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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

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MFPG
The Role of Coatings in the Prevention of Mechanical Failures

Proceedings of the 23rd Meeting of the
Mechanical Failures Prevention Group,
held at the National Bureau of Standards,
Gaithersburg, Maryland, October 29-31, 1975

Edited by

T. R. Shives and W. A. Willard

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FOREWORD

The 23rd meeting of the Mechanical Failures Prevention Group was held October 29-31, 1975, at the National Bureau of Standards in Gaithersburg, Maryland. The program was organized by the MFPG committee on the Mechanisms of Failure under the chairmanship of Professor Elmer E. Klaus of The Pennsylvania State University. The Mechanisms committee, the session chairmen, and especially the speakers are to be commended for the excellent program.

The papers in these Proceedings are presented as submitted by the authors on camera ready copy, except for some minor editorial changes. In addition to the papers, the Proceedings include the discussions of the talks. The discussions were recorded at the meeting and have been edited to improve readability.

Appreciation is extended to Mr. T. Robert Shives and Mr. William A. Willard of the NBS Metallurgy Division for their editing, organization, and preparation of the Proceedings, to Mrs. Sara R. Torrence of the NBS Office of Information Activities for the meeting arrangements, to Mr. Harry C. Burnett of the Metallurgy Division for general coordination and registration, to Mr. Paul M. Fleming of the Metallurgy Division for handling financial matters, and to the entire staffs of the Metallurgy Division and the NBS Institute for Materials Research for their assistance in many ways. Special thanks are accorded to Mrs. Marian L. Slusser of the Metallurgy Division for her diligent efforts in transcribing the recorded discussions.

ELIO PASSAGLIA
Executive Secretary, MFPG

Chief, Metallurgy Division
National Bureau of Standards

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SESSION IV: CHEMICAL COATINGS

* Indicates speaker when a paper had more than one author.

ABSTRACT

These Proceedings consist of a group of eighteen submitted papers and discussions from the 23rd meeting of the Mechanical Failures Prevention Group which was held at the National Bureau of Standards in Gaithersburg, Maryland on October 29-31, 1975. The central theme of the Proceedings is the role of coatings in the prevention of mechanical failures, with emphasis on polymer coatings, metal coatings, solid film lubricants, and chemical coatings.

Key words: Barrier film; chemical coatings; failure prevention; mechanical failure; metal coatings; plated coatings; polymer coatings; solid film lubricants; sputtered coatings; wear

UNITS AND SYMBOLS

Customary United States units and symbols appear in many of the papers in these Proceedings. The participants in the 23rd meeting of the Mechanical Failures Prevention Group have used the established units and symbols commonly employed in their professional fields. However, as an aid to the reader in increasing familiarity with and usage of the metric system of units (SI), the following references are given:

NBS Special Publication, SP330, 1974 Edition, "The International System of Units."
ISO International Standard 1000 (1973 Edition), "SI Units and Recommendations for Use of Their Multiples and of Certain Other Units."
E380-76 ASTM Metric Practice Guide (American National Standard Z210.1).

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Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

SESSION I

POLYMER

COATINGS

Chairman: E.E.Klaus

The Pennsylvania State University

THE FRICTION AND WEAR OF POLYMERIC COATINGS ON METAL

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Abstract

Polymeric coatings on metals wear and/or debond when rubbed. Information on wear is available from tests using bulk polymers which usually have a different structure than do thin films. The bond strength requirements for rubbing surfaces appear to be greater than that developed by the technology centered in adhesives and composite materials industries. Many of the factors involved in wear life and bonding are summarized in the paper. Recent and broad ranging references are given for each of the major points in the paper.

Keywords: Adhesion; coatings; friction; metal; polymers; wear.

A frequently quoted ancient author of papers on friction is Amontons [1] a French engineer. More often than not his conclusions are cited so that they may be differed with in the modern paper. It is not usually mentioned, however, that many of the conclusions of Amontons were based on research using a lubricant. In fact the lubricant used was pork fat, or "suet" [2], and this produced a coefficient of friction of 0.2. This number has been faithfully carried down to the modern day by countless handbooks and textbooks, and is now taken as the best estimate for dry friction.

Polymeric films stand in the long succession of lubricants beyond suet. This evolution has included lubrication: by liquids alone, by liquids containing boundary additives, by liquids containing solid lubricants, by solid lubricants attached to surfaces by various adhesives, and finally by polymeric films themselves. Obviously each step marked progress toward the achieving of some goal including economy.

Polymeric coatings can be considered either protective coatings or lubricants depending upon the industry. They are protective when applied to optical surfaces where scratching must be prevented. They are lubricants when they prevent seizure of machine elements. They can be considered mere conveniences in other instances. They are used because they do not collect dust as does a liquid lubricant film. They can be touched by clothing or hands without undesirable asthetic consequences. They can be used near food without adding visible "dirt" or toxicity to the food. They do not migrate or evaporate as does a liquid. They can be operated over a wider range of temperature than many liquids.

Finally they can add corrosion protection, electrical resistivity, color, and liquid barrier capabilities to surfaces.

Historically thin polymeric films had two separate uses as lubricants in machinery. The first is as a binder for such solid lubricants as graphite, MoS_2, and others. The second is as a film without fillers. The two films can be distinguished, however, in terms of the severity of service each is subjected to. Solid lubricants are usually attached to a metal surface by a thermo-setting polymer and more recently by silicone resin [3]. This is a consequence of the fact that solid lubricants find themselves in situations where high temperatures are generated and only thermo-setting or silicone polymers will survive. However, thermo-setting polymers are usually mildly abrasive to the counter surface. In terms of wear of the counter surface this is usually not of severe consequence since graphite and MoS_2 also wear the counter surface [4] by way of impurities. Simple polymeric layers on the other hand are often of the linear polymer or thermo-plastic polymer group. These are cheaper than composite layers and very useful for many light duty applications.

In some instances solid lubricants are bonded with linear polymers [5] and in other instances films of linear polymer are lubricated by liquids [6]. It is not clear that these formulations offer long wear life. In this paper we will consider only the simple films of a few linear polymers.

Linear Polymer Films

Thin films of polymer on metal are usually on the order of 100 Å to 4000 Å thickness. This is to be distinguished from the wall thickness of polymer sleeve bearings which is often in the order of 1/10 of the shaft diameter. Since thin films are so very thin, the system must be constructed to avoid too many episodes of local high wear rate. Furthermore, thin films rely upon good bonding with the adherend (substrate) far more than do the polymer bearings. Thus, there are two problems. Good bonding of films, and film integrity.

Very thin films of polymer on metal are sometimes used to achieve a low coefficient of friction. A linear polymer is very soft as compared with a metal and its behavior is analogous to that of a thin film of soft metal on a harder substrate [7]. The behavior of a soft film between a sphere and flat surface is described in the model of Tabor which is expressed in terms of $F = A \times s$. With a hard substrate the contact area is low and shear strength is high, and with a soft substrate the contact area is high but the shear strength is low, both yielding a moderate friction force. On the other hand, when a thin soft film of low shear strength is placed upon a hard backing the contact area is also small, leading to a low friction force.

Whereas the model is described in terms of a sphere of radius about

100 times the film thickness, the principle applies as well to contact stress of flat surfaces in the order of the strength of the polymer. Apparently the proper conditions for low friction are, a real contact area nearly equal the apparent area and a soft film which is too thin to extrude from between the hard sliding bodies. This condition produces a coefficient of friction [9] of about 0.12 for coatings of several polymers (high density polyethylene, polypropylene, polyvinylidene fluoride, FEP, and E.T.F.E.) and values as low as 0.03 for low density polyethylene and polytetrafluorethylene. However, when asperity radius becomes smaller than 1/10 of film thickness or if contact pressures become much less than about 50% of the strength of the polymer, the coefficient of friction returns to values in excess of 0.35. Thus in the lightly loaded rubbing of close fitting parts a polymer film, other than Teflon, may produce a higher friction than between two metal surfaces.

The Wear of Polymeric Films

Polymer films wear by several mechanisms, as follows:

1. A progressive, mild wear by non-repeating passage of paper, cloth, metals, human hands, etc. The most likely mechanism of polymer loss in this case is abrasion.

2. A relatively slower loss of polymer due to repeated passage of a counter surface. This is found in conveyors, hinges, etc. In these instances transfer of polymer from the deposited film to the counter surface is usually achieved, and this occurs in the first few passes [10]. Continued rubbing consists in an exchange of the transferred film between the rubbing surfaces and by shearing of the thin transferred film. However, contaminants including water may produce a "debond" of transfer film [11,12] which then is removed from the system in long ribbons and/or flakes. Retention of the transfer film is vital to long life of the polymer coated component [13].

3. At high speeds and loads there may be thermal degradation of the polymer. In this case, characteristic gases are evolved from the rubbing surfaces and a discontinuous or particulate wear debris is formed. This case is not predicted by the well-known PV limit. (At this point it may be useful to point out that the PV limit is not regarded as applicable to thin films of polymer whatever the loss mechanism [14].)

4. Loosening of the polymeric film from the substrate (adherend) causes large regions of polymer to be removed from the system, and these regions are often larger than a local area of contact distress. The loss of large regions of film is usually the consequence of progressive debonding. Either there was poor strength originally due to improper displacement of adsorbed gas during the coating process, or the film may have been permeated by a fluid which preferentially wet the interface.

Film Deposition

Highly adherent polymeric films have been achieved with only limited success. Most often it is attempted with a number of recipes for "couplers" purporting to achieve the DeBruyne-Zisman criteria—namely—the liquid polymer must wet the solid completely and spontaneously [15, 16]. The majority of recent developments in coupling agents has apparently been in the field of composite materials where good bonding between fibers (or particles) and a matrix is thought to be desirable [16].

Whereas most papers on bond strength focus on any available improvement some researchers are searching for the theoretical maximum bond strength. In some work bond strength equal to the cohesive strength (tensile strength) of the polymer is reported. Higher bond strengths seem unnecessary, but interesting. For example, polymeric films can become attached so firmly to metals during sliding that upon separation of the bodies some metal (aluminum) has been found attached to the polymer (PTFE) [17]. The polymer-metal bond in vacuum was found to be chemical in nature, not vanderWaals forces as is often supposed. In air the bond is probably between the polymer and the metal oxide, and attack by water upon the oxide is the probable cause of loss of bonding [18]. Here obviously are challenges for the industrial chemist.

Another concern in the search for high bond strength is the optimum surface roughness of metals to be coated. Rough surfaces promote spreading of liquid, apparently fulfilling the DeBruyne-Zisman criterion. On the other hand, rough surfaces trap more air between the polymer and substrate than does a smooth surface and this decreases average bond strength [19].

After surface preparation the polymer may be applied in many ways such as by spraying or dipping. However, as mentioned above a polymer film can also be applied by rubbing a block of polymer against the surface to be coated. In many instances rubbing apparently produces a stronger bond than other methods but the reason is not well understood.

The testing of film durability can be done by a number of methods. Perhaps the best understood test is the peel test. This test is difficult to use as a manufacturing quality control test because a precise setup is required. On the other hand, for production quality control a roller test is often used and this test may be called by several names including the blister test. Presumably the blister test tests a material in fatigue in some manner since blisters are found to grow by repeated loading. It is not known whether this is a consequence of migration of contaminants under the film by the action of the roller, or whether the bond between the polymer and the metal substrate ruptures in fatigue. Surprisingly little is known about the stress state in a blister test and whether it approximates practice. Very little of an analytical nature is published for the blister test. On the other hand, considerable information is available for the peel test [20], usually treating the film as a visco-elastic substance.

Increasing the Life of Polymeric Films

The answer to questions on wear life depends upon the mechanism of wear. If wear is primarily due to abrasion then a polymer film may be improved by including in it a distribution of hard fillers such as glass beads. If debond is the problem then the chemistry of interfaces must be considered. If all else fails a little suet may help!

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DISCUSSION

R. S. Miller, Office of Naval Research: At what temperatures or under what conditions does the siloxane polymer change from organic to inorganic and what is the size distribution of the particles?

K. C. Ludema: That subject is dealt with in a paper by Benzing, McConnell and Chow. Mr. McConnell is here--perhaps he can comment.

B. D. McConnell, USAF Materials Laboratory: I don't know the particle sizes of the material after the conversion, but the temperature range for changing from the organic to the inorganic is somewhere in the neighborhood of 800 F. This is based more on a high temperature paint formulation than on our solid film work.

A. J. Babecki, NASA, Goddard Space Flight Center: A lot of the ball bearings in spacecraft applications incorporate a Teflon ball cage, and lubrication is brought about by transfer of the Teflon from the cage to the balls and to the races. But one of the problems we have with that kind of lubrication is the continual buildup of this transferred material which eventually causes high friction within the bearing, or at least roughness in the bearing. Can this continual transfer be minimized by precoating the metal surfaces with Teflon or something else?

K. C. Ludema: I can point to the work by Tabor, et al, and a couple of others who show that the nature of the transfer film in Teflon varies according to strain rate and temperature. A buildup is due to low operating temperatures or high strain rate in the polymer. This buildup is also usually a consequence of the test configuration. If a piece of polymer is kept pressed against a piece of glass and made to go around in a circle, the buildup never develops. In a ball bearing, there may be a particle carried around that gets into the track.

