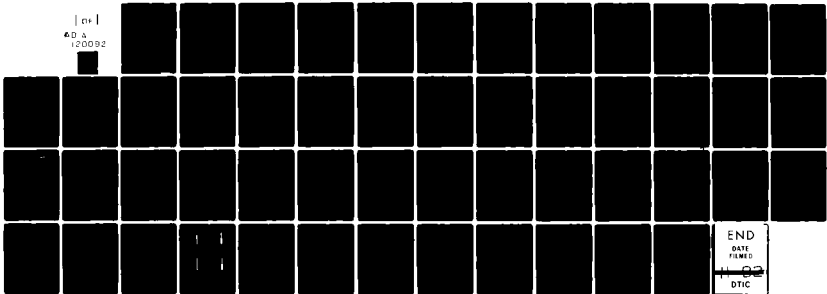


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FINAL REPORT
1 April 1979 - 30 September 1981

SOLID LUBRICANTS FOR IMPROVED WEAR RESISTANCE

James P. King and Yayesh Asmerom

**Pennwalt Corporation
Central Research and Development
King of Prussia, PA 19406**

July 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Detailed studies including synthesis, characterization and evaluation of antimony thioantimonate, $SbSbS_4$, 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		

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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 examined¹⁻⁴ 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.² 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 purity, and higher yield compared with the original method.³ 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 possibly 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.

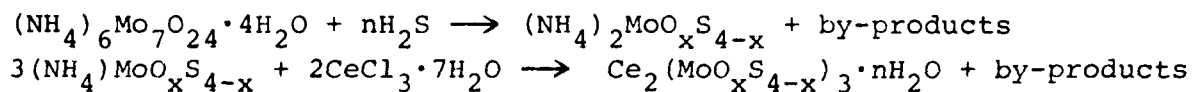
D. CERIUM OXYTHIOMOLYBDATES

1. General

Numerous attempts to prepare cerium thiomolybdate, $\text{Ce}_2(\text{MoS}_4)_3$, gave products with elemental analysis corresponding to cerium oxythiomolybdate complexes, $\text{Ce}_2(\text{MoO}_x\text{S}_{4-x})_3 \cdot n\text{H}_2\text{O}$, 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



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 $\text{Ce}_2(\text{MoO}_{1.2}\text{S}_{2.8})_3 \cdot 6\text{H}_2\text{O}$ by elemental analysis. The material was found to be amorphous by X-ray diffraction.

Tables I through IV summarize the performance data of $\text{Ce}(\text{MoO}_{1.2}\text{S}_{2.8})_3 \cdot 6\text{H}_2\text{O}$ 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

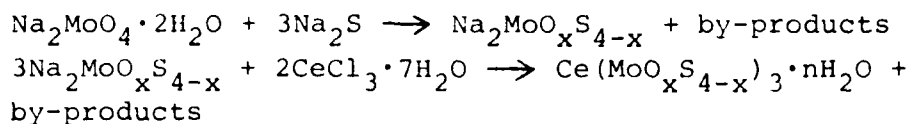
complex again shows superior antiwear characteristics and comparable extreme pressure properties to those of molybdenum disulfide.

A lithium grease containing a mixture of 1% SbSbS_4 and 1% $\text{Ce}_2(\text{MoO}_{1.2}\text{S}_{2.8})_3 \cdot 6\text{H}_2\text{O}$ 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.

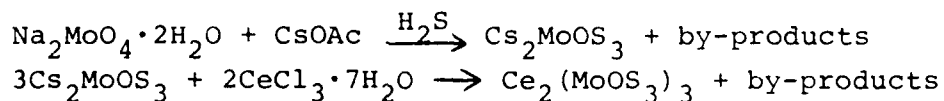
The cerium complex was also evaluated in an aluminum complex grease. The Shell Four-Ball weld points and load wear indices of this grease containing 5% MoS_2 and 5% $\text{Ce}_2(\text{MoO}_{1.2}\text{S}_{2.8})_3 \cdot 6\text{H}_2\text{O}$ are recorded in Table I. It appears that the cerium complex shows slightly superior EP performance to MoS_2 .

3. Reaction of Sodium Molybdate with Sodium Sulfide



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



The synthesis of cesium oxythiomolybdate, Cs_2MoOS_3 , was carried out as reported in the literature⁵ 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 $\text{Ce}_2(\text{MoOS}_3)_3 \cdot n\text{H}_2\text{O}$ starting from Cs_2MoOS_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 Cs_2MoOS_3 in 2:3 molar ratio at room temperature. A light brown solid was isolated (about 50% yield) whose analysis (Ce:Mo:S = 2:2.2:5.7) did not correspond to the expected composition, $\text{Ce}_2(\text{MoOS}_3)_3 \cdot n\text{H}_2\text{O}$. 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 Cs_2MoOS_3 and Selected Samples of Cerium Oxythiomolybdate Complexes

a. Cesium Oxythiomolybdate - Cs_2MoOS_3

Thermogravimetric analysis of cesium oxythiomolybdate was carried out both in air and nitrogen at a heating rate of $5^\circ\text{C}/\text{minute}$. 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 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 Cs_2MoOS_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.

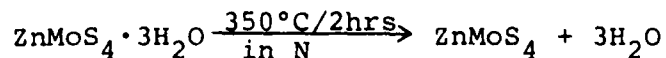
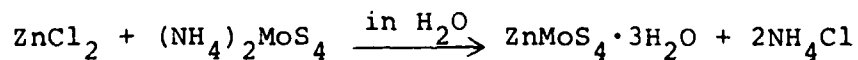
E. ZINC THIO- AND OXYTHIOMOLYBDATES

1. General

Synthesis and characterization of three stoichiometric zinc thio- and oxythiomolybdates - $\text{ZnMoS}_4 \cdot 3\text{H}_2\text{O}$, $\text{ZnMoOS}_3 \cdot 3\text{H}_2\text{O}$, and $\text{ZnMoO}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$ - 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, ZnMoO_2S_2 was found to be much superior to MoS_2 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 ZnMoO_2S_2 in air is shown in Figure IV.

2. Preparation of $\text{ZnMoS}_4 \cdot 3\text{H}_2\text{O}$ and ZnMoS_4



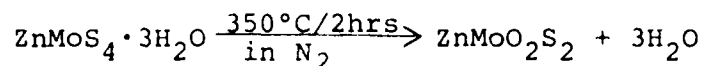
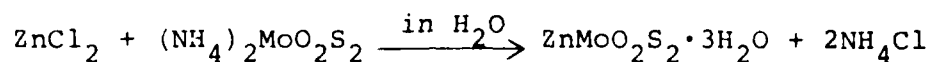
A sample of 5.0 g $(\text{NH}_4)_2\text{MoS}_4$ (prepared as described in the literature⁶) was dissolved in 100 ml distilled water. The resulting solution was slowly added with an aqueous solution of ZnCl_2 (2.6 g in 20 ml distilled water). A black solid formed immediately. The reaction

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 $\text{ZnMoS}_4 \cdot 3\text{H}_2\text{O}$: 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 $\text{ZnMoO}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$ and ZnMoO_2S_2

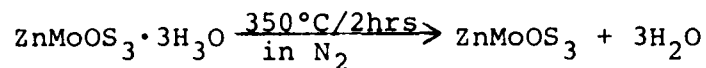
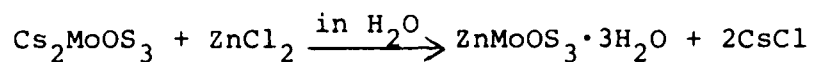


An aqueous solution of ZnCl_2 (5.38 g in 50 ml distilled water) was slowly added to a solution of $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ (9.0 g in 100 ml distilled water; the compound was prepared as described in the literature^{6,7}) resulting in slightly exothermic reaction. A dark brown solid formed 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 $\text{ZnMoO}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$: 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 $\text{ZnMoOS}_3 \cdot 3\text{H}_2\text{O}$ and ZnMoOS_3



A solution of 15.4 g $\text{Cs}_2(\text{MoOS}_3)$ (prepared as described in the literature⁵) in 100 ml distilled water was treated with a ZnCl_2 solution (4.4 g in 30 ml distilled water). The reaction mixture was refluxed 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 $\text{Zn}(\text{MoOS}_3) \cdot 3\text{H}_2\text{O}$: 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 $\text{ZnMoO}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$ with favorable results, as follows:

Skin irritation test: Non irritating

Eye irritation test: Mildly irritating without washout

Acute dermal LD50 (rabbits) >2g/kg

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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 Indices¹
of Cerium Oxythiomolybdate² in Lithium and Aluminum
Complex Greases on Chrome Tool Steel Balls (AISI-52100)

