual turning of ratchet wheel).
7. Drive motor was started and test run to 30 seconds, or to failure if prior to 30 seconds. Failure was indicated by rupture of pin or rapid torque increases above 40 in-lb and excessive noise.
8. Test pin was cleaned with xylene and acetone before making visual observation.

Four-Ball Testers

The extreme pressure and antiwear properties of the greases were determined on Shell Four-Ball EP and Wear Testers. These testers consist of steel spherical specimens sliding against each other. Weld points and load wear indices were determined in a series of runs (10 sec., 1800 rpm at 77°F) conducted at various loads, and scar diameters were measured after each run in accordance with ASTM-D-2596.
prevention characteristics were determined by measuring wear diameters of test specimens after each run at specified rpm, load, temperature and duration (ASTM-D-2266). Two alloys—chrome tool steel AISI-C-52100 and stainless steel AISI-440C—were used.

RESULTS AND DISCUSSION

Abrasive Wear Study

Abrasive wear tests were conducted with the Falex machine for the three base greases (MIL-G-10924, MIL-G-24139, and MIL-G-81322), the three base greases with 5% MoS₂, the three base greases with 5% SbSbS₄, and same modified greases containing abrasive particles. The results for the abrasive wear resistance imparted by 5% concentration of SbSbS₄ in MIL-G-10924 and MIL-G-24139 greases are presented in Figure 1. It can be observed that severe wear and surface damage occur with either MIL-G-10924 or MIL-G-24139 (both containing 5% grit); however, SbSbS₄ virtually eliminates such wear and surface damage. Wear effects were also noted with MIL-G-81322 in the presence of abrasive particles, although the base grease is originally formulated to provide some degree of protection from surface damage in sliding contact. The presence of SbSbS₄ further improved the antiwear properties of this grease. The presence of MoS₂ in all the three base greases also provides some degree of surface protection; however, by visual observation the results are not as evident in all cases as those obtained with SbSbS₄.

Extreme Pressure and Antiwear Properties

As indicated earlier, all three base greases studied had been fully formulated at the source in order to meet the military specifications, i.e., they contained additives. Our primary interest was to improve abrasive wear resistance of these greases by incorporation of SbSbS₄; however, the extreme pressure and antiwear properties were also obtained in order to determine whether these performance properties were further improved by the presence of SbSbS₄.

We found that the weld points and load wear indices of MIL-G-10924 could be considerably improved by the presence of 1 to 5% SbSbS₄. At 5% concentration of MoS₂ no increase in weld point of this grease was observed; however, its load wear index was somewhat higher than the base grease. Indeed, the EP properties of the base grease containing 1% SbSbS₄ were found to be superior to those of the same base grease containing 5% MoS₂. The antiwear characteristics of
The base grease containing 1% SbSbS4 showed slight improvement over its base grease. The experimental data are recorded in Table I. A graphical comparison of the data obtained on these greases is presented in Figure 2.

The weld point and load wear index of MIL-G-24139 containing 1% SbSbS4 were significantly higher than those of the base grease. The weld point and load wear index of the base grease containing 3% SbSbS4 were lower than that of the same base grease containing 1% SbSbS4. The wear prevention characteristics of samples of the base grease containing 1% SbSbS4 and 3% MoS2, respectively, were comparable and were a dramatic improvement over the base grease on both chrome tool and stainless steels. The experimental data are recorded in Table II and a graphical presentation is shown in Figure 3.

Because of insufficient supply of MIL-G-81322 grease available to us at this time, load wear indices were not determined. The weld point of MIL-G-81322 containing 1 and 3% SbSbS4 showed 25 and 100% improvements over the base grease, respectively. With 3% MoS2 a weld point increase of 56% was observed. The base grease, as originally formulated, showed good wear prevention characteristics on chrome tool steel. No significant improvement of wear prevention characteristics on both chrome tool and stainless steels was achieved by incorporation of MoS2 or SbSbS4 into the base grease. The results are listed in Table III.

CONCLUSIONS

1. The abrasive wear resistance of both MIL-G-10924 and MIL-G-24139 greases was dramatically improved by incorporation of low concentrations of SbSbS4.

2. The extreme pressure and antiwear properties of three base greases—MIL-G-10924, MIL-G-24139, and MIL-G-81322—were greatly enhanced by using SbSbS4 as a solid additive. At a lower concentration this additive outperformed MoS2 in all cases.

3. Antimony thioantimurate showed good response to both chrome tool steel AISI-G-52100 and stainless steel AISI-440C in all three base greases investigated.

4. The presence of SbSbS4 in these three base greases does not adversely affect other properties such as water washing out, rust prevention, drop point, etc. (Investigation of some of these properties is planned).