E. E. Klaus, The Pennsylvania State University: Mechanistically, to what do you attribute the order of magnitude change in friction between high and low density polyethylene?

K. C. Ludema: I go to the explanation of Tabor, apparently supported by others working in the polymer field. Tabor sees in low density polyethylene and Teflon smooth molecular profiles. This means that the molecules can shear or slip over each other much more easily than those with bulky side groups.

E. E. Klaus: You mean crystallinity has nothing to do with it?

K. C. Ludema: That's correct. There isn't a great amount of crystallinity in either of those anyway.

E. E. Klaus: Generally, the difference in friction is attributed to the difference in crystallinity. In fact the high density polyethylene has an average of 5 methyl side chains per thousand carbon atoms versus 40 per thousand for the low density material. That doesn't seem like a whole lot of side chains to blame it on.

R. S. Miller: If you have a service application in which the temperature can vary and wear can occur at all temperatures, how do you best pick a polymer to minimize the wear rate? Can you correlate such things as the glass transition temperature of the polymeric film with wear?

K. C. Ludema: I don't think there is a single criterion one can use. If you consider the glass transition temperature you are totally frustrated by the fact that polyethylene with a glass transition temperature of about -120 C lasts a lot longer than polymethylmethacrylate with a glass transition temperature of +105 C. Wear rate is not correlatable with glass transition temperature or with any other visco-elastic quantity.

S. A. Karpe, David Taylor Naval Ship Research and Development Center: What is the effect of pressure on the shear strength in these films?

K. C. Ludema: You may refer to the work of R. C. Bowers (Reference no. 9 of this paper) who has done as much as anybody in the field.

S. A. Karpe: What is the effect of counterface surface topography?

K. C. Ludema: C. W. Jennings (Reference no. 19 of this paper) has explored this, although not in sliding contact. He tested the glue bond between two pieces of metal by running a series of tests varying the surface roughness of the metals and testing the mechanical strength of the bond. It is his conviction that surface roughness is a factor in the strength of the bond largely because it influences wettability. As far as the surface roughness of the counterface is concerned, there is conflicting evidence as to the influence on wear.

S. A. Karpe: Most of our discussion here has been on bulk polymers. Do thin films behave in a similar manner?

K. C. Ludema: All of our friction information is from bulk polymers. Very little work has been done studying the wear mechanisms of thin films.

S. Jahanmir, Massachusetts Institute of Technology: You mentioned the thickness of the films you used as ranging from 100 to 4,000 angstroms. First, I would like to know why you selected this range, and second, is there any optimum range that exists for a particular type of coating and a particular substrate or for a particular sliding condition?

K. C. Ludema: I quote 100 to 4,000 angstroms because that's what is in the literature. Now, for optimum film thickness, it appears that film thickness has one effect when it comes to wear--the thicker the film the longer the life--and has an opposite effect on bonding. In the dynamics of debonding, there is an optimum film thickness above which debonding is more likely to happen.

E. E. Klaus: You were non-commital on the surface roughness. A year or two before the date you quoted, at the last ASLE-ASME International Lubrication Conference, there were three papers which all seemed to indicate that a surface roughness of about 15 μin seemed to be an optimum. Could you tell us what the surface roughnesses were in the polymer studies?

K. C. Ludema: It was in that area, but I don't remember the specific numbers.

E. E. Klaus: Well, at least in one paper that dealt with solid and liquid lubricants, one got the impression that if you considered surface roughnesses on either side of 15 μin, the results were quite different from those obtained at 15 μin.

K. C. Ludema: I looked for the possibility that there might be a minimum or a maximum to the right of which and to the left of which there would be opposite behavior or similar behavior and I could find no correlation. Lancaster, with the Royal Aeronautical Establishment in England, feels that surface roughness is of no consequence where there is transfer because transfer simply fills up all the little holes and the surface becomes smooth. I don't quite believe that, but it must be considered as a possibility. Therefore, surface roughness would be thought to be more important for thermosetting resins which do not form a transfer film very readily and, again we didn't find any sensible correlation there.

A. W. Ruff, National Bureau of Standards: Does the wear rate or the wear mechanism or both depend on the nature of orientation of the transferred polymer film?

K. C. Ludema: The effect of orientation is very transient. In about the first 1/8 in of travel, original orientation makes a big difference, but ever thereafter the surface is oriented in the sliding direction. The sliding process orients the polymer so it doesn't matter what the initial orientation was.

A. W. Ruff: I was thinking of reciprocal sliding.

K. C. Ludema: In reciprocal sliding, there is a reorientation problem on either end. There are big globs of polymer worn off on either end of the travel.

S. A. Karpe: I think that polyethylenes are two-phase materials; i.e., they are partly amorphous and partly crystalline. If you use the amorphous shear strength in Tabor's adhesion theory of friction instead of the bulk shear strength, there is a beautiful correlation for friction coefficients. In our work, we have found a range of surface roughness of the metal counterface between about 15 and 35 μin where the coefficient of friction of the polymers is constant. For very smooth surfaces, there are very slight increases in the coefficient of friction due, we believe, to an effect of reinforcing actions of the polymer asperities or surface contact regions. At surface roughness values greater than 35 μin, there is mechanical entrapment of the polymer in the metal surface causing an increase in the coefficient of friction.

PERFORMANCE STUDIES OF POLYMER PROCESSED MECHANICAL AND STRUCTURAL COMPONENTS

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A technique which has become known as "dry powder painting" is one of the major advances made in the application of coatings. This technique is based upon the deposition of specially formulated, thermoplastic or thermosetting, heat-fusible powders on metallic substrates. Since there are no solvents present, the coating can be cured immediately after application. One of the most obvious advantages of this method is the absence of pollution and safety problems associated with organic solvents that are used in most liquid paint systems. A second advantage is that coatings may be obtained by this process from materials that cannot be applied by liquid paint techniques because of their poor solubility in organic solvents. Dry powder techniques are readily adaptable to current production methods and are easily learned by product finishing personnel. Because of special requirements in particle size, particle size distribution, and other properties, dry powder coatings are generally more expensive than liquid paint systems. However, in view of the advantages of dry powder processes over wet painting techniques the overall cost differences are probably minimal. In addition as much as 95% of the dry powder material can be utilized if a powder recovery system is used.

Advantages similar to those reported for dry powder techniques are also claimed for electrocoating. This process can be compared to electroplating of metals, and, like the dry powder method, it also avoids the use of organic solvents.

Dry Powder Techniques

1. Fluidized Bed Method

Until now most of the powdered paints have been applied by fluidized bed techniques. In the fluidized bed method a dense cloud of powder is created by passing air through the perforated bottom of a powder reservoir. At the correct flow rate the cloud of powder behaves like a liquid that tends to "wet" all surfaces of an object immersed in it. An agitator or vibrator is normally employed to maintain the uniformity of powder and to prevent channeling of air. Usually the part to be coated is preheated so that the coating particles can fuse and adhere to the hot surface. When large objects are coated, the cure must usually be completed in separate ovens. The fluidized bed method is best suited for the application of relatively thick coatings--10 to 60 mil--to small objects.

2. Electrostatic Deposition of Dry Powders

The second method of dry coating technology, electrostatic deposition of dry powders, is carried out by two different procedures. The first procedure employs a fluidized bed as described above and an electrostatic field that imparts a charge of the powder particles. The fluidized bed is maintained by an air flow of low pressure (approximately 5 cfm/ft^2 at 2 to 5 psi), and the charge is supplied by electrodes at an applied voltage of 60 to 90 kv. The object to be coated is grounded and passed over or through the fluidized bed of charged powder. It has been found that even nonconductive materials can be coated by this method without the use of conductive prime coats. A major inherent limitation is the absence of uniformity of the charged cloud on a vertical plane. As a consequence only articles that are relatively flat can now be coated by this process. However, it is believed by some that this process will eventually become the major means of depositing dry powder materials.

The most advanced method of electrostatic deposition of dry powder is the spray procedure. In this method a metered amount of powder is fed to a spray gun by compressed air, and, as the particles pass through a region of air ionized by the d-c potential of an electrode, they become charged. The part to be coated carries a charge opposite to that of the coating particles and the powder is attracted to it. The sprayed coating, which may be as thin as 1 mil, is then fused or cured in an oven. This process is especially suited for large parts and parts with complex shapes. Coating thickness is limited by the loss of attraction of the powder to the substrate surface as the coating builds up.

3. Applications of Fluidized Bed and Electrostatic Spray Techniques

Numerous plastics have been formulated as dry powder coatings. Epoxy resins are the most widely used at present, but the following resins are also being employed or considered for use: poly (vinyl chloride), poly (vinyl fluoride), polyester, nylon, polyethylene, polypropylene, acrylic, chlorinated polyether, cellulose acetate butyrate, fluorocarbons, and alkyd melamine. In industry, powder coatings are being used to coat a wide range of objects such as appliances, metal furniture, electrical equipment, and pipes.

It has been shown that powder coatings technology has considerable promise for numerous aircraft applications. In fact, a few Local Process Specifications (LPS) covering fluidized bed and electrostatic spray applications have already been issued at two of the seven Naval

Air Rework Facilities. In addition, the Naval Air Development Center is carrying out numerous studies devoted to the evaluation of electrostatic spray method. In one study at the Naval Air Development Center, spline assemblies were powder-spray coated with nylon 11 and examined for performance life on a spline wear tester. Under the test conditions the nylon-coated assembly remained operational four times longer than the control. A coating formulation for spline applications is now commercially available. Powder coating techniques have also been used in studies to overcome other problem areas in aircraft maintenance. Fatigue failure resulting from repeated stressing is a major problem in the operation of aircraft. Tests have shown that powder coatings of poly (vinyl chloride), nylon 11, and epoxy are effective in increasing the resistance to flexure fatigue failure. A similar increase in fatigue life was also observed for nylon 11 coated Ti-6Al-4V alloy substrate. A number of components electrostatically coated with nylon 11 are already being field tested on operational aircraft. These include aluminum and magnesium wheels, access panels, tie down chains, leading edge panels, antenna covers, bell cranks, spline assemblies, and wing-fold lock/unlock levers. Increased resistance to erosion and corrosion are sought.

4. Plasma Spray Techniques

Although most of the dry powders which are organic polymers are applied by fluidized bed and electrostatic spray methods, steady progress has been made in developing plasma spray equipment that can be used with organic polymers. In this procedure a torch is used which produces and controls a high velocity inert gas stream, usually argon, at temperatures ranging from 5,000° to 15,000°F. The resultant gas stream consists of a mixture of free electrons, positive ions, atoms, and molecules. The plastic powder is fed into the plasma stream at an angle of approximately 20° so that the dwell time of the material in the flame is exceedingly brief. The hot gas melts the plastic powder without decomposition and forces it onto the substrate. Dense, pore-free coatings can be obtained by proper control of process parameters such as voltage, current, arc gas flow, powder feed rate, and spray distance.

An obvious advantage of this method is that the coating can be applied and cured in one step thereby avoiding subsequent heat treatments characteristic of other dry powder processes. The heat treatments are often objectionable if the temperature necessary to achieve cure is sufficiently high to cause metallurgical changes in the substrate. For example, tests have shown that 7075-T78 aluminum alloy loses 10 percent of its tensile strength at 275°F. The application of similar coatings by plasma spraying did not result in loss of mechanical properties of the substrate. It has been observed that during plasma spraying substrate temperatures were as low as 185°F for coating with epoxy resin and 200°F for coating with nylon 11 resin. An additional advantage is that by this method the coatings can be applied to parts that are too large to be cured in an oven or which cannot be conveniently removed from a larger structure. The NADC mobile plasma spray unit provides for repairs of plastic coatings in the field.

Table I presents a status report for several applications involving polymer powder materials.

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TABLE I
APPLICATIONS STATUS REPORT

COMPONENT	AIRCRAFT BUREAU #	DATE INSTALLED	REPORTING CUSTODIAN	STATUS
Tow Tractor	JG-75 #003593	May 1972	NAF, Warminster	Inspected Nov 1974 after 30 months service, no corrosion or chipping.
Lateral Control Cables	RA-5C #149276	16 Nov 1973	RVAH-13 Key West NARF-JAX	After two full Westpac tours, cables were outperforming adjacent uncoated cables. No corrosion.
Rudder Boot Assy	T-2 #144218	Sep 1973	NAF, Warminster	Applied over fiberglass boot. Condition good as of Nov 1974.
Fairing Assy, Rudder Trim	S-2 #148883	June 1972	NAF, Warminster	14 months service, coating in perfect condition aircraft now located in Point Mugu, CA.
Emergency L/G Blowdown Accumulator	A-7 All par A-7	Feb 73 on a production basis	NARF-JAX	Plasma spray coating (nylon) being applied to all PAR-A-7 since Feb 73 by IAFB-135 and LES 170/172.

DISCUSSION

A. J. Babecki, NASA, Goddard Space Flight Center: The coating of magnesium with nylon sounds like a good idea for spacecraft applications. We use a lot of magnesium, and we do have a corrosion problem. How thick are these nylon coatings?