<u>Grease Composition</u>	<u>Weld Point kg</u>	<u>Scar Diameter Before Weld mm (kg)</u>	<u>Load Wear Index</u>
Lithium Grease	140	2.64 (126)	18.3
Lithium Grease + 5% MoS ₂	250	2.90 (224)	30.4
Lithium Grease + 5% Cerium Complex	250	2.02 (200)	41.4
Lithium Grease + 1% SbSbS ₄ + 1% Cerium Complex	400	1.61 (315)	59.5
Aluminum Complex Grease (ACG)	100	2.10 (70)	11.8
ACG + 5% MoS ₂	190	2.24 (160)	35.5
ACG + 5% Cerium Complex	200	2.10 (160)	40.2

1. ASTM-D-2596

2. Ce₂(MoO_{1.2}S_{2.8})₃·6H₂O

Table II. Shell Four-Ball Weld Point and Load Wear Index¹
of Cerium Oxythiomolybdate² in Lithium Grease
on Stainless Steel Balls (AISI-440C)

<u>Grease Composition</u>	<u>Weld Point kg</u>	<u>Load Wear Index</u>
Lithium Grease	80	3.5
Lithium Grease + 5% MoS ₂	100	6.1
Lithium Grease + 5% Cerium Complex	100	10.4
Lithium Grease + 1% SbSbS ₄ and 1% Cerium Complex	140	11.8

1. ASTM-D-2596

2. $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$

Table III. Shell Four-Ball Wear Prevention Characteristics¹ of Lithium Grease Containing Additives on Chrome Tool Steel Balls (AISI-52100) and Stainless Steel Balls (AISI-440C)

<u>Grease Composition</u>	<u>Wear Scar Diameter on 52100 Balls mm</u>	<u>Wear Scar Diameter on 440-C Balls mm</u>
Lithium Grease	0.70	3.96
Lithium Grease + 5% MoS ₂	0.65	2.34
Lithium Grease + 5% Cerium Complex ²	0.40	1.38
Lithium Grease + 1% SbSbS ₄ and 1% Cerium Complex ²	0.43	0.84

1. ASTM-D-2266 - 1200 rpm, 167°F, 40 kg for one hour

2. Ce₂(MoO_{1.2}S_{2.8})₃·6H₂O

Table IV. Effect of Concentration of $Ce_2(MoO_{1.2}S_{2.8})_3 \cdot 6H_2O$ in
Lithium Grease on Wear Scar Diameters¹

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

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% $Ce_2(MoO_xS_{4-x})_3 \cdot nH_2O$ prepared from ammonium oxythiomolybdate
- III. Lithium Grease + 5% $Ce_2(MoO_xS_{4-x})_3 \cdot nH_2O$ prepared from cerium oxythiomolybdate