5. The use of SbSbS4 as a solid additive in these greases
These results with SBSBS₄ as extreme pressure and anti-wear agent indicate potential for significant impact covering major improvements for lubricating greases, especially the current MIL-G-10924 (GAA) improvements being pursued by the U. S. Army Mobility Equipment Research and Development Command (DRDME-GL), Fort Belvoir, Va.

ACKNOWLEDGMENT

This work was supported by the Office of Naval Research. The guidance and encouragement provided by Commander Harold P. Martin is greatly appreciated.

REFERENCES


Table 1. Weld Points, Load Wear Indices, and Wear Scar Diameters of MIL-G-10924 Grease Containing Additives

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Weld Point, $^1$ kg</th>
<th>LWI$^1$</th>
<th>Wear Scar$^2$ Diameter, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-G-10924 Grease (GAA)</td>
<td>160</td>
<td>29.3</td>
<td>0.62</td>
</tr>
<tr>
<td>&quot; + 1% SbSbS$_4$</td>
<td>250</td>
<td>39.4</td>
<td>0.59</td>
</tr>
<tr>
<td>&quot; + 5% SbSbS$_4$</td>
<td>315</td>
<td>56.7</td>
<td>0.59</td>
</tr>
<tr>
<td>&quot; + 5% MoS$_2$</td>
<td>160</td>
<td>38.4</td>
<td>0.57</td>
</tr>
</tbody>
</table>

1. ASTM-D-2596 - AISI 52100 Steel
2. ASTM-D-2266 - 1200 rpm, 40 kg, 167°F for one hour on AISI 52100 steel
Table II. Weld Points, Load Wear Indices and Wear Scar Diameters of MIL-G-24139 Grease Containing Additives

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Chrome Tool Steel 52100</th>
<th>Stainless Steel 440-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weld Point¹ kg</td>
<td>LWI¹</td>
</tr>
<tr>
<td>MIL-G-24139 Grease (AMI)</td>
<td>126</td>
<td>14.1</td>
</tr>
<tr>
<td>&quot; + 1% SbSbS₄⁴</td>
<td>315</td>
<td>38.1</td>
</tr>
<tr>
<td>&quot; + 2% SbSbS₄</td>
<td>---</td>
<td>----</td>
</tr>
<tr>
<td>&quot; + 1% MoS₂</td>
<td>---</td>
<td>----</td>
</tr>
<tr>
<td>&quot; + 5% MoS₂</td>
<td>200</td>
<td>27.9</td>
</tr>
</tbody>
</table>

1. ASTM-D-2596
2. 40 kg, 77°F and 1800 rpm for 5 min.
3. 20 kg, 77°F and 1800 rpm for 5 min.
4. The presence of SbSbS₄ in MIL-G-24139 did not cause copper corrosion according to ASTM-D-130 (212°F for 1 h).
Table III. Weld Points and Wear Scar Diameter of MIL-G-81322 Grease Containing Additives

<table>
<thead>
<tr>
<th>Grease Composition</th>
<th>Chrome Tool Steel 52100</th>
<th>Stainless Steel 440-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weld Point (^1) kg</td>
<td>Wear Scar Diameter (^2) mm</td>
</tr>
<tr>
<td>MIL-G-81322 Grease (MOB)</td>
<td>160</td>
<td>0.41</td>
</tr>
<tr>
<td>&quot; + 1% SbSb(_S_4)</td>
<td>200</td>
<td>0.39</td>
</tr>
<tr>
<td>&quot; + 3% SbSb(_S_4)</td>
<td>315</td>
<td>0.56</td>
</tr>
<tr>
<td>&quot; + 5% Mo(_S_2)</td>
<td>250</td>
<td>0.41</td>
</tr>
</tbody>
</table>

1. ASTM-D-2596
2. 40 kg, 77\(^\circ\)F, and 1800 rpm for 5 min.
3. 20 kg, 77\(^\circ\)F, and 1800 rpm for 5 min.
Figure 1. Effect of SbSbS₄ on Abrasive Wear

The outstanding wear resistance properties imparted by SbSbS₄ to greases containing grit particles (primarily SiO₂ 60-80 μ) are illustrated by these Falex pins:

- a = grease MIL-G-24139 with 5% grit
- b = " " " " and 5% SbSbS₄
- a' = " MIL-G-10924 " " and 5% SbSbS₄
- b' = " " " " and 5% SbSbS₄
Figure 2. Wear Scar Diameter vs. Load; AISI-C-52100 Steel Balls; 25°C, 1800 rpm, 10s

1. MIL-G-10924 (GAA)
2. GAA + 5% MoS₂
3. GAA + 1% SbSbS₄
4. GAA + 5% SbSbS₄
Figure 3. Wear Scar Diameter vs. Load; AISI-C-52100 Steel Balls; 25°C, 1800 rpm, 10s

- 1. AMI (MIL-G-24139)
- 2. AMI + 5% MoS₂
- 3. AMI + 1% SbSb₄
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