M. J. Devine: Our experience indicates that with the plasma deposition of nylon, a film of 1 to 2 mils in thickness can be produced. With the fluidized bed process, normally the thickness is from 5 to 11 mils. With the electrostatic process, the thickness is in the range of 4 to 5 mils. Without the nylon coating on the control lever that I showed, corrosion developed on the inner bore as well as on the outer surface in the proximity of the bearing. But once we applied the nylon to the entire assembly and pressed the bearing in, there was no evidence of corrosion after 36 months.

N. Glassman, David Taylor Naval Ship Research and Development Center: What was the thickness of the paint on the treated panel on the ground support equipment?

M. J. Devine: About 4 mils.

N. Glassman: How thick was the nylon?

M. J. Devine: The nylon was about 8 to 10 mils thick. It was applied by the fluidized bed method.

N. Glassman: Did I understand you to say that you were using an antifretting compound on the strands of the wire rope cable?

M. J. Devine: The compound that we introduced into the internal area was MIL-G-81322, a synthetic hydrocarbon. It is probably the best available antifretting compound for such applications.

N. Glassman: Is it an oil or a grease?

M. J. Devine: It is a nonsoap thickened grease. During the impregnation process, however, it's cut back to a slurry consistency with about 50% hexane. The hexane is driven off before the polymer is applied.

J. E. Stern, NASA, Goddard Space Flight Center: Did you have any special process for cleaning the cables before you coated them after you had impregnated them with the antifretting compound?

M. J. Devine: The only procedure that we followed was to wipe the excess grease off with a cloth saturated with hexane.

J. E. Stern: Were there any problems in bonding or in getting a dense coating without any cracks, breaks, or openings?

M. J. Devine: No, I think that is what is unique about the process. It violates the concept that we all follow that the surface must be very, very clean. There is no evidence that that coating, which is then fused, can be easily removed from the cable.

J. E. Stern: What was the effect on the stiffness and the structural behavior of the cable after it was coated?

M. J. Devine: There was no significant effect on stiffness. We exposed both the treated and untreated cable to a salt fog environment. At various intervals we ran load tests by pulling the cables over a 1/4 in diameter pulley with a 300 pound load. After 600 hours the conventional cable broke during the load test, whereas after 1670 hours, the treated cable showed no evidence of damage.

E. E. Klaus, The Pennsylvania State University: Can you comment on the quantities of the antifretting material in the cable?

M. J. Devine: No, we fill all those internal areas between individual wires. Part of the fretting problem comes from the interaction of the wires. Therefore, if the process is going to be effective, it must protect those individual wires, so all the internal spaces must be filled. There must be a tight film around the cable to eliminate the material from being pumped from the internal areas. To have it there initially is one thing, but to maintain it there continually is more important.

L. F. Fehrenbacher, USAF Materials Laboratory: Have you done any work with higher temperature polymers such as polyimides which may be more environmentally resistant?

M. J. Devine: We have written a number of papers about polyimides in solid sections, especially for antifriction bearing applications, both as retainers and as land inserts. We have not attempted to apply the polyimides by any of the techniques presented here. We are using polyphenylene sulfide for higher temperature applications. We do have articles out for field tests, but we don't have any field test data as yet. We are also working with a number of Teflon or modified Teflon-type products, but again, there are no significant field test results.

L. F. Fehrenbacher: How do you determine which process--plasma, fluidized bed, or electrostatic--to use?

M. J. Devine: Sometimes it will depend on the size of the article, but usually the available clearances will determine the process.

If the clearance is small, the plasma process will probably have to be used.

L. F. Fehrenbacher: If all of the three techniques could be used in a given application, do you have enough data to indicate which would give the best results?

M. J. Devine: There is just a little indication. A very important test is the water vapor transmission test in which an attempt is made to determine how much moisture will penetrate a film in a given period of time. Test results on polyurethane paints indicate moisture penetration of about 5 grams per 100 centimeters per 24 hours. With the plasma applied nylon, it runs about 3 and with the electrostatic processed nylon, it's down to somewhere between 1 and 2. It appears for a very non-porous film that, based on the water vapor transmission data, the electrostatic process gives the best film.

L. F. Fehrenbacher: Do you get a denser film with the electrostatic process?

M. J. Devine: It appears to be, based on limited data.

A. J. Babecki: What kind of temperatures do the substrates reach with each of these application processes?

M. J. Devine: The highest substrate temperatures will be encountered with the fluidized bed process. In this process a layer of powder is held in suspension in a drum-like arrangement. The part to be coated is heated in an oven above the melting point of the powder before the part is inserted into the powder to fuse the coating on. In the case of nylon-11, the temperature is above 400 F for the fluidized bed process. For the electrostatic process, the temperature is between 385 and 400 F. For the plasma process, the temperature of the substrate is significantly lower. In this process, the heat is used to melt the boundary layer of the plasma. The melt is then flowed onto the substrate surface. It is quite possible that nylon-11 could be applied to ordinary newspaper or cardboard without damaging the substrate.

E. J. Deemer, Naval Air Systems Command Representative, Atlantic: Is there any possibility of glass bead impregnation in the nylon-11 coatings to increase resistance to erosion?

M. J. Devine: Your point is well taken, but at present we do not know. Professor Ludema may have something to add.

K. C. Ludema, University of Michigan: In one proprietary process that I know of, where paper slides over these polymers, glass beads will increase the life of the film by a factor of 10.

J. E. Stern: Have you done any experimentation with sputtered coatings? If you did, what kind of coatings were they and what kind of results did you get from them?

M. J. Devine: In October of 1973, Gentner and Newhart presented a paper at the Mechanical Failures Prevention Group meeting in Boulder, Colorado (The Role of Cavitation in Mechanical Failures, Proceedings of the 19th Meeting of MFPG, Boulder, Colorado, 1973, NBS Special Publication 394). They discussed the application of tungsten carbide and silicon carbide blended with type 304 stainless steel sputter-coated on aircraft compressor blades. The coatings reduced the effects of erosion on the leading edge, while the geometry of the blade, both on the fore side and the back side, was maintained. They found that sputtered coatings on titanium prevented the formation of titanium oxides for thousands of hours at elevated temperatures. The major problem with sputtered coatings is in setting up a production facility. For compressor blades, we are talking about processing only one or two a day.

J. E. Stern: Have you tried any sputtered polymers on any of your devices?

M. J. Devine: No, I have not. Spalvins at NASA Lewis has done work in that area.

W. F. Byrnes, Naval Air Engineering Center: When the tractor panels that had been fluidized bed-coated were damaged, could they be repaired without removing the first coating?

M. J. Devine: They can be repaired. In fact, the plasma process can be used to repair coatings applied by either the fluidized bed or the electrostatic process. However, we are trying to develop a much simpler technique to effect repairs. The main drawback in repairing with the plasma process is blending the colors so they will match.

W. F. Byrnes: Would this be done at the depot level?

M. J. Devine: We would have to do this at the depot level using the plasma process. However, the technique that we are working on in the laboratory is very close to being completed. This technique would enable repairs to be made at any level of maintenance.

NYLON 11 AS A LUBRICANT
AND CORROSION PREVENTATIVE COATING

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The working bearing surfaces of Sea Plow IV, a vehicle designed to lay cable in a 4-ft trench in the ocean floor, must be protected from corrosion, internal friction plus abrasion from sand, mud and silt. Examination of this problem suggested that a coating of nylon 11, applied electrostatically as a dry powder, could afford protection against all of these conditions. Conventional application techniques were modified to permit application of the coating at dockside. Results have been excellent as evidenced by Sea Plow IV's more than one year of troublefree operation.

Keywords: Abrasion; Corrosion protection; Friction; Marine environment; Powder coating; Salt water; Solid lubrication.

American Telephone & Telegraph company and its overseas partners began laying voice communications cables on the ocean floor over twenty years ago. Currently a new cable, known as TAT 6, is being put into place between the United States and France. Early cables were merely placed on the ocean floor. But this subjected sections near each coast to damage from fishing trawlers. Now the cables are buried at each end, essentially along the continental shelf, in a trench about 4-ft deep. An ocean-floor traversing vehicle called Sea Plow IV is performing this operation off the coasts of France and Rhode Island. This paper deals with the materials and techniques used to protect the working bearing surfaces of this machine from corrosion, friction and abrasion.

Bell Telephone Laboratories were consulted on this problem. The essential requirements were that the Sea Plow IV operate reliably in 1,000 fathoms of sea water. In addition to the chemical attack by sea water, the machine had to be protected against many other types of corrosion including stress, galvanic, crevice and pitting. To operate satisfactorily the lead screw and attitude control mechanism required lubrication and protection from tolerance destroying abrasion from the sand, silt and mud plowed to form the trench. Finally the working surfaces also had to be protected against abrasion by the cables themselves.

Several years previously we had consulted the Naval Air Development Center about the problem of protecting and lubricating bearing surfaces required to operate under high load conditions in a sea water environment. The Center demonstrated a method of electrostatically applying a dry powder coating of nylon 11 on aircraft splines. We contacted the manufacturer of the electrostatic equipment, Interrad Corporation, and talked to various powder vendors. Based on the Navy's experience in which nylon 11 has withstood 100,000 psi stress in an undersea environment for years, we selected this nylon 11 from Rilson Corporation.

The problem of application was less straightforward. In the Navy applications relatively small parts are coated in the shop where conditions for surface preparation, priming, application and curing could be closely controlled. Our problem was to coat large sections of a 30-ft long vehicle on a Baltimore dock, with only torches and a heat-treating furnace available for curing the powder.

Fortunately the equipment manufacturer was able to provide a recently developed, portable, fully transistorized powder spray unit. In addition, the miniaturized high voltage generator necessary to charge the powder particles, was located right in the spray gun. This eliminated the need for stringing a bulky 70 KV cable along the exposed dock.

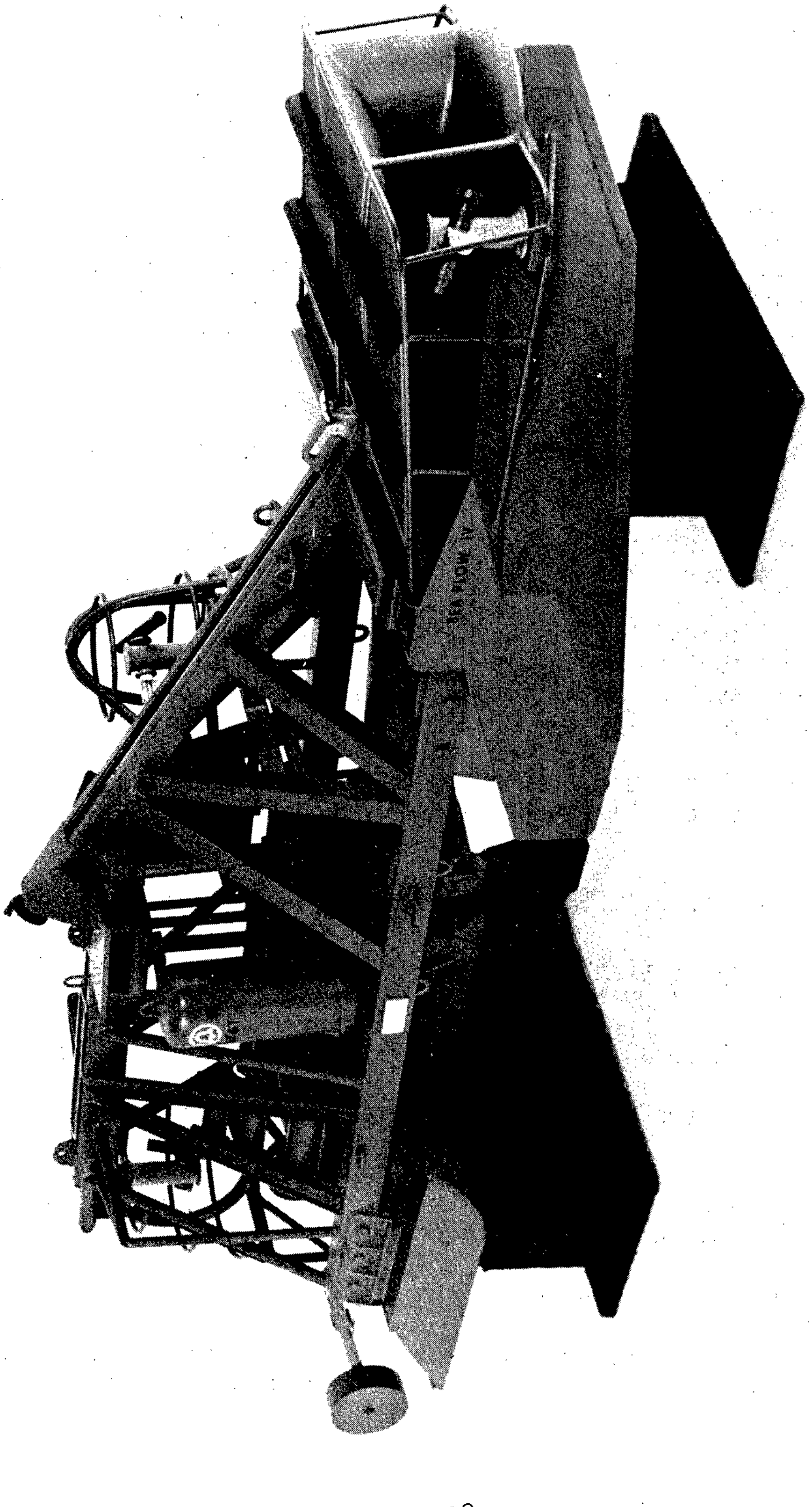
Personnel at Bell Telephone Laboratories Guilford Center further adapted this equipment. Wands were developed to extend the spray gun nozzles in order to deliver powder inside several tubular parts.