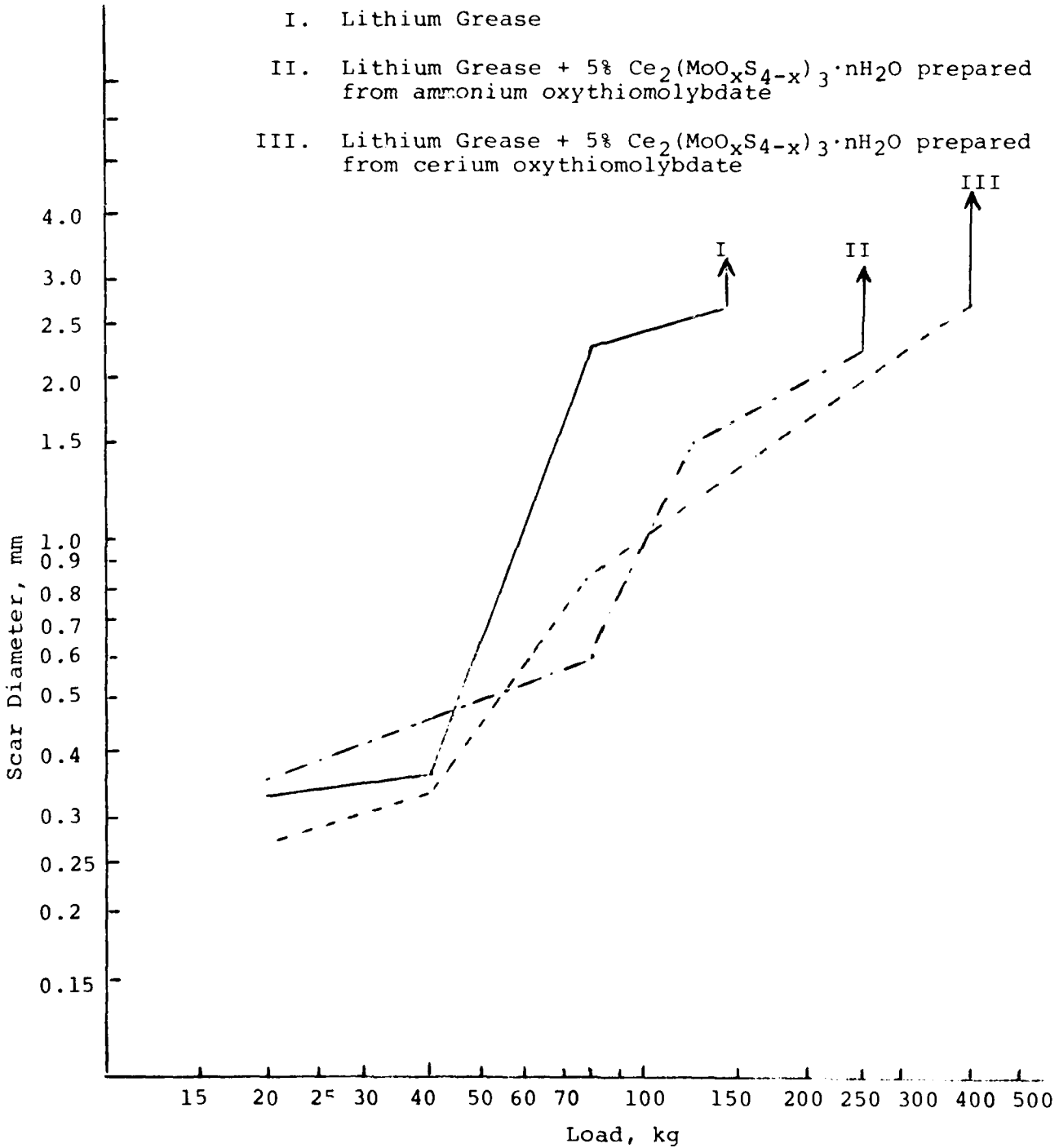


Figure II. Thermogravimetric Analysis of Cs_2MoOS_3 in Air and Nitrogen

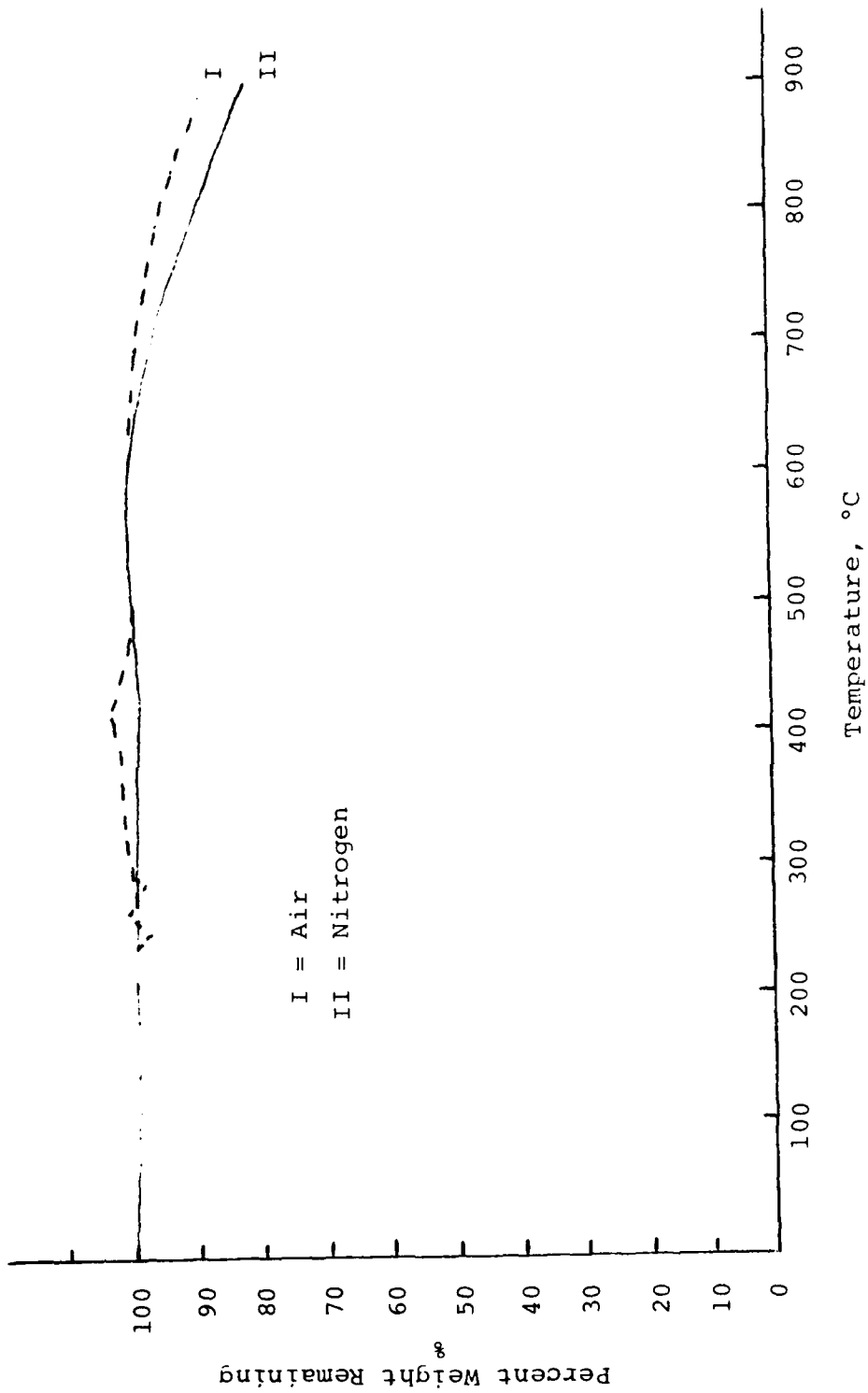


Figure III. Thermogravimetric Analysis in Air of Cerium Oxythiomolybdate Complexes Prepared By Two Different Methods

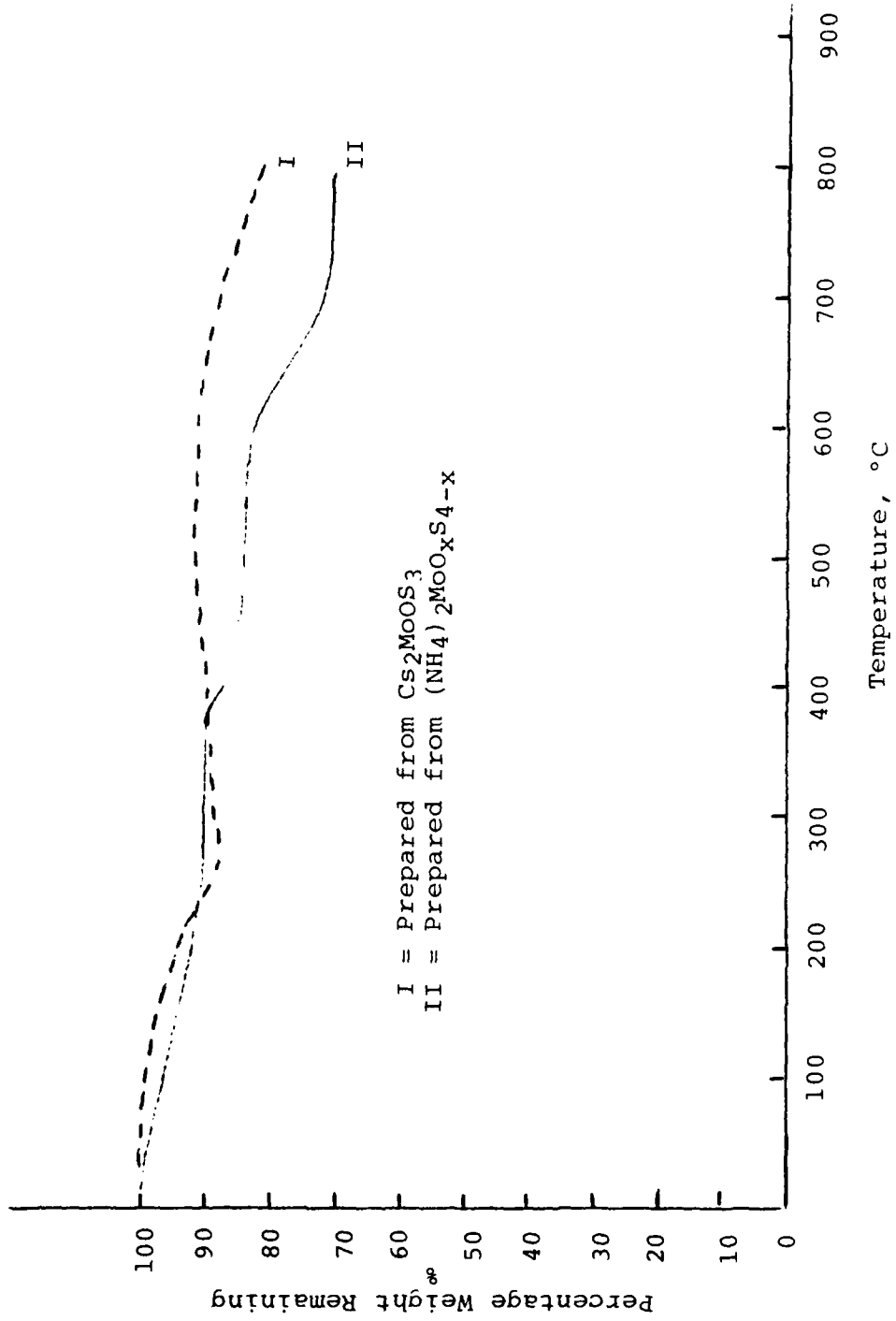


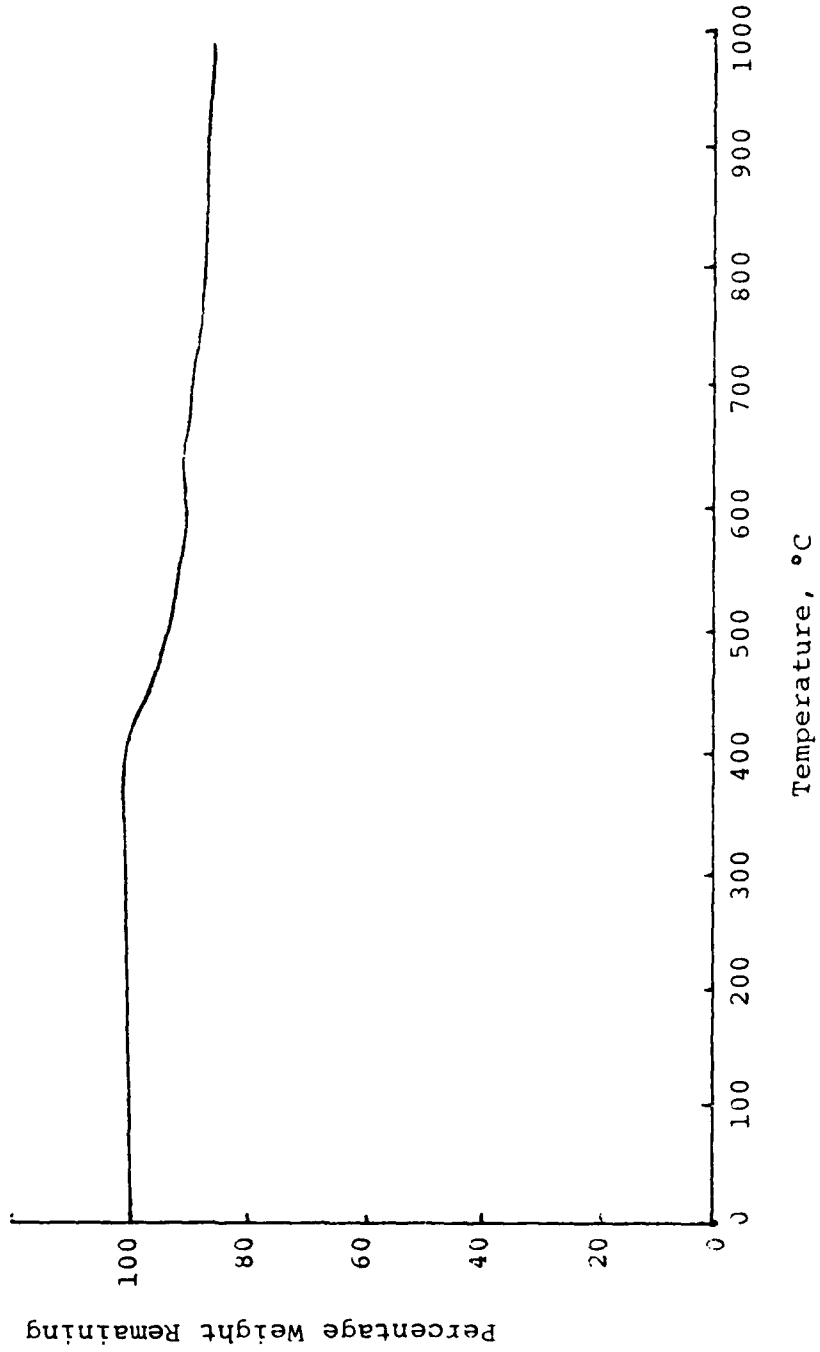
Table V. Lubricant Properties of Thio- and Oxythiomolybdate Complexes

Grease Composition	Weld Pt. kg	LWI ^a	Wear Scar Diameter, MM ^b			
			Before	After		
			52100 SS 440	52100 SS 440		
Lithium Grease (L.G.)	140	18.3	0.70	3.96	---	---
L.G. + 5% MoS ₂	250	80.4	0.65	2.34	---	---
L.G. + 5% ZnMoS ₄ ·3H ₂ O	250	37.4	0.42	0.44	0.38	0.38
L.G. + 5% ZnMoOS ₃ ·3H ₂ O	315	52.0	0.44	0.53	0.50	1.50
L.G. + 5% ZnMoO ₂ S ₂ ·3H ₂ O	315	60.6	0.40	0.84	0.48	0.61

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 $ZnMoO_4S_2$ in Air





Investigation of Extreme-Pressure and Antiwear Properties of Antimony Thioantimonate

JAMES P. KING (Member, ASLE) and YAYESH ASMEROM
Pennwalt Corporation
King of Prussia, Pennsylvania 19106

Detailed studies including synthesis, characterization and evaluation of antimony thioantimonate, SbSbS₃, have been carried out. The amorphous complex chalcogenide was prepared by a solution precipitation method. As a solid lubricant additive in various greases, this material exhibits superior extreme pressure and antiwear properties as demonstrated by the Four Ball wear points and load wear indices on both AISI 52100 and AISI 440C steels. Antimony thioantimonate appears to be compatible with all the base greases investigated including a silicone grease in which very few additives show good response.

INTRODUCTION

Continuing advances in technology require the development of lubricant systems capable of meeting the challenge presented by increasing speeds, 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 crucial 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 hydrocarbon 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 chalcogenides previously synthesized were examined (1), (2), (3), (4) for their performance as extreme-pressure and antiwear additives in

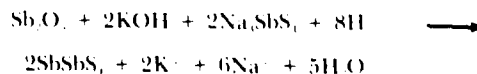
greases, solid-film lubricants and fluids. As extreme-pressure and antiwear additives, these complex chalcogenides were superior to simple sulfides, including MoS₂. One composition, arsenic thioantimonate—which was well characterized and evaluated (2)—was found to be an outstanding solid lubricant. When the safety of all inorganic arsenic compounds came under question, development of arsenic thioantimonate was terminated.

A study was then undertaken to determine the potential of antimony thioantimonate, SbSbS₃, as a solid-lubricant additive. This report covers investigation of the lubricating properties of SbSbS₃ 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 solution by a precipitation procedure similar to that used to prepare arsenic thioantimonate (1). An alkaline solution of Sb₂O₃ was added to an aqueous solution of sodium thioantimonate (Na₂SbS₃·9H₂O). The resulting solution was filtered to remove a small amount of NaSb(OH)₄, and the filtrate was slowly neutralized with a 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 vacuo at 75°C. to constant weight. Sodium thioantimonate solution was prepared by refluxing a mixture of sodium sulfide, sulfur and antimony trisulfide (3:1.05:1 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:



The ammonium trisulfide of 97-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 I.

Test Methods

Four-Ball Tests

The extreme-pressure and antiwear properties of the greases were determined on Shell Four-Ball EP and Wear Testers. These testers provide for sliding steel vs steel (AISI-52100 vs AISI-52100 and AISI-149C vs AISI-149C) with spherical specimens. Weld points and load wear indexes were determined in a series of runs (10 s, 1800 rpm, 77 F) conducted at various loads, and scar diameters were measured after each run in accordance with ASTM D 2596. Wear prevention characteristics were determined by measuring scar diameters of test specimens after each run at 1200 rpm, 40 kg, 167 F for one hour. This test is described in ASTM D 2266.

Falex Machine

The load-carrying capacities of certain selected grease samples were measured on a Falex machine using AISI-C-3135 steel pins and AISI-C-1137 V-blocks. The testing procedure is similar to ASTM D 3233.

Oxidation Test

Antioxidant properties of some greases were determined in an oxidation bomb under pure oxygen at 210 ± 2 F for 100 h. Relative antioxidant ability was rated by measuring the drop in oxygen pressure after 100 h. This test is described in ASTM D 942.

Copper Corrosion

A copper strip was allowed to remain in contact with the lubricating grease containing the complex sulfide for a period of 24 h 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 5309.2 of FIMS No. 791a.

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 34.2 percent S; Calcd Sb 65.5 percent and 34.5 percent S). The density determined at 23°C is 3.55 g/cc. The thermal stability of SbSbS₂ has been investigated by thermogravimetric analysis. When SbSbS₂ is heated in air at 9.1 mm, 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 840 F is exceeded. At 750 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 36 h, the sample had lost 9.1 percent of its original weight, which closely approaches the theoretical weight loss for conversion of Sb₂S₃ to Sb₂S₅, and the resulting product was identified as crystalline Sb₂S₅ by X-ray diffraction analysis.

Results and Discussion

Lubricating Properties of SbSbS₂ 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 molyb-

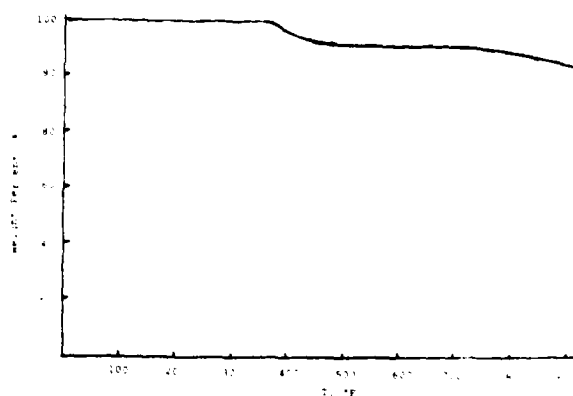


Fig. 1—Thermogravimetric analysis of SbSbS₂ in air

GREASE	THICKENER (%)	FLUID
A. Lithium Grease	Litham 12 OH Stearate (6)	Naphthene mineral oil
B. Clay Grease	Clay (5)	Paraffinic mineral oil
C. Silicone Grease	Lithium Stearate (12)	Methylphenyl silicone
D. Aluminum Complex Grease	Aluminum Complex (7.5)	Paraffinic mineral oil

*No other chemical agents were included in these greases, so the effect of specific additives could be determined.

denium disulfide in the same base greases were also determined. The weld points and wear load indices with chrome-tool steel balls (AISI-52100) were determined for base greases, base greases containing 5-percent antimony thioantimonate, 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, antimony thioantimonate (SbSbS₃) has antiwear and EP properties superior to those of molybdenum disulfide. In fact, even the 1-percent SbSbS₃ 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 SbSbS₃ or 5-percent MoS₂, were determined on a Four-Ball Wear Tester at 40 kg, 167 F, 1200 rpm for one hour. The results for 52100 steel vs 52100 steel and 440C stainless steel vs 440C stainless steel are recorded in Table 3. The wear prevention characteristics with chrome-steel balls (AISI 52100) showed a slight improvement for the greases containing SbSbS₃ and MoS₂ over the corresponding base greases in most cases. There is no significant difference in antiwear properties at 40-kg load between SbSbS₃ and MoS₂ in all four greases.

The effect of antimony thioantimonate concentration on the lubricating properties of a lithium grease was investigated. The weld points and load-wear indices of a lithium grease containing 0.5 to 5.0-percent antimony thioantimonate were determined. For comparison, the weld points and load-wear indexes of the same base grease containing 1 to 5-percent MoS₂ were also obtained. The results are listed in Table 4. These results suggest that high-performance EP greases can be formulated with considerably lower concentrations of SbSbS₃ than of MoS₂. The results of various properties of lithium grease containing 5-percent SbSbS₃ and 5-percent MoS₂ are recorded in Table 5.