Although more conventional methods of metal pretreatment such as phosphating or chromate rinsing may have been preferable, our location and the equipment available limited the pretreatment to sandblasting.

Because we were unable to closely control preheat and cure temperatures, the degree of cure was checked by eye and by feel. After sandblasting parts were preheated at 650 F for one hour. The heated parts were primed, by dip or brush and immediately sprayed with nylon 11 powder. The coating was cured by reheating for 20 minutes at 650 F. If the coating appeared under cured, the part was heated again until we were satisfied that cure was complete.

Among the parts coated in this manner was a lead screw and its 15-ft tube, the U-bolts through which the vehicle is towed by the surface vessel. Clearance between the mating threads of the lead screw was 30 mils. The coating could not exceed this thickness. Minimum coating thickness was established at 8 mils.

Compared to the controlled conditions of a conventional in-plant coating line, our application technique was rather crude. Nevertheless, thanks to the ingenuity of everyone involved, including equipment and material suppliers, the coating has proved to be effective. It permitted the designers of Sea Plow IV to use tool steel for critical parts instead of much more costly aluminum-bronze. Perhaps more importantly, it has enabled the machine to operate reliably in a most difficult environment. The Sea Plow IV has been in almost continuous service for over a year. During that time there have been no reports of malfunction or corrosion.



DISCUSSION

R. A. Mollicone, USAF Materials Laboratory: Have you done any work with composites?

G. H. Kitchen: Marty, do you want to respond to that?

M. J. Devine, Naval Air Development Center: We did do a few experiments with composite materials. One was actually made into a structural component--a fuel tank section. It was tested to failure in bending fatigue. It had approximately 95% leakage, mostly at the seams. We took this essentially expended specimen and coated the entire surface area including all the seams externally with the nylon by plasma deposition. It was again tested in fatigue; the leakage had been reduced to about 5% of what it was before.

It is also possible to apply these powders on fibers to improve their ultraviolet radiation resistance.

R. A. Mollicone: Does anyone have any background information in regard to high temperature (300-350 F) applications with loading?

M. J. Devine: I think 250 F is about the upper temperature limit for nylon-11 for continuous service. At higher temperatures (500 to 700 F) materials such as aromatic polyimides and the polyphenylene sulfides must be considered.

R. A. Mollicone: What is the effect of a 250 F temperature on moisture absorption of the structural graphite epoxies or boron epoxies?

M. J. Devine: At 250 F, nylon will be effective for extended periods.

J. Kruger, National Bureau of Standards: How good is the erosion or abrasion resistance of this coating?

G. H. Kitchen: The abrasion resistance even to sand is excellent.

J. Kruger: Do you have any information regarding the bio-fouling of this coating?

G. H. Kitchen: We have found that there is definitely a significant reduction in the buildup of inorganic salts on metal parts.

J. Kruger: What about barnacles?

G. H. Kitchen: The things that we bring up are fairly clean. Marty, do you want to comment on barnacles? Your equipment is in shallow water.

M. J. Devine: After three years, our equipment was clean.

N. Glassman, David Taylor Naval Ship Research and Development Center: What is the function of the primer that you mentioned?

G. H. Kitchen: The primer is a plastic-like material that is used to coat the substrate to a thickness of about half a mil. It has a very tacky, rough surface that permits a mechanical bond of the nylon-11 to it rather than to the metal substrate.

N. Glassman: You talked about using this material on electroless nickel. That wasn't because of corrosion, was it?

G. H. Kitchen: No.

G. E. DeLong, Naval Air Systems Command Representative, Pacific: Was your primer inhibited?

G. H. Kitchen: No.

M. J. Devine: George DeLong made a very important point. Nylon-11 is not a chemical conversion coating. It is really a barrier film. If the coating is disrupted so that water can penetrate to the base metal, there will be a site for corrosion to take place if there is no inhibited primer. For maximum corrosion protection, it is very important to include an inhibited primer prior to the application of a polymer film.

G. H. Kitchen: If the nylon-11 coating is disrupted and moisture penetrates to the metal, corrosion will start. But the corrosion doesn't spread under the nylon-11 like it does under other coatings.

A. J. Babecki, NASA, Goddard Space Flight Center: From the standpoint of spacecraft applications, do either of you gentlemen know anything about the coefficient of friction of this nylon surface against itself or against metals?

M. J. Devine: We have run comparative experiments using nylon on steel and grease on steel and found no difference in the heat inputs.

MECHANICAL DESIGN CONCEPTS FOR COATED NUCLEAR FUEL PARTICLES

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Abstract: Retention of fission products in microspherical coated particles depends upon the mechanical integrity of the coatings. Mechanical design concepts have been developed over a 15 year period which led to the fabrication of highly successful multiple coated particles such as the TRISO coated particles. An overview of this development is described.

Key words: Computer modeling on a microscale; elasto-plastic micropressure vessels; failure predictability through small size; microencapsulated coated fuel particles.

Millions of curies of radioactive isotopes are the product of fissions in a typical power reactor. These fission products are isotopes of dozens of elements from the periodic table, representing solid, vapor, and gas species.

Ideally, there should be a zero release of fission products to the coolant and to the environment. Great progress has been made in fulfilling that goal through the use of many independent containment components (fission product release barriers) in a reactor system. Failure of one fission product barrier should not compromise the goal of zero release to the environment by the system.

The primary barrier responsible for fission product retention is the fuel element. Typically it retains 99.999 percent of the fission products generated. Some reactors have had retention exceptional to the requirements, such as the Peach Bottom gas cooled reactor, a test reactor of 40 MWth. Its performance was evaluated by the reactor operator, the Philadelphia Electric Company (1) and showed the release to be 0.003 fraction of the AEC required limits.

Liquid cooled reactors generally use fuel elements having long tubular metallic cladding with welded enclosures to assure retainment, or fuel cermet layers bonded between metal sheets with side enclosures (picture frames). A typical light water reactor may have 1,000 to 40,000 individual elements. This approach to fission product retainment is the oldest and most developed.

Another retainment concept is the subject of this paper, the use of tiny microspherical fuel particles, each with its own coating for fission product retention. This concept has been applied to gas cooled reactors such as the helium cooled, graphite moderated Ft. St. Vrain reactor in Colorado. The total number of coated particles in the 851 MWth core is 10^{12} particles. Failure prediction is improved because of the great number of nominally identical particles. Failure of one particle is found to be essentially independent of failure of another. The individual failed particles with coatings not structurally intact release only a fraction of their fission product inventory, largely the fission gases krypton and xenon.

A typical example of a multilayer coated particle for use in a helium cooled graphite reactor is shown in Figure 1, "Cross section of a Typical Multi-coated Particle". Many variations are possible for specific applications, but the design concepts are basically like this. It is the mechanical integrity of the outer three layers that is important.

Prevention of mechanical failure and loss of structural integrity of the coatings on fuel particles determines the fractional release of fission products to the helium coolant of a nuclear reactor. Coated particle development over a 15 year period improved the fraction failed in a long operating time from 0.8 to 0.00001. The history of this remarkable improvement shows the value of applying mechanical analysis and statistics to help in performance testing evaluation and production process development.

This coated microspherical fuel particle has been successfully developed over a period of approximately 15 years by many laboratories in several countries. A few of the major contributors to this development will be mentioned, but many will not for practical reasons. The omission is not meant to be a reflection on the value of their contributions.

The history of the development of this reliable concept began with attempts to blend ceramic (oxide or carbide) fuel powders into a graphite matrix in the early concepts of ROVER, HTGR, and MGCR reactors.

The design requirements for the ROVER nuclear rocket emphasized tight dimensional tolerances of extruded graphite fuel, as well as strength and density. The fraction of the uranium fissioned was very low, and the fission product retainment without fuel particle coating was adequate for tests at the rocket test site for periods of one hour or less. However, moisture in air during storage, assembly, shipping, and test preparation was found to deteriorate the fuel strength. The individual fuel grains were than spheroidized and given a single pyrocarbon layer to protect the uranium dicarbide kernels from hydrolysis. This was the major solution to the problem of loss of strength by hydrolysis. A ROVER type particle is shown in Figure 2.

Further development sponsored by the USAEC showed that the simple one layer pyrocarbon coating fractured readily with greater uranium burnup than required for ROVER but required for power reactors, such as the Gas Cooled Reactors. One early mechanical model was devised and was described by Prados and Scott (2) of ORNL. Sources of stress were defined. The fuel kernel swelled since each uranium atom fissioned produced two fission product atoms. Further, 14 percent of the fission product atoms at high burnups are the inert gases krypton and xenon. The gases can create tremendous internal pressure inside the pyrocarbon coating if there is no provision for gas expansion space inside the coating.

Thus the two layered, or BISO fuel, was conceived. The cross section of a typical one is given in Figure 3. A somewhat sooty porous inner buffer layer is deposited on the fuel microsphere kernel, and the buffer layer is coated with a gas tight outer pyrocarbon layer. The porous buffer layer provides gas expansion space.

The first core loading in the Peach Bottom reactor used the single pyrocarbon layer coated particles as in Figure 2 and had particle failures in 0.8 of the particles. Core 2 operated more successfully using the BISO coated particles. It is estimated that less than 0.01 fraction of these particles failed.

The main function of the intermediate porous buffer coat in Figures 1 and 3 is to reduce mechanical stresses and structural damage to the outer layers due to recoil fission product ions from the fission events near the surface of the fuel kernel. The outer pyrocarbon coat was modeled as a microspherical hollow pressure vessel. Thus, it was necessary to measure its creep strength at operating temperatures. Price and Bokros of GA (3) reported creep properties and densification and related them to irradiation. Isotropic pyrocarbon was found to be the most desirable pyrocarbon. They measured the effect of a high fluence of fast neutrons on dimensional changes of pyrocarbon of various densities, etc. There appears to also be an enhanced mechanical creep due to irradiation. Prados and Godfrey (4) of ORNL continued evolving a more complicated code called STRETCH to accommodate these observations.

Another material effect was observed. Some fission product elements such as Ba and Sr are not as well retained by isotropic pyrocarbon as other fission products. DeNordwall and Sayers (5) reported a 10^2 to 10^4 improvement in retention of these fission products if a silicon carbide layer is introduced. Barr (6) also observed cesium retention to be improved when sandwiched between two pyrocarbon layers. Silicon carbide was also found to be stronger than pyrocarbon. Considering these and other factors, the multicoated particle concept known in the USA as a TRISO coated particle was developed. Figure 1 shows one example of this type.

The principal purpose of the inner pyrocarbon coat is to be able to coat the silicon carbide over a buffer coat without silicon carbide penetrating the buffer and filling its desirable porosity.

Mechanical analysis then became much more complicated. Multicoat analytical modeling by Kaae (7), Walther (8), and Stevens (9), capable of analyzing this four coated particle significantly advanced earlier codes. The current analytical code (7) is designated TRISO II. It was necessary to account for the differential thermal expansion between silicon carbide and pyrocarbon during processing and operating temperature changes. The strength of the silicon carbide is greater and has less creep than pyrocarbon. Complex stress and strain relationships were developed.

The current status is that several versions of mechanical design codes based on elastic, plastic, and irradiation behavior at operating temperatures are capable of predicting coated particle failure rates for a broad range of dimensional and property variations as well as the uranium burnups.

The eventual successful development of the TRISO coated particle was achieved through an iterative process of mechanical design analytical concept definition, mechanical materials property measurements, testing particles in a reactor, evaluating coating failure, evaluating fission product retention, and remodeling the analytical models for redesign. Several modern analytical codes are based on elasto-plastic behavior in fabrication and operation of multi-layer coated particles.

Through iterative comparison of analytical models with irradiation test evaluation, the basic mechanical concepts have been retained, but modifications to the material behavior functions were necessary. A recent treatment by Gulden (10) of GA is particularly interesting since it recognizes the effect of variations of buffer coating thickness and kernel diameters on the prediction of particle coating failure as compared to experimental results.

The time dependence of stresses analyzed by Gulden using the GA TRISO II code is given in Figure 4. The silicon carbide layer in this nominal design with average dimensions is always in compression and will not fail. Initial compressive stress in the silicon carbide layer is desirable and is obtained by use of differential contraction of the outer pyrocarbon layer upon the silicon carbide. The combined effects of stress relief through creep, shrinkage of the outer pyrocarbon with irradiation, and internal gas pressurization led to an early stress reversal in the silicon carbide followed by a decreasing compressive stress behavior. It is critical to the coated particle coating integrity that the silicon carbide not be in tension. The effective strength before rupture of the silicon carbide is estimated by Gulden to be 30,000 psi through comparison with empirical results. When the silicon carbide tensile stress exceeds 30,000 psi the particle coating fails.

The variation of buffer thickness and kernel diameters was found to be critical through analysis by Gulden (10). The total porous volume in the buffer layer, and thus the internal gas pressure at high uranium burnup fractions depends upon these dimensional variations determined at the time of fabrication. Variations in the silicon carbide tensile stresses resulted. The smaller the porous volume the greater the tensile stress in the silicon carbide. A high probability of failure occurs above 30,000 psi stress.