A lithium grease containing different extreme-pressure

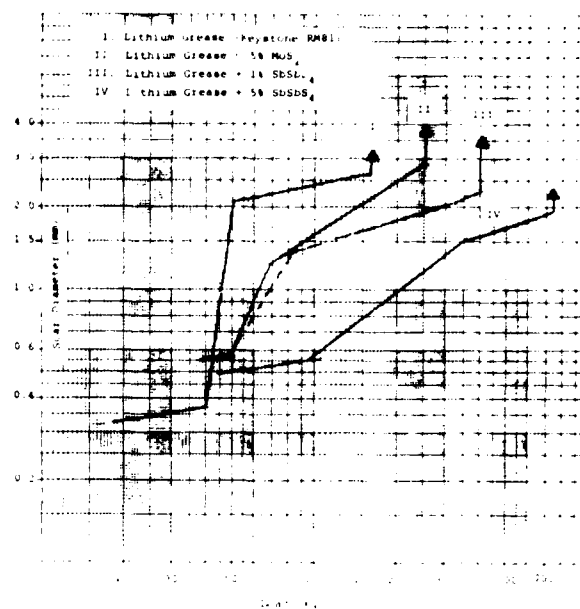


Fig. 2—Wear scar diameter vs load; AISI-C-52100 steel balls; 25°C, 1800 rpm, 10 s.

additives, including both inorganic 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 antimony thioantimonate were demonstrated.

Preliminary evaluation of the load-carrying properties of various base greases containing antimony thioantimonate (SbSbS₃) and MoS₂ were carried out on a Falex machine. The results are recorded in Table 6.

Lubricating Properties of SbSbS₃ on Stainless-Steel AISI-440C

In general, corrosion-resistant metals or alloys are diff-

TABLE 2—WELD POINTS AND LOAD WEAR INDICES* OF ANTIMONY THIOANTIMONATE IN VARIOUS GREASES

	WELD POINT kg	SCAR DIAMETER BEFORE WELD mm(kg)	LOAD WEAR INDEX
Lithium Grease	140	2.64 (126)	18.3
Lithium Grease + 5% MoS ₂	250	2.90 (224)	30.4
Lithium Grease + 1% SbSbS ₃	400	2.38 (315)	43.0
Lithium Grease + 5% SbSbS ₃	760	2.20 (740)	98.3
Silicone Grease	126	2.17 (100)	15.7
Silicone Grease + 5% MoS ₂	190	1.44 (160)	33.1
Silicone Grease + 5% SbSbS ₃	560	1.96 (500)	74.9
Clay Grease	200	2.74 (180)	26.2
Clay Grease + 5% MoS ₂	250	2.72 (224)	38.8
Clay Grease + 5% SbSbS ₃	560	1.86 (500)	78.1
Aluminum Complex Grease	100	2.10 (70)	11.8
Aluminum Complex Grease + 5% MoS ₂	190	2.24 (160)	35.5
Aluminum Complex Grease + 5% SbSbS ₃	448	2.02 (400)	83.7

*ASTM D2796—AISI 52100 steel balls

GREASE COMPOSITION	WEAR SCAR	WEAR SCAR
	DIAMETER ON AISI-C-52100 BALLS (mm)	DIAMETER ON AISI-440C BALLS (mm)
Lithium Grease	0.70	3.96
Lithium Grease + 5% SbSb ₃	0.63	0.78
Lithium Grease + 5% MoS ₂	0.65	2.34
Silicone Grease	1.99	—
Silicone Grease + 5% SbSb ₃	2.11	—
Silicone Grease + 5% MoS ₂	2.11	—
Clay Grease	0.69	—
Clay Grease + 5% SbSb ₃	0.65	0.57
Clay Grease + 5% MoS ₂	0.64	0.84
Aluminum Complex Grease	0.65	2.27
Aluminum Complex Grease + 5% SbSb ₃	0.65	1.14
Aluminum Complex Grease + 5% MoS ₂	0.63	2.59

*ASTM D-2266.

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 SbSb₃ have been evaluated with AISI-440C stainless-steel balls in a Shell Four-Ball FP 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 SbSb₃ in four greases, the weld points of stainless-steel balls showed improvements of 100 to 300 percent over the same greases containing 5-percent molybdenum disulfide. Experimental results are given in Table 7. The scar diameter vs load graphs shown in Fig. 4 and 5 indicate that the greases containing SbSb₃ 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 SbSb₃ are greatly improved over those of the base grease and the base grease containing 5-percent MoS₂.

The wear prevention characteristics of 5-percent SbSb₃ 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 scar diameters for the lithium grease and the lithium grease containing 5-percent MoS₂ were 400 and 300 percent larger than for the same base grease containing 5-percent SbSb₃. In fact, the wear scar diameter of the lithium grease containing 5-percent SbSb₃ 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 (2.59 vs 2.27 mm). However, the presence of 5-percent SbSb₃ in the same silicone grease resulted in 100-percent improvement over the base grease (see wear data in Table 3).

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 SbSb₃ 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 SbSb₃ on various alloys and in a variety of greases has been quite universal. It is interesting to note that lithium grease containing 5-percent SbSb₃ 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.

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-

GREASE COMPOSITION	WELD POINT (kg)	LOAD-WEAR INDEX
Lithium Grease	110	18.3
Lithium Grease + 0.5% SbSb ₃	200	25.8
Lithium Grease + 1% SbSb ₃	400	43.0
Lithium Grease + 1% MoS ₂	126	17.6
Lithium Grease + 3% SbSb ₃	620	57.0
Lithium Grease + 3% MoS ₂	162	26.5
Lithium Grease + 5% SbSb ₃	760	98.4
Lithium Grease + 5% MoS ₂	250	30.4

PROPERTIES	LITHIUM GREASE	LITHIUM GREASE + 5% SbSbS ₃	LITHIUM GREASE + 5% MoS ₂
Penetration (ASTM D 217)			
Unworked	253	315	—
Worked, 60 strokes	285	269	—
Drop point (ASTM D 566) F	365	369	370
Oxidation Stability (ASTM D 942)			
Psig O ₂ pressure drop in 100 hours 210 F	10	7	34
Lubrication Properties			
Extreme-pressure properties (ASTM D 2596)*			
Load wear index	18.3	98.3	30.4
Weld point, kg	160	760	250
Wear prevention characteristics (ASTM D 2266)*			
40 kg load, 1 hour, 1200 rpm at 167 F	0.70	0.63	0.65
Falex F.P. lbs (ASTM D 3233) [†]	< 300	2250	1850
Copper Corrosion 24h at 212 F	pass	pass [‡]	pass

*ASTM D 2100

†ASTM C-3135 steel pin vs ASTM C-1137 v-blocks

‡With 1% thiazazole type of additives. The Shell Four-Ball weld point of the resultant grease was 920 kg

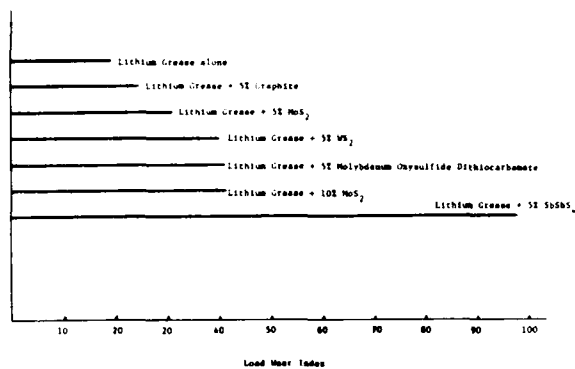


Fig.3—Load wear indexes of various solid additives in lithium grease (ASTM C-52100 steel balls).

GREASE + ADDITIVE	FAILURE LOAD (lbs)
Lithium Grease	< 300
Lithium Grease + 5% MoS ₂	1850
Lithium Grease + 5% SbSbS ₃	2250
Silicone Grease	< 300
Silicone Grease + 5% MoS ₂	< 300
Silicone Grease + 5% SbSbS ₃	< 300
Clay Grease	2850
Clay Grease + 5% MoS ₂	2850
Clay Grease + 5% SbSbS ₃	3200
Aluminum Complex Grease	1000
Aluminum Complex Grease + 5% MoS ₂	1700
Aluminum Complex Grease + 5% SbSbS ₃	2100

*ASTM D 3233

GREASE COMPOSITION	SHELL FOUR-BALL WELD POINT (kg)	LOAD WEAR INDEX
Lithium Grease	80	3.50
Lithium Grease + 5% SbSbS ₃	450	48.4
Lithium Grease + 5% MoS ₂	100	6.14
Silicone Grease	80	2.9
Silicone Grease + 5% SbSbS ₃	400	28.8
Silicone Grease + 5% MoS ₂	80	3.28
Clay Grease	100	5.04
Clay Grease + 5% SbSbS ₃	250	19.2
Clay Grease + 5% MoS ₂	80	7.01
Aluminum Complex Grease	100	2.43
Aluminum Complex Grease + 5% SbSbS ₃	250	18.3
Aluminum Complex Grease + 5% MoS ₂	100	3.98

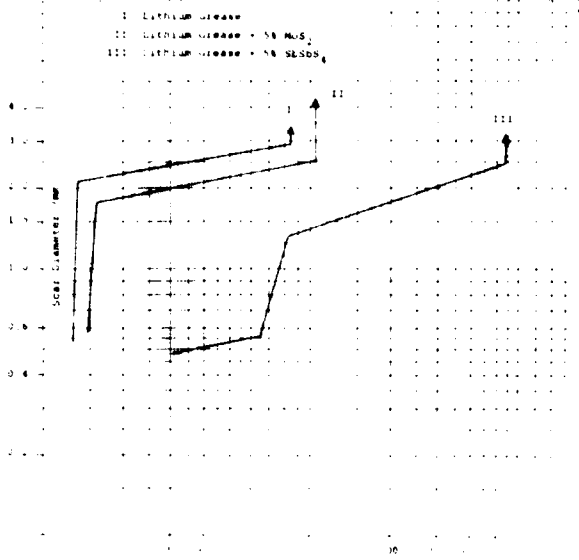


Fig. 4—Scar diameter vs load: AISI-440-C stainless-steel balls, 25°C, 1800 rpm, 10 s.

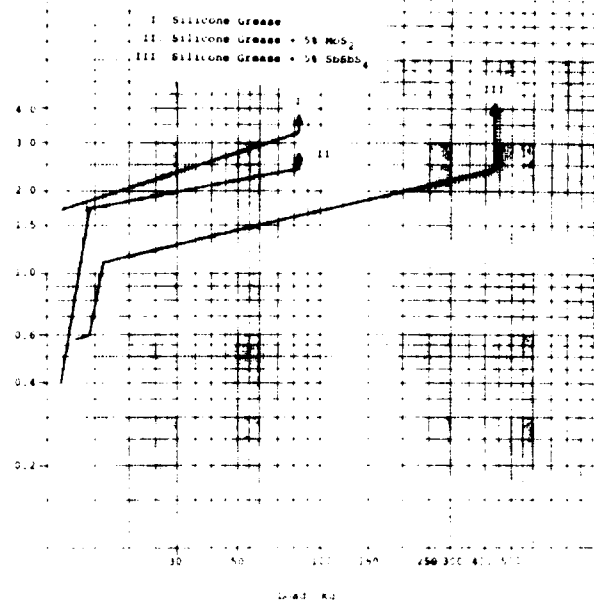


Fig. 5—Scar diameter vs load: AISI-440-C stainless-steel balls, 25°C, 1800 rpm, 10 s.

TABLE 5. COMPARISON OF STEEL FOUR BALL WEAR RESULTS OF SbSbS ₂ AND MoS ₂ ON CHROME STEEL AND STAINLESS-STEEL BALLS																
GREASE AND ADDITIVE	TEST BALL COMPOSITION	WEAR SCAR DIAMETER IN MILLIMETERS (D ₅₀ , 1800 rpm RUNS AT THE FOLLOWING APPLIED LOADS IN KILOGRAMS)														
		40	50	60	80	100	126	160	200	250	400	450	500	560	710	760
		Lithium Grease + 5% MoS ₂	52100 ^a	0.56	0.56		1.35				2.55	weld				
	440	2.00	2.13		2.38	weld										
Lithium Grease + 5% SbSbS ₂	52100		0.50					1.00		1.48		1.74		2.18	weld	
	440	0.50	0.52	0.55	1.26			1.88		2.40	weld					
Clay Grease + 5% MoS ₂	52100	0.36		0.77	0.68	0.85		2.04		weld						
	440	1.84		1.87	2.10	2.28	weld									
Clay Grease + 5% SbSbS ₂	52100	0.47			0.71	0.72		1.23		1.46			weld			
	440	1.53		1.60	1.71	1.73		2.28	2.89	weld						
Silicone Grease + 5% MoS ₂	52100	0.88		0.96	0.90	0.97		1.44	weld							
	440	2.29		2.51	weld											
Silicone Grease + 5% SbSbS ₂	52100	0.64	0.73			0.73		1.16	1.32	1.66		1.96	weld			
	440	1.18		1.51		1.63		2.06	2.22	weld						
Aluminum Complex Grease + 5% MoS ₂	52100		0.50		0.57	1.93		2.24	weld							
	440	2.48	2.62	3.28	weld											
Aluminum Complex Grease + 5% SbSbS ₂	52100		0.37		0.51			0.89	1.20		2.02	weld				
	440	1.27		1.36	1.60	1.68		2.60	weld							

^aChrome steel AISI 52100

^bStainless steel AISI 440C

ductive for use under extremely high loads where the conventional solid lubricants are found to be inadequate.

ACKNOWLEDGMENTS

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DISCUSSION

JOSEPH P. CERINI
C.C.L. Company Incorporated
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 $SbSbS_4$ 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 Sb 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 Sb_2Sb_4 ?

In the preparation of complex chalcogenides such as $FeMoS_4$, the resultant product is really a mixture of FeS_2 and MoS_2 but in an intimately mixed state due to co-precipitation. Physically mixing FeS_2 and MoS_2 , 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 $SbSbS_4$ relative to MoS_2 ?

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DISCUSSION

M. B. PETERSON (Member, ASLE)
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 MoS_2 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. MoS_2 does not yield a particularly high weld load when used in greases. Have the authors compared their results with organic sulfides such as di-benzyl, di-phenyl, or di-octyl?
2. Do the authors intend a direct comparison with MoS_2 ? 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 company 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 MoS_2 with antimony thioantimonate—the reason that we listed the performance data of MoS_2 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 D1. 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 Sb_2S_3 lattice. Intercalation 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	
	WELD POINT, kg
Lithium Grease	140
Lithium Grease + 5% MoS ₂	250
Lithium Grease + 5% Dibenzyl Disulfide	180
Lithium Grease + 5% Diphenyl Disulfide	160
Lithium Grease + 5% Dioctyl Disulfide	126*
Lithium Grease + 1% SbSbS ₄	400
Lithium Grease + 5% SbSbS ₄	760

*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 perfor-

mance 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.

APPENDIX II

EFFECT OF ANTIMONY THIOANTIMONATE IN GREASES ON ABRASIVE WEAR

J. P. King
Pennwalt Corporation
King of Prussia, PA 19406

Yayesh Asmerom
Pennwalt Corporation
King of Prussia, PA 19406

M. J. Devine
General Technology
Havertown, PA 19086

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 ($SbSbS_4$) in three base greases—MIL-G-10924, MIL-G-24139, and MIL-G-81322—was investigated. The presence of $SbSbS_4$ 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 $SbSbS_4$ 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

Abrasive wear is well recognized as the primary cause of surface damage for military vehicles and equipment as well as industrial machinery.¹ This form of wear is encountered when foreign materials, e.g., sand, grit or other hard

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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 (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 SbSbS_4 in several military greases was conducted with the objective of selecting one or more of these greases to be formulated with 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 SbSbS_4 . The extreme pressure and antiwear characteristics of these greases with and without SbSbS_4 and MoS_2 as additives were determined and compared.

PREPARATION OF ANTIMONY THIOANTIMONATE (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 μ and the following composition:

SiO ₂	68%
Fe ₂ O ₃	5%
Al ₂ O ₃	16%
CaO	3%
MgO	1%
Na ₂ O	5%
Ignition Loss	2-3%

TEST METHODS

Falex Machine

The abrasive wear study was carried out on a Falex machine using AISI-C-3135 steel pins (R_p87-91) and AISI-C-1137 V-blocks (R_c20-24). 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. Wear

prevention characteristics were determined by measuring ball 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-81392), 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% SbSbS_4 showed a 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% SbSbS_4 were significantly higher than those of the base grease. The weld point and load wear index of the base grease containing 5% MoS_2 were lower than that of the same base grease containing 1% SbSbS_4 . The wear prevention characteristics of samples of the base grease containing 1% SbSbS_4 and 5% MoS_2 , 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 points of MIL-G-81322 containing 1 and 3% SbSbS_4 showed 25 and 100% improvements over the base grease, respectively. With 5% MoS_2 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 MoS_2 or SbSbS_4 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 SbSbS_4 .
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 SbSbS_4 as a solid additive. At a lower concentration this additive outperformed MoS_2 in all cases.
3. Antimony thioantimonate showed good response to both chrome tool steel AISI-C-52100 and stainless steel AISI-440C in all three base greases investigated.
4. If the presence of SbSbS_4 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), the use of SbSbS_4 as a solid additive in these greases

she is definitely beneficial.

5. 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.