Two failure modes are postulated. When the tensile stress in the silicon carbide exceeds 30,000 psi, the stored elastic energy in the multicoated shell is released and the crack propagates through all three outer layers. The buffer coat serves to decouple mechanical reactions between the kernel and the outer coatings. It will not propagate a crack initiated in the outer coatings nor transmit strain from the expanding kernel to the outer coats. Therefore it is not mechanically involved in a failure mode analysis since it does not store elastic energy or transmit a crack. However, it can release stored fission gases if the outer coatings crack. Bursts of fission gas activity release have been experimentally associated with intentional cracking of individual irradiated coated particles. The other failure mode begins with the chemical attack of the inner pyrocarbon layer by a fuel kernel moving ("amoeba" effect) up a temperature gradient and results in an unbalanced stress. This second mode of failure also leads to a sudden cracking of all three outer layers and a burst of fission gas release.

Following the burst of fission gas release is a slower release of a wide variety of gas, vapor, and solid fission products.

The main criterion is to maintain the integrity of a very high fraction of the fuel particle coatings throughout their life in spite of severe conditions of:

- temperature
- internal gas pressure
- radiation damage.

The use of 10^{12} of individually coated fuel particles permits the use of statistical techniques in analyzing fuel bead performance that results in specification of fuel particle coating tolerances in production. The failure prediction of 10^3 to 10^4 clad tubular fuel pins gives less predictability, and a greater release fraction with each failure.

Test results have been applied in developing computer codes which are able to evaluate the effects of changes in coating layer designs and predict coated particle performances.

- codes also consider the variability of coatings on a statistical basis.

Fuel particle coating developments are continuing to improve the coating performance and also to improve the understanding of the design parameters of importance.

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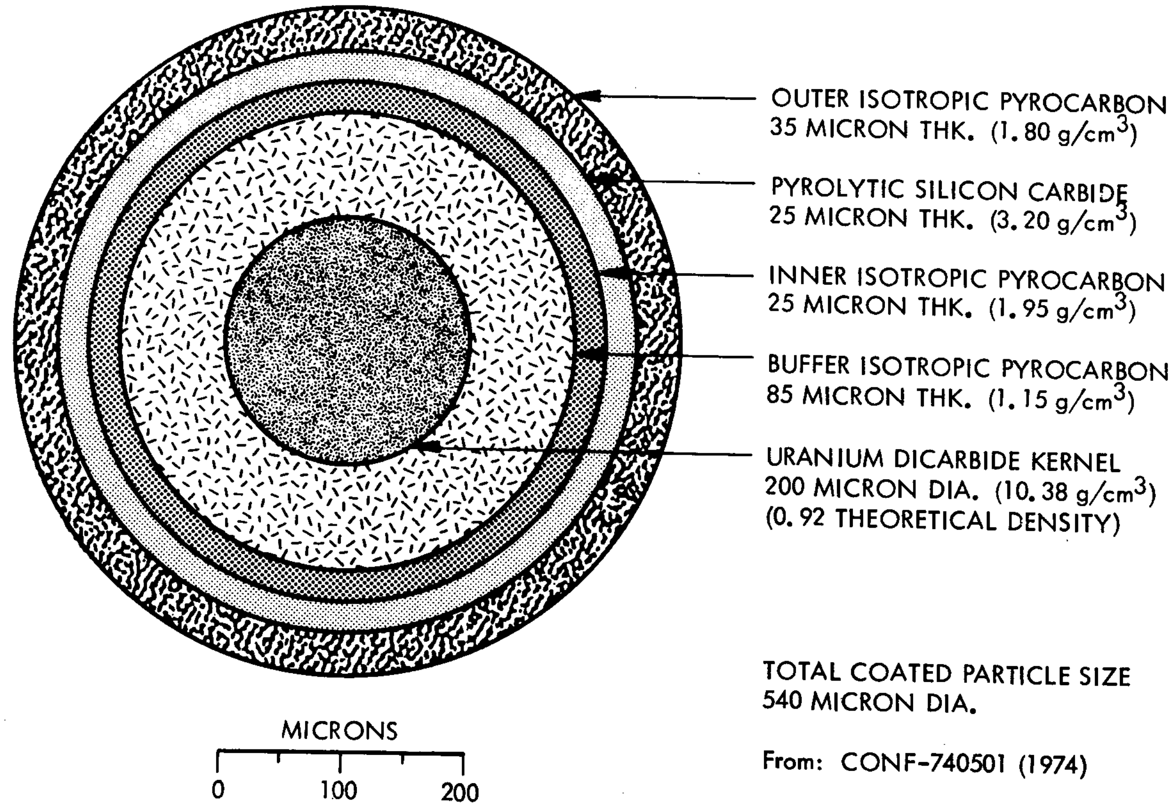
Reference VHTR Initial Fissile Particle Design (Triso Coat)

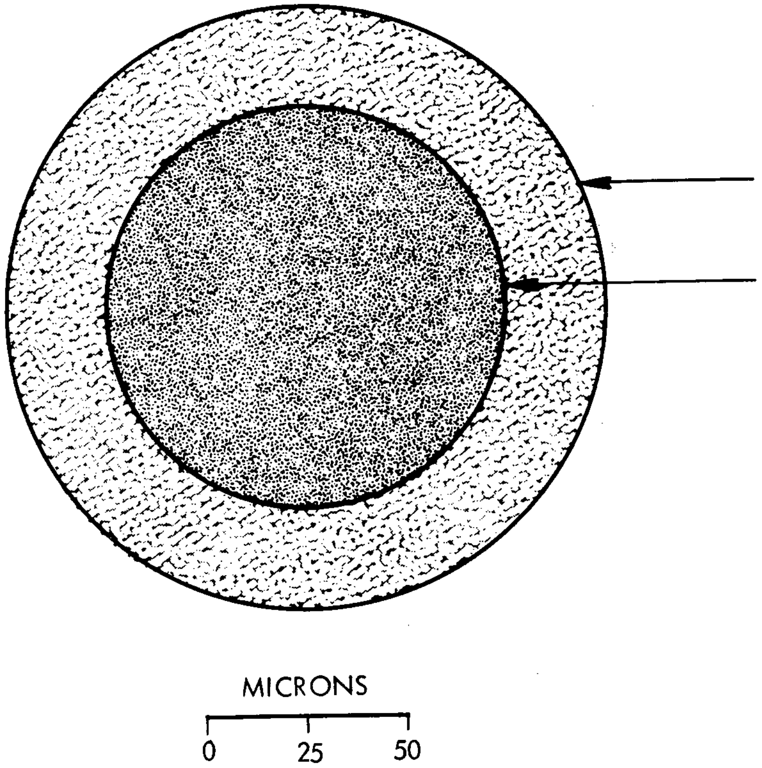


TOTAL COATED PARTICLE SIZE
540 MICRON DIA.

From: CONF-740501 (1974)

Figure 1. Cross Section of a Typical TRISO Multi-coated Fuel Particle

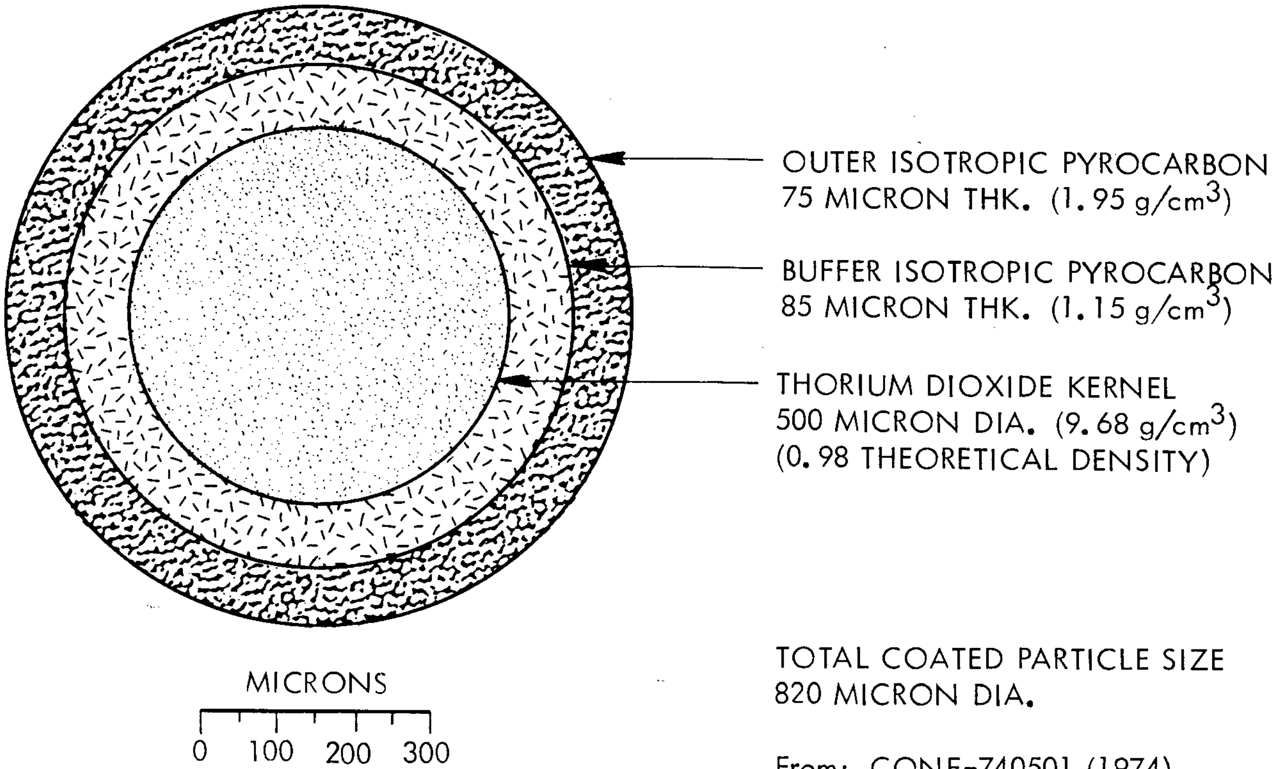
Reference Particle Design for the NERVA Reactor



From: WANL-TNR-230 (Vol. II APP)
(1972)

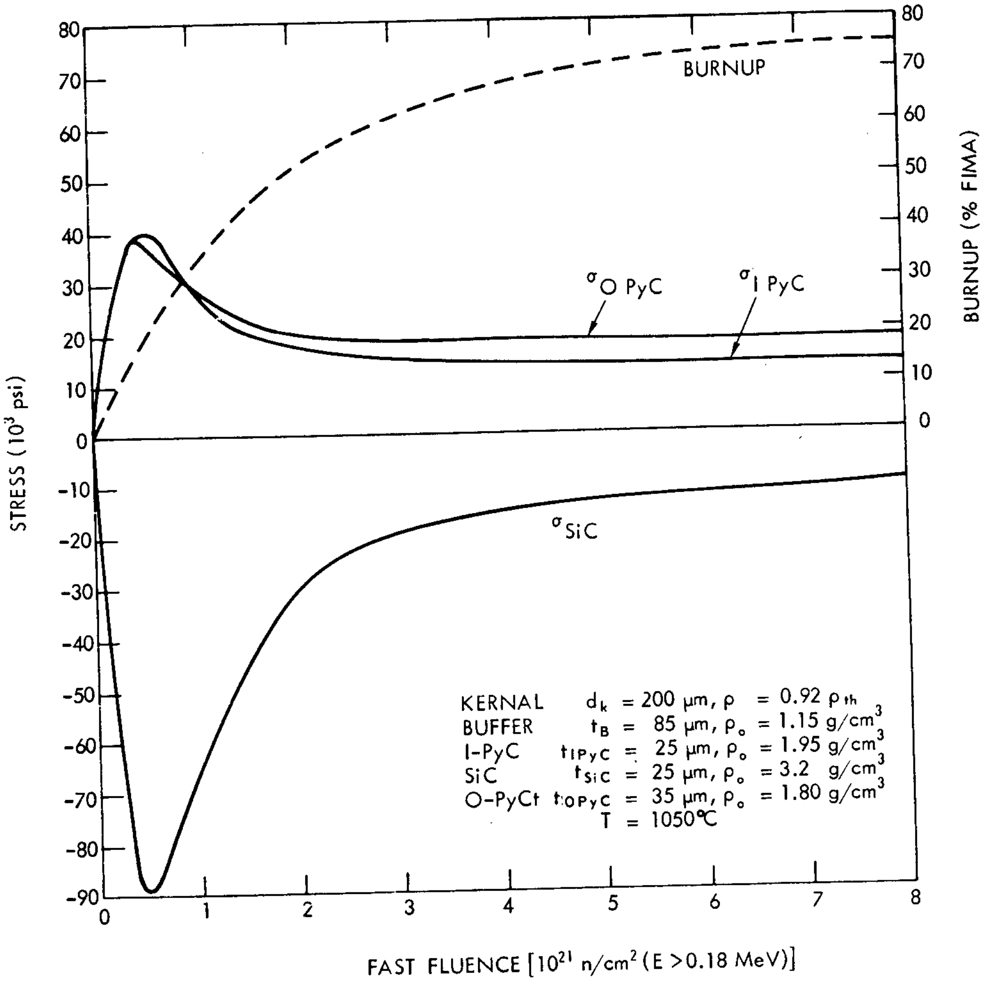
Figure 2. Cross Section of a Typical ROVER Single-coated Fuel Particle

Reference VHTR Fertile Particle Design
(Biso Coat)



From: CONF-740501 (1974)

Figure 3. Cross Section of a Typical BISO Two-coated Fuel Particle



STRESS INCREASE WITH FAST FLUENCE

Figure 4. Coating Stresses in TRISO Coated Particles with Increasing Fast Neutron Exposure (and burnup).