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

Grease Composition	Weld Point, ¹ kg	LWI ¹	Wear Scar ² Diameter, mm
MIL-G-10924 Grease (GAA)	160	29.3	0.62
" + 1% SbSbS ₄	250	39.4	0.59
" + 5% SbSbS ₄	315	56.7	0.59
" + 5% MoS ₂	160	38.4	0.57

-
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

Grease Composition	Chrome Tool Steel 52100			Stainless Steel 440-C	
	Weld Point ¹ kg	LWI ¹	Wear Scar Diameter ² mm	Wear Scar Diameter ³ mm	
MIL-G-24139 Grease (AMI)	126	14.1	2.17	3.48	
" + 1% SbSbS ₄	315	38.1	0.58	2.18	
" + 2% SbSbS ₄	---	---	0.56	---	
" + 1% MoS ₂	---	---	0.64	2.55	
" + 5% MoS ₂	200	27.9	0.57	2.15	

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

Grease Composition	Chrome Tool Steel 52100		Stainless Steel 440-C	
	Weld Point ¹ kg	Wear Scar Diameter ² mm	Wear Scar Diameter ² mm	Wear Scar Diameter ⁴ mm
MIL-G-81322 Grease (MOB)	160	0.41		2.31
" + 1% Sbsbs ₄	200	0.39		2.19
" + 3% Sbsbs ₄	315	0.56		1.88
" + 5% MoS ₂	250	0.41		1.90

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.

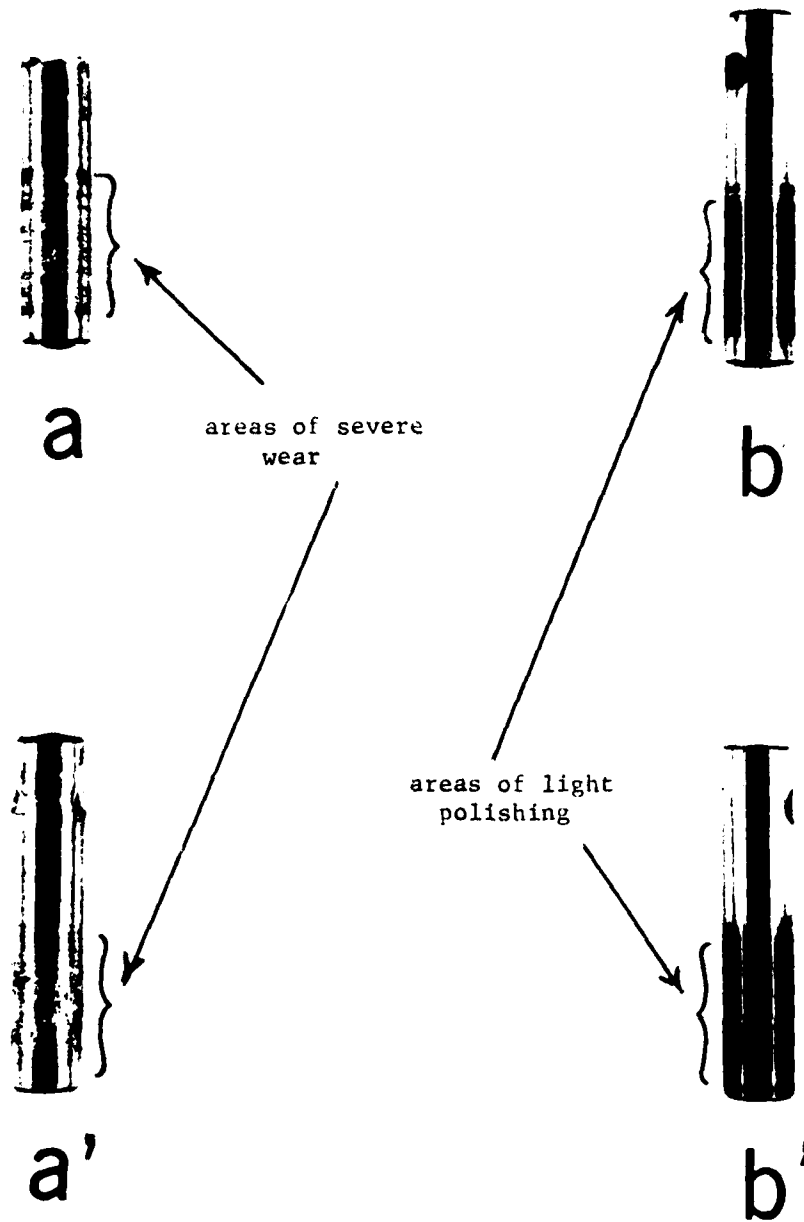


Figure 1. Effect of SbSbS₄ on Abrasive Wear

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 " " "
- b' = " " " " and 5% SbSbS₄

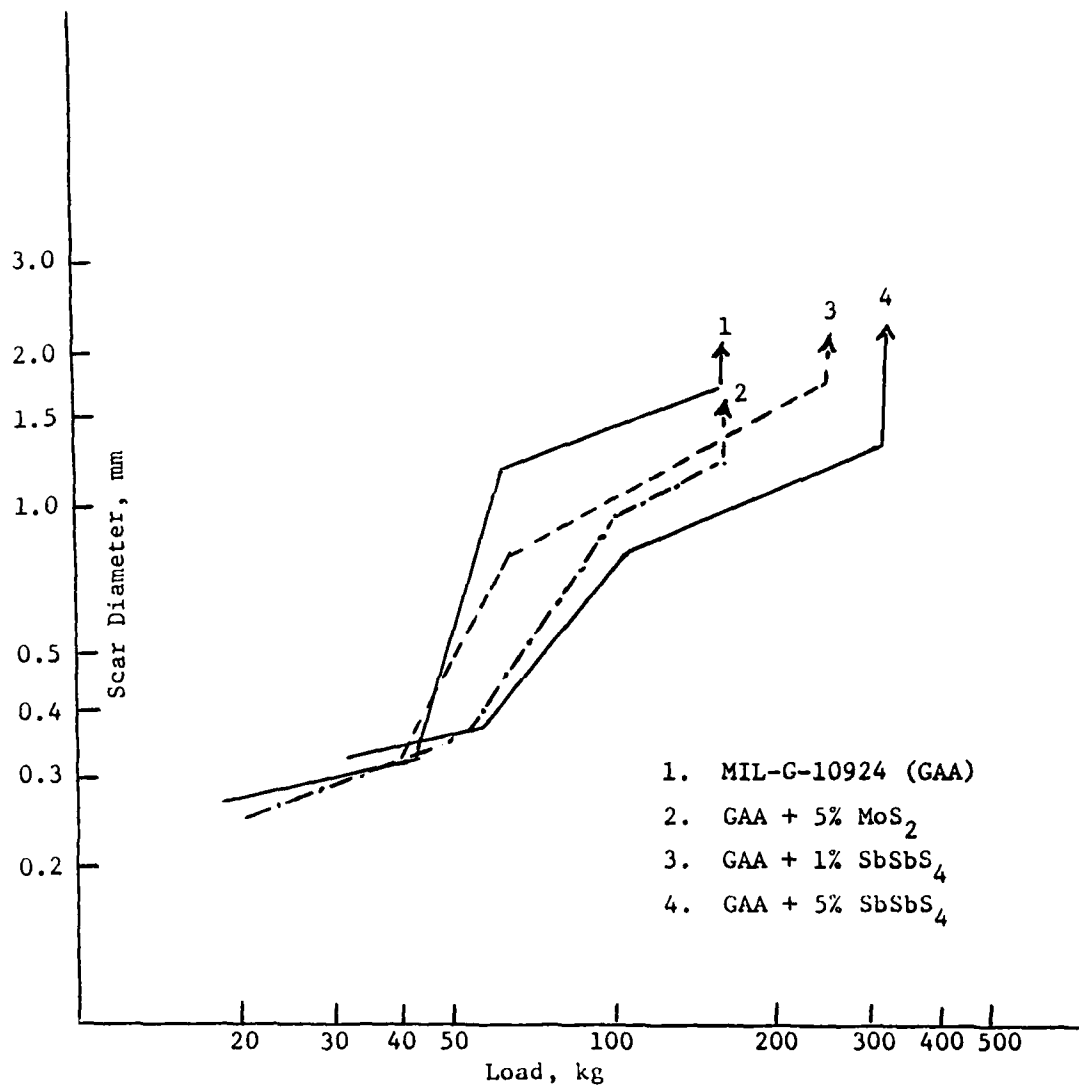


Figure 2. Wear Scar Diameter vs. Load; AISI-C-52100 Steel Balls; 25°C, 1800 rpm, 10s

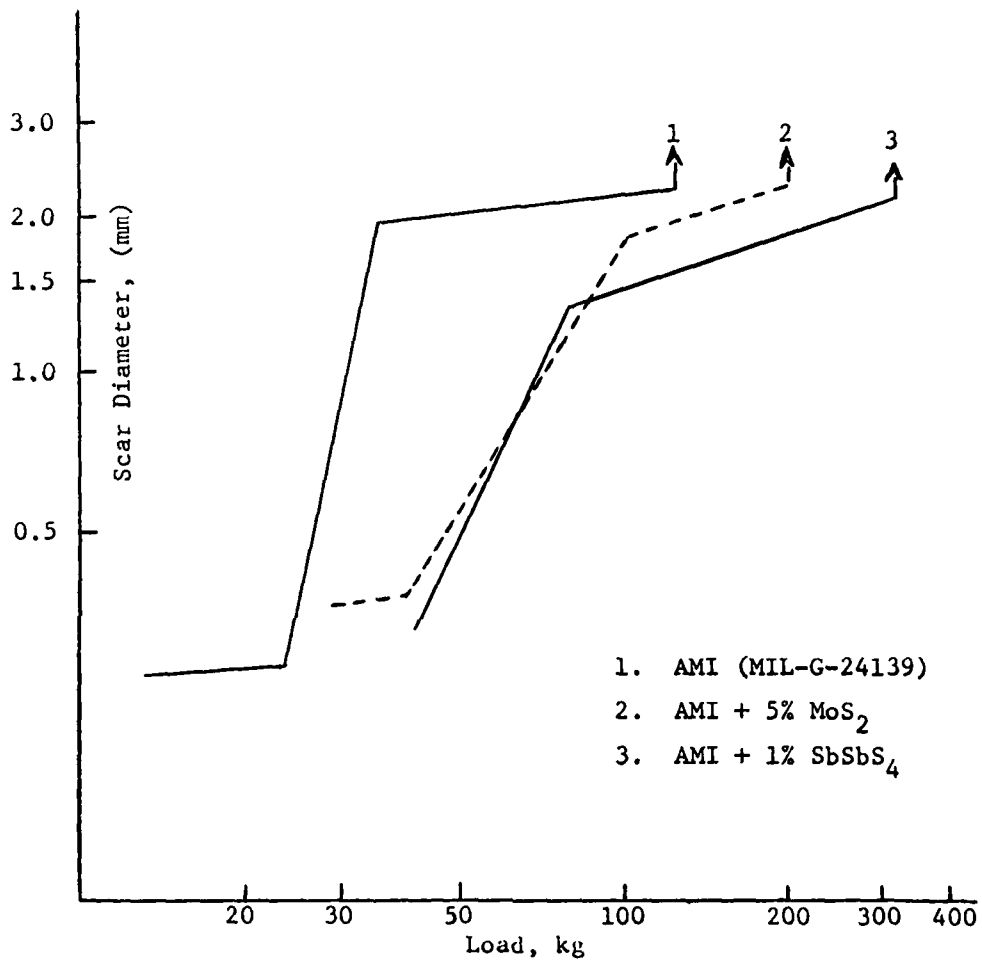


Figure 3. Wear Scar Diameter vs. Load; AISI-C-52100 Steel
Balls; 25°C, 1800 rpm, 10s

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Mr. M. Keith Ellingsworth
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Arlington, VA 22217

Mr. R. G. Brown
Code 2382
DTNSRDC
Annapolis, MD 21402

Dr. J. Dell POSL 1
Air Force Wright Aeronautical Laboratories
Wright- Patterson Air Force Base
Dayton, OH 45433

M. J. Devine
General Technology
2560 Prescott Road
Havertown, PA 19083

A. J. D'Orazio, Code PE-72
Naval Air Propulsion Center
Trenton, NJ 08628

Mr. Jim Dray
Head, Friction & Wear Branch
DTNSRDC
Annapolis, MD 21402

F. C. Gale
NAVMAT
Code OOKB, CP5, Room 606
Washington, DC 20360

Mr. Richard R. Graham, II
Code 5243, Bldg. NC4
Naval Sea Systems Command
Washington, DC 20362

Mr. Al Harbage, Jr.
Code 2723
DTNSRDC
Annapolis, MD 21402

Mr. Martin Kandl
Code 5231
Naval Sea Systems Command
Washington, DC 20362

S. Karpe
David W. Taylor Naval Ship R & D Center
Ship Materials Engineering Department
Annapolis, MD 21402

Dr. R. N. Katz
Army Materials and Mechanics Research Center
Watertown, MA 02172

Lt. Col. R. Kerr, USMC
Mobility and Logistics Division
Development Center
MCDEC
Quantico, VA 22134

L. Kociuba, Code 92A3
Naval Air Engineering Center
Lakehurst, NJ 08733

A. J. Koury - AIR-4111D
Naval Air Systems Command
Washington, DC 20361

Dr. George Mayer
Director, Metallurgy and
Materials Science Division
Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709

B. D. McConnell - MLBT
Air Force Wright Aeronautical Laboratories
Wright-Patterson Air Force Base
Dayton, OH 45433

W. McGovern
U. S. Army MERDC
Fort Belvoir, VA 22060

D. V. Minuti
Code 606B
Naval Air Development Center
Warminster, PA 18974

Dr. Jim D. Murday
Code 6170
Naval Research Laboratory
Washington, DC 20375

Mr. Cliff Mussen
PMS 396-223
Naval Sea Systems Command
Washington, DC 20362

Mr. A. B. Neild, Jr.
Head, Power Transmission Branch
DTNSRDC
Annapolis MD 21402

NASA-Lewis Research Center
Attn: Mr. Jim Kiraly
21000 Brookpark Road
Cleveland, OH 44135

J. W. Patten
Battelle Memorial Institute Pacific
Northwest Laboratories
Richland, WA 99352

Dr. Earl Quandt, Jr.
Head, Power Systems Division
DTNSRDC
Annapolis, MD 21402

Dr. A. W. Ruff
Metal Science and Standards Division
National Bureau of Standards
Washington, DC 20234

Mr. Ken R. Sasdelli
Code 2723
DTNSRDC
Annapolis, MD 21402

R. Schmidt, AIR-320
Naval Air Systems Command
Washington, DC 20361

Dr. R. Schumaker, AIR-340
Naval Air Systems Command
Washington, DC 20361

David S. Siegel
Code 260
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

L. Stallings,
Code 6061
Naval Air Development Center
Warminster, PA 18974

Mr. Richard Strucko
Code 2723
DTNSRDC
Annapolis, MD 21402

Dr. N. P. Suh
Massachusetts Institute of Technology
Department of Mechanical Engineering
Cambridge, MA 02139

Dr. Fred J. Tribe
Admiralty Marine Technology Establishment
Holten Heath, Poole, Dorset
U.K. BH166JU

Dr. E. Van Reuth
Defense Advanced Research Project Agency
1400 Wilson Blvd.
Arlington, VA 22209

Dr. Frank Ventriglio
Code 05R14
Naval Sea Systems Command
Washington, DC 20362

P. Wienberg, AIR-5304C
Naval Air Systems Command
Washington, DC 20361

Dr. R. D. Arnell
Department of Aeronautical &
Mechanical Engineering
University of Salford
Salford, U.K. M54WT

Professor Ralph A. Burton
Chairman, Mechanical and Aero-
space Engineering Department
North Carolina State University
3211 Broughton Hall
Raleigh, NC 27650

Professor N. S. Eiss, Jr.
Department of Mechanical Engineering
Virginia Polytechnic Institute
and State University
Blacksburg, VA 24061

Professor I. Etsion
Department of Mechanical Engineering
Technion, Haifa
Israel

Professor Hasselman
Virginia Polytechnic Institute
Department of Materials Engineering
Blacksburg, VA 24061

Professor William F. Hughes
Mechanical Engineering Dept.
Carnegie Mellon University
Pittsburgh, PA 15213

Professor Frederick D. Ju
Bureau of Engineering Research
University of New Mexico
Albuquerque, NM 87131

Professor T. Keith
Department of Mechanical Engineering
University of Toledo
Toledo, OH 43606

Professor Francis E. Kennedy, Jr.
Thayer School of Engineering
Dartmouth College
Hanover, NH 03755

Professor Alan O. Lebeck
Bureau of Engineering Research
University of New Mexico
Albuquerque, NM 87131

Professor Fred F. Ling
Department of Mechanics
Rensselaer Polytechnic Institute
Troy, NY 12131

Professor K. Ludema
Department of Mechanical Engineering
University of Michigan
Ann Arbor, MI 48105

Professor W. Kenneth Stair
Associate Dean for Research
University of Tennessee
Knoxville, TN 37916

Dr. H. Wilsdorf
Department of Materials
University of Virginia
Charlottesville, VA 22901

Batelle Columbus Laboratories
Attn: Dr. Richard Jentgen
505 King Avenue
Columbus, OH 43201

BHRA Fluid Engineering
Attn: Dr. Bernard S. Nau
Cranfield, Bedford
England MK430AJ

Franklin Research Center
Attn: Mr. Harry Ripple
Twentieth & Parkway
Philadelphia, PA 19103

Wear Sciences
Attn: Mr. Marshall Peterson
925 Mallard Circle
Arnold, MD 21012

Westinghouse R&D Center
Attn: Dr. Ian McNab
1310 Beulah Road
Pittsburgh, PA 15235

Mr. Edward L. Wiehe
TRW, Inc.
1 Space Park
Redondo Beach, CA 90278

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