DISCUSSION

R. M. Thomson, National Bureau of Standards: Why did you use silicon carbide, which is a ceramic, for the strengthening agent instead of something like tungsten or stainless steel which wouldn't have the thermal shock properties that the ceramic has?

M. Tobin: The substitution of zirconium carbide for silicon carbide is under current development. The main reason for this planned replacement pertains to the limit of the processing temperatures to 1800 C for 2 hours or less for TRISO particles containing silicon carbide. Beyond this limit, the particle will be chemically destroyed. The particle kernal will attack the silicon carbide. Silicon carbide at 2000 C has a very high silicon pressure. Zirconium carbide has a melting point in contact with carbon as a ZrC-carbon eutectic of 2890 C. It is much more refractory than SiC. Tungsten carbide is another possible replacement for silicon carbide.

R. S. Miller, Office of Naval Research: How were creep properties of the beads measured?

M. Tobin: Jack Bokros made little coin-like discs of carbon and fluidized them in a conical bed of graphite. He coated pyrocarbon on the disc, and then assumed that the structure was the same as would be obtained on a little tiny ball. Most of his creep work was done with the coatings from these discs. The coatings were removed from the discs and tested in graphite furnaces.

A. J. Babecki, NASA, Goddard Space Flight Center: Is the hammer made just of pure carbon or is some kind of binder used?

M. Tobin: Just pure carbon. It is produced by Pure Oil Company of Decatur, Texas. It is a reconstituted graphite that has been heat treated at 2500 C. There are two major kinds of manmade graphite. Primary graphite is produced by heating pitch to form coke. The coke is then crushed to powder and mixed with more pitch and then heated to a very high temperature. Most graphites are of this type. Highly specialized graphites are made by grinding primary graphite into a powder, classifying it, and possibly treating it. Sometimes it is then mixed with a thermoplastic or a thermosetting binder and molded or extruded and then thermally processed into another graphite which is more isotropic and stronger than the primary graphite. This material is a reconstituted or secondary graphite with superior properties. All the graphite parts used in the nuclear rocket program were of that type.

A. J. Babecki: Do you know if there are any ball bearing components made of this material?

M. Tobin: I heard it works fine as raceways. It is a dimensionally stable material and therefore may be desirable for some bearing applications. This secondary graphite costs about 25 times as much as primary graphite, and for this reason, it is not used unless necessary.

A. J. Babecki: Is the application of this material to bearings done under NASA sponsorship?

M. Tobin: No, this was a very minor effort sponsored by the manufacturer.

SESSION II

METAL
COATINGS

Chairman: J.Kruger

National Bureau Of Standards

NICKEL-PHOSPHORUS ALLOY COATINGS FOR WEAR RESISTANCE

Christian E. Johnson
Fielding Ogburn

National Bureau of Standards
Washington, DC 20234

Electroless nickel coatings are nickel alloys generally with a nominal composition of 8 wt % phosphorus, applied to metal substrates from a nickel solution by an autocatalytic chemical process. They are used for protecting steel from corrosion and wear, and are generally more corrosion and wear resistant than electroplated nickel.

Heat treatments can increase significantly the wear resistance and hardness of electroless nickel. This occurs by precipitation hardening and the precipitation of a nickel phosphide. The hardness depends on the heat treatment and on the alloy composition and often attains a Knoop hardness of 900-1000, equivalent to the hardness of electrodeposited chromium.

Tests by several laboratories show improved wear resistance with appropriate heat treatment and in some circumstances, the electroless nickel coatings have a higher wear resistance than electrodeposited chromium. Wear resistance of electroless nickel can also be improved by the incorporation of small particles of hard material into the coating during the plating process.

Keywords: Auto-catalytic nickel; auto-catalytic nickel, hardness of; auto-catalytic nickel, wear of; electroless nickel; electroless nickel, hardness of; electroless nickel, wear of; nickel, auto-catalytic; nickel, electroless; nickel-phosphorus alloy; and wear resistant alloy.

Coatings of nickel-phosphorus alloys are used to provide hard, wear resistant surfaces and with other characteristics have contributed to their use in a wide variety of applications.

The coatings are formed by a chemical process in which sodium hypophosphite reacts with nickel ions in a solution on a catalytic surface to produce nickel metal. Since nickel is a catalyst for the process, the formation of nickel can continue after coverage of the original surface and coatings can be built up to substantial thicknesses. In the plating trade, both the process and the coating are referred to as electroless nickel, though the proper designation is now considered to be autocatalytic nickel. Actually these terms include processes which produce materials other than nickel-phosphorus alloys, but will not be discussed further.

These nickel-phosphorus coating materials contain up to 15 wt % phosphorus. As-plated, they are supersaturated solutions of phosphorus in nickel and are often considered to be amorphous or a metallic glass though it has been shown by electron diffraction that at some compositions they are very fine grained. Subsequent heat treatments at appropriate temperatures will convert the metastable material to Ni_3P and nickel to form a substantially harder and more wear resistant material.

Economically, electroless nickel plating is more expensive than conventional electroplating; but the process has the advantage that the coating has a more uniform distribution and it can be applied to components whose shapes are not suitable for electroplating. In addition, the nickel-phosphorus alloys are more corrosion resistant, harder, and more wear resistant than electrodeposited nickel. Because of these characteristics of the process and the material, electroless nickel-phosphorus coatings are used on such items as heat exchangers, pumps, oil field drilling equipment, high pressure gas bottles, shipboard equipment, hydraulic cylinders, gears, printing press beds, and as a protective surface for stainless steel. A complete list would include many other applications where corrosion resistance and/or wear resistance are required.

Gutzeit and Mapp [1] reported data on the rate of penetration of electroless nickel-phosphorus coatings by over 100 different solutions. Generally, these coatings are corroded by reagents which attack unalloyed nickel but usually at a slower rate. This corrosion resistance should be dependent on the alloy composition and heat treatment, but most corrosion data do not specify the composition or are only for one composition.

Because of the relation between hardness and wear resistance, and because of the relative ease of measuring hardness, hardness data is often used in lieu of wear data and an understanding of the hardness characteristics of the nickel-phosphorus alloy is pertinent to the understanding of the wear characteristics.

As deposited, electroless nickel-phosphorus coatings vary in Knoop hardness from about 500 to 700 for a 100g load depending primarily on the phosphorus content (Fig. 1). After a simple heat treatment in air at 200°C for 8 hours, there may be some hardening of the material, again depending on the phosphorus content. After heat treatment at 400°C for 1/2 hour, the hardness is generally in the range of 900 to 1000 HK_{100} (Fig. 1) resulting from precipitation hardening in which nickel phosphide, Ni_3P, precipitates. The precipitation hardening process is further illustrated in Fig. 2 in which hardness is plotted as a function of the time at 400°C. The falling off of hardness of the low phosphorus alloy after the initial hardening is probably associated with recrystallization of the nickel [2] and agglomeration of nickel phosphide as shown by Brenner [3] for heat treated alloys higher in phosphorus content. The high phosphorus material then consists essentially of small grains of nickel dispersed in a matrix of nickel phosphide, Ni_3P.

Hardness as a function of the heat treatment temperature is shown in Fig. 3. It is evident that the alloys generally encountered, with 6 to 10 wt % phosphorus, reach maximum hardness with heat treatments at about 400°C. Above 400°C, the hardness decrease becomes less pronounced with increasing phosphorus content. Heat treatments of 400°C are generally used for hardening electroless nickel-phosphorus and the hardness obtained is of the same order as that obtained on conventional chromium coatings and sometimes harder. It is not unreasonable to speculate that still harder material could be obtained with an appropriate cycle of heat treatment.

Wear tests have been reported by at least 5 laboratories [4,5,6,7, and 8]. These results are not directly comparable, because each laboratory used a different test or different test conditions, although there is no disagreement with the qualitative relationships between the heat treatment and phosphorus content of the material and its wear performance.

Our own data, obtained with a Taber Abraser, are summarized in Table 1. In brief: heat treatment at 400°C improved the wear resistance of the nickel alloy, although the wear resistance of electroplated chromium was still better. In relating wear resistance of a material to that of chromium, it should be borne in mind that the properties of electroplated chromium are not single valued. That is, the wear resistance and other properties of chromium are dependent on the chromium plating process.

According to Gutzeit [4] and Randin and Hintermann [5], the wear resistance of electroless nickel-phosphorus increases considerably as the temperature of the heat treatment is raised, reaching that of hard chromium at 600°C.

Turns and Browning [6] report increasing wear resistance with increasing temperature of heat treatment up to about 480°C. Their Taber Abraser test rated chromium better than heat treated nickel-phosphorus.

Weightman and Pearlstein [7] obtained similar results using a Falex wear test except that nickel-phosphorus heated at 400°C was better than chromium. Parker [8] and Cohen [9] (Table 3) obtained the same results.

During the deposition of electroless nickel-phosphorus, one can incorporate small particles of alumina or other hard material into the coating. Parker [8] tested the wear resistance of such composite coatings containing various hard particles. He reports that as-plated, these coatings were as wear-resistant as chromium and aluminum hardcoat, and more wear-resistant after heat treatment at 260-290°C (Table 2).

In summary: The nickel-phosphorus coatings have been used in pumps, compressors, molding and extruding dies for plastics, in order to reduce galling type wear in machinery, etc. These applications have evolved by experience and trial and error. In recent years interest in these coatings for wear resistance have lead to laboratory testing and developments which are expected to lead to better wear performance.

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TABLE 1

Wear Tests
(NBS)

Specimen	Number of runs	Cycles Per run	Type of Wheel	Weight loss* mg/1000 cycles	Thickness loss* µm/1000 cycles
Electroless nickel as-plated	5	5000	CS-10	9.1	0.42
	4	2500	CS-17	20.6	0.95
	1	5000	CS-17	14.6	0.67
Electroless nickel after 1 hr at 400°C	5	5000	CS-10	7.6	0.35
	4	2500	CS-17	17.0	0.78
	1	5000	CS-17	13.5	0.62
Chromium	5	5000	CS-10	2.0	0.10
	2	2500	CS-17	8.4	0.43
Chromium after 1 hr at 400°C	5	5000	CS-10	3.0	0.15

*1000g load

TABLE 2

COMPOSITE ELECTROLESS NICKEL TABER WEAR RESISTANCE [8]

Particle		Deposit Taber Wear Index	
	Hardness Knoop	As-Plated	Heat Treated°
None	--	18	8
+ Graphite	Soft	15	8
+ Chromium Carbide	1735	8	2
+ Tungsten Carbide	2080	3	2
+ Aluminum Oxide	2100	10	5
+ Titanium Carbide	2470	3	2
+ Silicon Carbide	2500	3	2
+ Boron Carbide	2800	2	1
+ Diamond (Du Pont)	7000 Est.	2	2
Aluminum Hardcoat	--	2	---
Hard Chromium	1000	3	--

Taber Wear Index = weight loss mg/1000 cycles
(Average of 5000 cycles, CS-10 wheels — 1000g load)
°10-16 hr. at 290°C (554°F)

TABLE 3

Falex Wear Tests [9]

V-Blocks		Rotating Pins			
Surface	Hardness	Deposit	Heat Treat °C/hrs.	Hardness	Wear mg
SAE 1141	HRB-100	SAE 3140	--	HRB-86	21.0
SAE 1141	HRB-100	Bright Chromium	288/3	HV 1000	1.5
SAE 1141	HRB-100	Electroless Nickel$^{\Delta}$	345/2	HK 850	0.5
Bright Chromium	HV_{100}1000	Bright Chromium$^{\square}$	288/3	HV_{100}1000	7.3
Electroless Nickel	HK 850	Electroless Nickel$^{\Delta}$	345/2	HK 850	1.3

Load — 200 lb.
Duration — 11 min.
Lubrication — Synthetic oil.

$^{\square}$Thickness — 50 μm
$^{\Delta}$Thickness — 38 μm

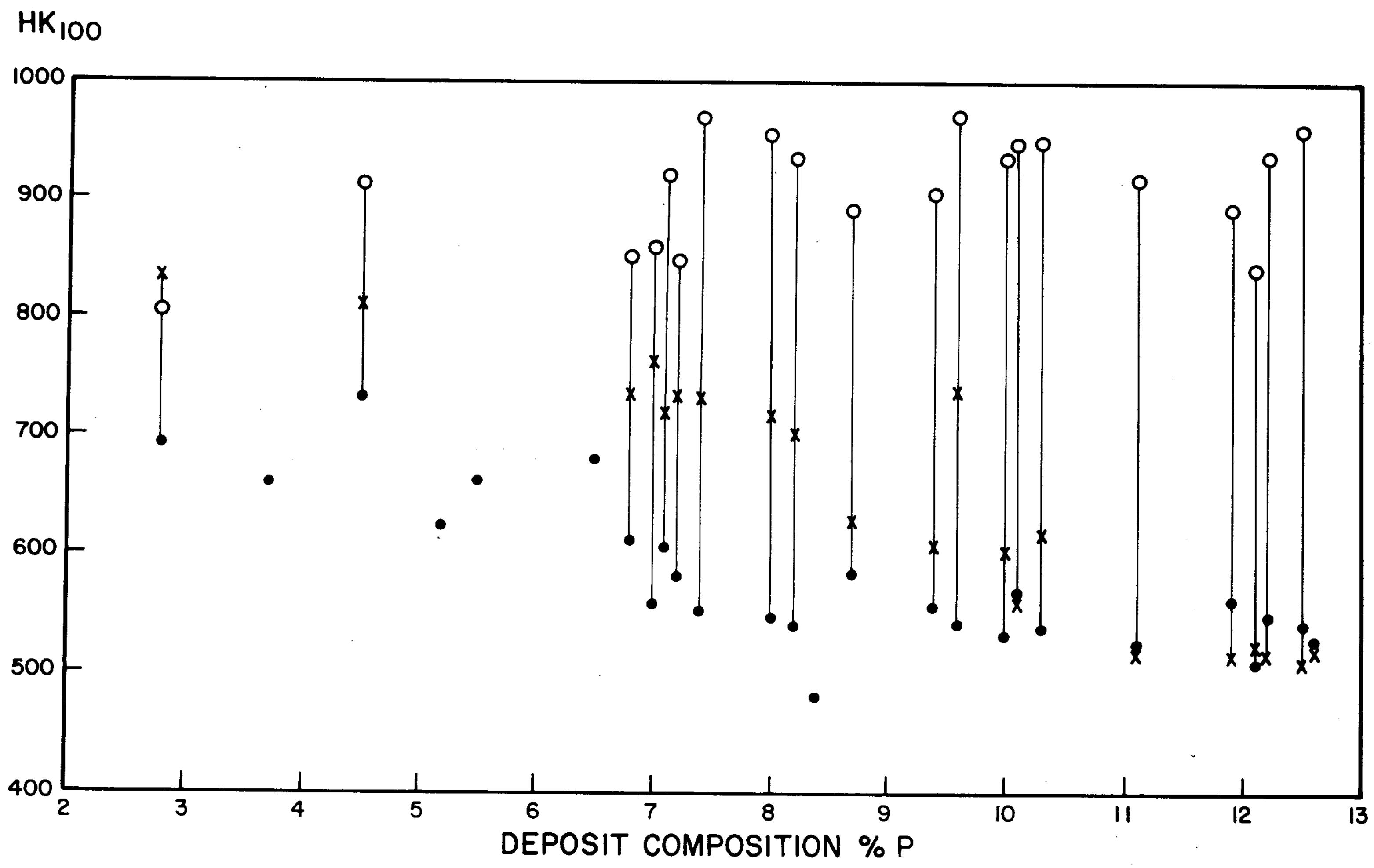

Figure 1. Hardness of Ni-P Alloy
● as-plated
x after 8 hours at 200°C
o after 1/2 hour at 400°C

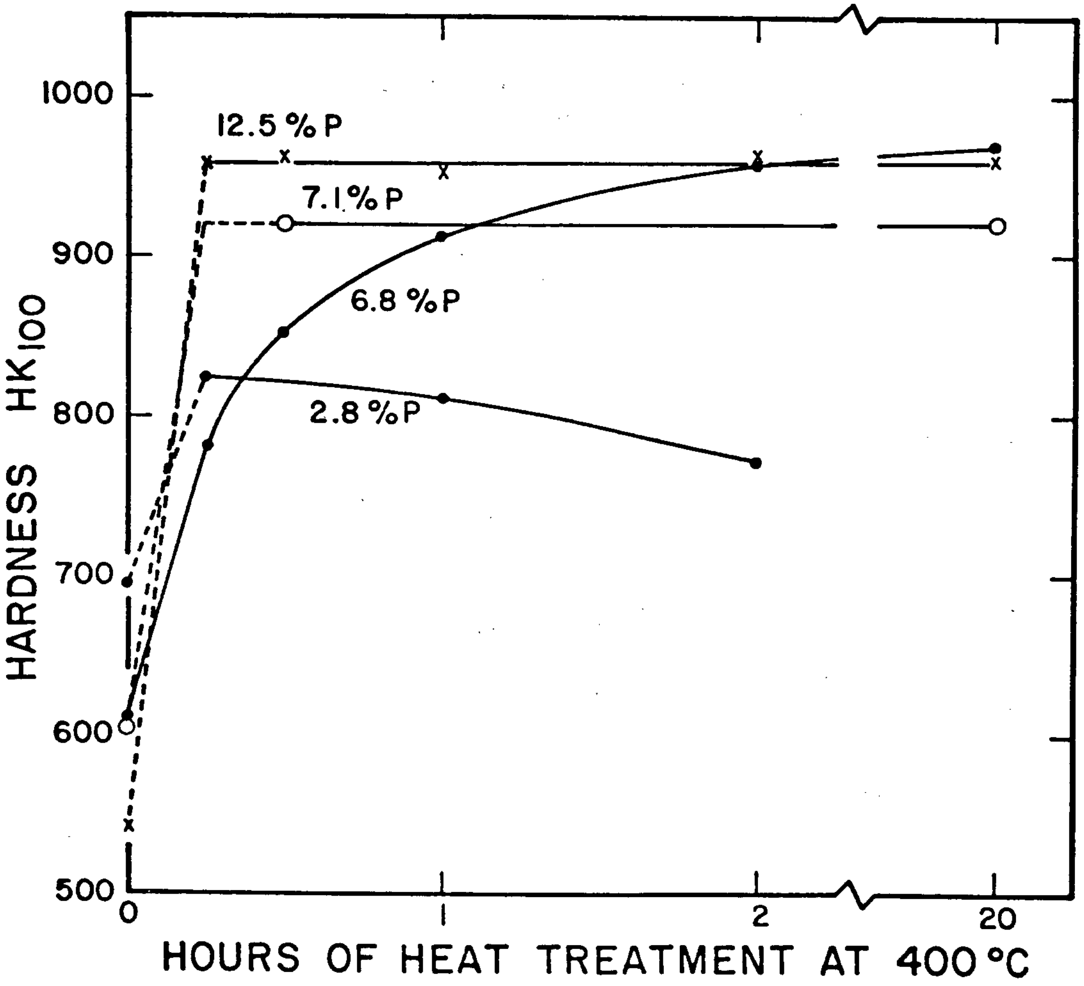

Figure 2. Effect of duration of heat treatment at 400°C on hardness.

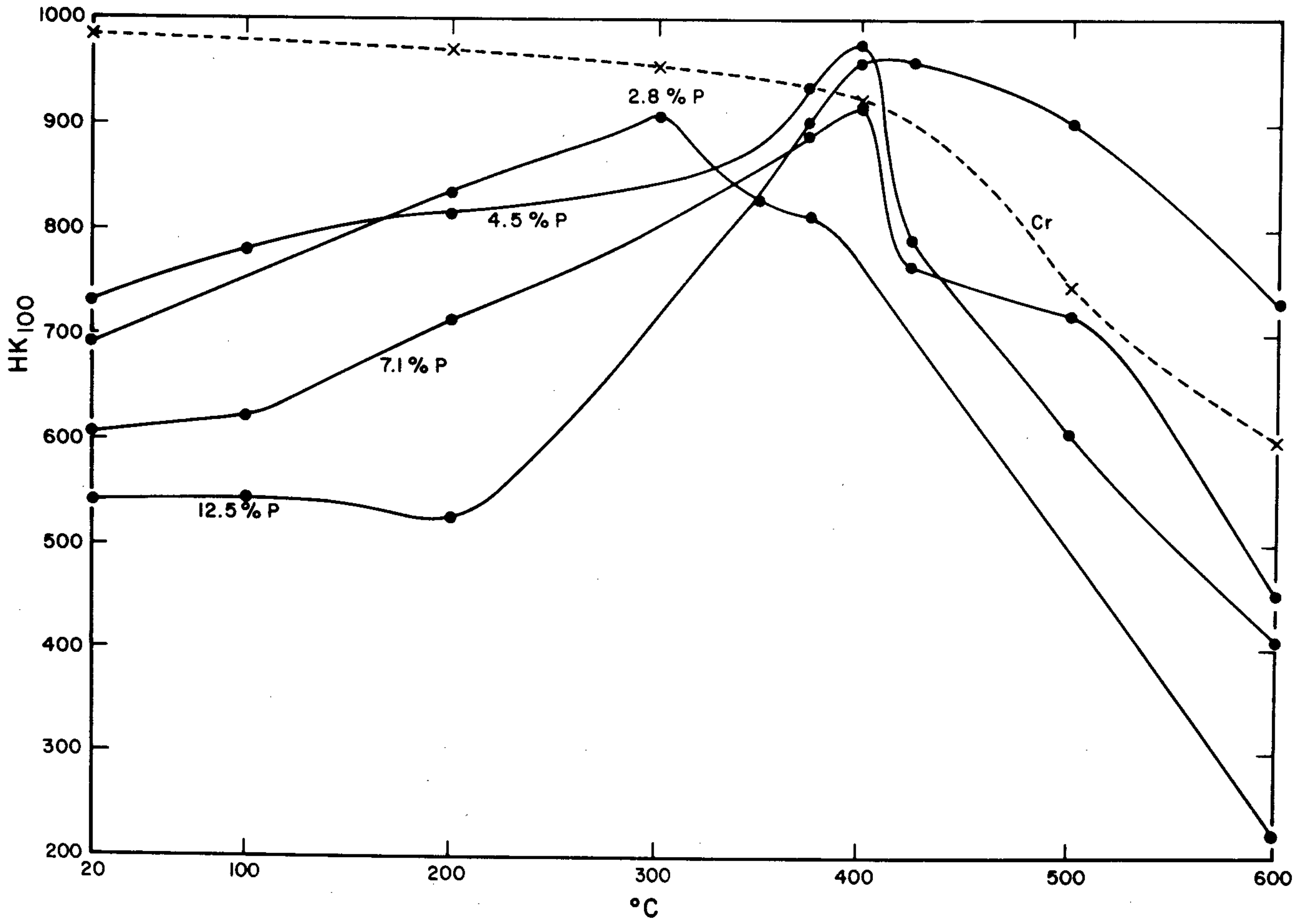

Figure 3. Hardness vs. temperature of heat treatment.
24 hours at 100°C and 200°C.
20 hours at 300°C - 600°C.
1 hour for Chromium at all temperatures.

DISCUSSION

R. E. Maringer, Battelle, Columbus Laboratories: You stated that the heat treatment of the electroless nickel plate is sometimes called a stress relief treatment. I believe that that is wrong. We did some experiments some years ago in which we took a thin sheet of prepared beryllium and plated Kanigen electroless nickel on it. Our purpose was to compare thermal expansion coefficients, but we found that after it came out of the plating bath, it stayed perfectly straight. As soon as it was heat treated, it deformed. Instead of stress relieving the material, the heat treatment built up the stress. For most applications this doesn't make any difference.

C. E. Johnson: Were you heat treating in air?

R. E. Maringer: I believe so, although it may have been in argon.

C. E. Johnson: If the heat treating atmosphere was hydrogen, I am sure the stresses would increase. My statement about stress relieving referred to the high phosphorus alloy.

A. J. Babecki, NASA, Goddard Space Flight Center: At what phosphorus content is there a change in the ferromagnetism of the nickel in nickel-phosphorus alloys?

C. E. Johnson: Above about 8% phosphorus, the ferromagnetism of the nickel diminishes significantly. After heat treating, the alloys we examined become ferromagnetic, regardless of the phosphorus content.

A. J. Babecki: Can the adhesion of the as-deposited plating be improved by heat treatment?

C. E. Johnson: Adhesion does increase with heat treatment.

CHROMIUM DEPOSIT STRUCTURE HAS A PROFOUND INFLUENCE ON PROPERTIES

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Abstract

The optimum structure of chromium electroplate should be specified for each individual application. Crack-free chromium supplies good corrosion protection and good wear resistance for some applications. Customary hard chromium is preferred for resisting wear in other applications. High-crack-count chromium is mandatory for avoiding harmful effects on the fatigue strength of high-strength steel substrates. Each of these structures can be deposited by a new process that is 25 to 50 times faster than the customary rate for chromium plating.

Keywords: Corrosion; crack-free chromium; electroplating; fast plating; fatigue strength; grinding; hardness; stress; tensile strength; wear

Introduction

The chief functional uses for chromium electroplate involve resistance to wear, erosion, friction or galling, and protection of substrate metals from high-temperature oxidation or corrosion at ambient temperatures. For these purposes, chromium coatings characterized by a hardness of 800 to 1100 VHN and a crack count of 10 to 100 per cm (25 to 250 per inch) are usually applied on coating and drying rolls, cutting tools, engine cylinders, extrusion dies, glass forming molds, gun-tube bores, landing gear cylinders, piston rings, pump shafts, rods, and many other products. Thickness ranges from 2.5 to > 250 μm (0.1 to > 10 mils). The annual added-on value of these products by chromium plating is estimated at $250,000,000 to $500,000,000.

Chromium plate with a network of cracks numbering 5 to 100 per cm as intersects to any straight line on the surface is the most common of three alternative types because it was the first type developed commercially and is currently the only type available from the large majority of vendors equipped for chromium plating. These vendors and their customers have been neglectful of the potential advantages of two other types, which are termed (1) crack-free chromium and (2) high-crack-count chromium (> 250 cracks/cm or 650 cracks/inch).

Properties and Structure

Table 1 summarizes property data for three types of chromium. Crack-free chromium is characterized by a high density, a relatively low concentration of oxides (0.05 to 0.2 percent oxygen), and a high tensile strength. Conventional and high-crack-count chromium exhibit a low density, a high concentration of oxides (0.4 to 0.88 percent oxygen), and a low tensile strength.

Crack-free deposits are softer than conventional or high-crack-count chromium. Soft deposits exhibited a hexagonal structure, whereas chromium with a hardness of 1000 kg/mm^2 or more exhibited a body-centered cubic structure.(3) A mixture of bcc and hexagonal chromium was observed for deposits of intermediate hardness.

Some investigators have reported that wear resistance is independent of hardness. Others observed that soft deposits showed less wear than hard deposits, but a few reported improved resistance to wear or scratching when hardness was increased to about 1050 kg/mm^2.(2) During a recent study, crack-free chromium with a hardness of only 725 kg/mm^2, which was deposited on the bore surfaces of cylinders evaluated in an air conditioner assembly, showed only one-third as much wear as conventional chromium with a hardness of 875 to 925 kg/mm^2.(4) Phosphated steel piston rings were run in the chromium-plated, aluminum cylinders.

Applications

Where corrosion resistance is of primary importance, consideration should be given to crack-free chromium in preference to conventional deposits. Available data show that crack-free chromium furnishes better protection against humid, corrosion environments. Crack-free chromium also should be used for high-temperature service, particularly when parts such as molds for fabricating glassware are thermally cycled.

For good resistance to wear, either crack-free or conventional chromium may be satisfactory. The best kind of chromium for maximum wear resistance in a specific application can only be determined by making comparative tests. The nature of mating surface and its finish, the chromium surface finish, and lubrication conditions appear to have far more influence on wear than the hardness of the deposit. A lightly honed crack-free chromium with a micronodular surface (20 to 40 microinches) is better than a ground and lapped surface for some purposes.

To avoid the catastrophic consequences of structural damage during grinding, a low wheel speed, a relatively low pressure, and good lubrication are very important. A lightly honed, thin deposit (0.002 to 0.004 inch) may be better than a thicker, surface-ground deposit, and less costly. Failures attributable to surface grinding of 0.006 to 0.015-inch-thick deposits occur frequently. Chromium thickness on

Table 1. Properties of Electroplated Chromium(1,2)

Type of Chromium	Density, g/cm^3	Hardness kg/mm^2	Tensile Strength, kg/mm^2	Stress, kg/mm^2 (a)	Change in Fatigue Strength of Chromium Plated Steel, Percent (b)
Crack free	7.13 - 7.17	325 - 750	35 - 70	1.4 - 4.2	No data
Conventional (10 - 100 cracks/cm)	7.01 - 7.05	875 - 1130	15 - 17	7.7 - 42	-22 - -73
High crack count (>250 cracks/cm)	7.01 - 7.05	920 - 1130	~ 15	-1.2 - -12	-10 - 4

(a) A negative sign indicates compressive stress.

(b) A negative sign indicates a loss in fatigue strength for chromium-plated steel relative to the unplated steel.

cutting tools is sometimes limited to only 2.5 or 5 μm (0.0001 or 0.0002 inch) to eliminate the need for any surface finishing after plating.

Conventional chromium deposits are stressed in tension and reduce the fatigue strength of steel (and aluminum alloy) substrates, as shown in Table 1. The reduction in fatigue strength depends on the stress level in the chromium, and the fatigue limit of the steel.(5) A high stress (20 to 42 kg/mm^2) in chromium deposited on a high-strength steel (112 to 148 kg/mm^2) reduces fatigue strength as much as 65 to 73 percent.(6,7) On the other hand, high-crack-count chromium exhibits a compressive stress (-1.2 to -12 kg/mm^2) and has little or no harmful influence on the fatigue strength of the substrate. Thus components subjected to fatigue during service should be plated with high-crack-count chromium.

Plating Procedures

At least three procedures for depositing crack-free chromium have been developed. One uses 2.5 M chromic acid solutions containing 2.0 to 2.5 g/1 of sulfuric acid and maintained at 80 to 85 C.(1) Another uses 60-cycle pulsating current.(8) The third deposits crack-free chromium at a rate of approximately 20 μm/min, which is approximately 60 times faster than the usual rate for plating chromium.(9) This process uses high solution velocity (6 to 8 ft/sec) past cathode surfaces or a high rate of cathode rotation to sustain high current densities of 3 to 6 amp/cm^2 (20 to 40 amp/in^2), which is 10 to 15 times higher than normal. Cathode efficiency with these conditions is 45 to 55 percent. By comparison, crack-free or cracked chromium is deposited conventionally with an efficiency of 10 to 15 percent.

Conventional chromium with 5 to 100 cracks/cm is usually deposited in 1.5 to 3 M chromic acid solutions maintained at 45 to 55 C at current densities of 0.12 to 0.4 amp/cm^2 (0.8 to 2.6 amp/in^2). With a temperature of 50 C, variations in current density from 0.2 to 0.8 amp/cm^2 or shifts in the concentration of chromic acid have only a slight effect on hardness.(1) Sulfuric acid concentration is usually 1 percent of the chromic acid concentration unless fluosilicate ions are added to replace a part of the sulfate ions. Deposits from solutions containing fluosilicate ions are slightly harder than chromium deposited in chromic-sulfuric solutions.(2)

Compressively stressed chromium with a high crack count is deposited in 40 C, 2.5 M chromic acid solutions at a current density of 0.2 amp/cm^2.(6,10) A higher current density (0.4 amp/cm^2) can be used to deposit this type of chromium in 40 C chromic-sulfuric solutions(10) or 43 C chromic-sulfuric-fluosilicate solutions.(11) A fast plating method also has been developed for plating high-crack-count chromium.

Fast Plating Processes

Fast plating procedures were developed recently at Battelle-Columbus for depositing each of the three types of structures described in this paper. Table 2 summarizes the conditions. Deposits obtained at high current densities with fast solution flow (1.25 to 1.5 m/sec) were similar in structure and hardness to deposits obtained on piston rods rotated at a high rate (1.25 to 1.5 m/sec).

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Table 2. Fast Rate Procedures for Chromium Plating[a]

Type of Chromium	Plating Solution	Temp., C	Current Density, amp/cm^2	Cathode Efficiency, percent	Plating Rate, µm/min	Hardness kg/mm^2
Crack free	2.5 M CrO_3 0.025 M H_2SO_4	50	3.2-6.2	45-55	10-20	720-840
Low crack count (75-95 cracks/cm)	2.5 M CrO_3 0.025 M H_2SO_4	75	3.7	20	4.5	920-1030
High crack count (250 cracks/cm)	2.4 M CrO_3 0.03 M H_2SiF_6 0.02 M H_2SO_4	75	3.7	24	5.4	920-1020

(a) The solution flow rate or rate of mechanical rotation ranged from 1.25 to 1.5 m/sec.

DISCUSSION

E. Rabinowicz, Massachusetts Institute of Technology: I have only user's experience with chrome plating. But from what people tell me, the reliability of chrome plating is notoriously low. There might be a commercial outfit that does good chrome plating for you for years at a time, and then one week suddenly everything goes bad. Is that your experience?

W. H. Safranek: I have heard of a few similar cases. Chromium plating is very highly dependent upon the quality of the substrate, and this is one thing that is very rarely kept under control.

A. J. Babecki, NASA, Goddard Space Flight Center: When electrodepositing chromium, do you use the same intermediate layer to get good adhesion on different substrates such as cast iron, steel or aluminum?

W. H. Safranek: In the case of cast iron piston rings, the first operation is wet blasting. Then they are vapor degreased. Next they are cathodically activated at low voltage for a few seconds. Then they are plated. For high silicon content aluminum, we use an etching type alkaline cleaner in order to obtain a controlled micro-roughness on the surface. This operation is followed by rinsing, nitric acid desmutting, rinsing and zincate. Then, the material is chromium plated.

F. K. Sautter, Watervliet Arsenal: What is the residual stress in the crack-free chromium?

W. H. Safranek: Published data for tensile stress in a crack-free type chromium ranges from 1.4 to 4.2 kg/mm^2.

F. K. Sautter: You mentioned that crack-free chromium was particularly good for high temperature applications. It has been our experience that crack-free chromium cracks as soon as heat is applied.

W. H. Safranek: This happens in some cases. The magnitude of the difference in coefficients of expansion between the chromium and the substrate determine whether the plating will crack. Our experience for the crack-free type chromium relates primarily to its use in the glass mold forming application, and in that application it did very well. These are low chromium steel molds and the coefficients of expansion for the steel and the chromium are similar.

W. G. Thelen, David Taylor Naval Ship Research & Development Center: There are proprietary processes that supposedly seal the cracks in chromium with chromium oxide or other ceramics. Do these have any effect on wear in the plucking or scratching mode such as in a cylinder with piston rings?

W. H. Safranek: I can't really answer the question directly. Certainly they could have an effect and it might be a factor in accounting for inconsistencies in reports relating hardness to wear for a conventional type chromium--a low-crack-count type chromium. In some cases there could have been higher amounts of oxides retained in the cracks than in other cases. But I don't know anybody who has studied this particular aspect in any detail.

R. M. Thomson, National Bureau of Standards: I'm a little puzzled that you have not seized on the cracks as the primary characteristic of the quality of the chromium plate. One would think that the cracks would be sites for corrosive attack on the underlying substrate and that also they would be important stress raisers for the underlying substrate where fatigue might initiate. What are the criteria used to determine the quality of the plated product?

W. H. Safranek: Well, I didn't entirely neglect these subjects. I did point out that the crack-free type chromium does not provide paths for corrosive elements to get to the substrate. The literature does not contain a great deal of data demonstrating that the crack-free type chromium is very much better than a low-crack-count chromium. But we have quite a bit of data at Battelle. For chromium deposits on steel, in the 1/2 to 1 1/2 mil thickness range, the crack-free chromium is very much superior to the low-crack-count chromium. You are quite right about the effect of the cracks in the chromium being sites for fatigue cracks to start in the steel and this is exactly what happens with low-crack-count chromium. Now, when the crack-count goes up to 250 cracks per centimeter or more, the load is spread out over so many potential sites that the effect on failure of the steel no longer exists, or at least does not exist to the same degree. That is why the high-crack-count chromium causes no large reduction in the fatigue strength of the substrate.

G. H. Kitchen, Bell Telephone Laboratories: There are companies which supply chromium plated coatings in which the cracks are filled with molybdenum disulfide, graphite, Teflon, etc. Purportedly they heat treat the coatings and seal the solid lubricants in the chromium surface. Can you comment on that?

W. H. Safranek: Actually, I was not aware of it, so I can't comment. We have made some pretty sophisticated studies of the width of these cracks in the as-plated material. They are about 2 to 3 μin wide. I find it hard to believe that you can get very much material (lubricant) into these narrow cracks.

PLATED COATINGS FOR ELECTRIC CONTACTS

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ABSTRACT

Electrical contacts, such as those in separable connectors, are required to have low and stable contact resistance. For high reliability connector applications in low voltage circuits, gold is the preferred contact material because of its chemical inertness. Recent studies have shown that the most common gold electrodeposits, which contain cobalt or nickel as hardeners, are complex materials, containing 10% or more by volume of organic polymers, potassium compounds, and other substances. Failure in service can occur if the deposit is porous, since films may form on the surface by reaction of the base substrate metal with air pollutants at pore sites. The use of underplatings and smooth substrates can reduce the thickness of gold required for low porosity; inhibitor coatings may suppress corrosion reactions, and galvanically inert substrates can even eliminate pore corrosion. Wear-induced porosity is also a failure process, and contact lubrication is effective in its control. Degradation by diffusion of substrate metals, such as copper, to the surface where films form is controlled by barriers, like nickel underplate. The high cost of gold has led to the search for alternate contact materials. Palladium plate and the soft base metals, tin and solder plate, have achieved limited acceptance.

Key words: Contact lubrication; corrosion inhibitors; electrical contacts; gold plate; palladium; polymer in gold; porosity in gold; solder plate; tin-nickle alloy; tin plate; underplatings for gold; wear of gold.

Plated metal coatings are widely used on the contacts of current-carrying devices whose function it is to allow a circuit to be disconnected and reengaged, or to enable one member to be moved while in continuous contact with another. Such devices include connectors, slip rings, and switches. When voltage and current levels are low and high reliability is required, gold and some other noble metals, e.g., alloys high in gold content and rhodium plate, have become nearly universal as the contact coating. We describe one of these devices, the separable electronic connector, in some detail: design practices, materials selection, and its mechanisms of contact failure. We then briefly consider some lower cost metals that are candidate replacements for gold.

It is of interest to note that the value of separable electronic connectors manufactured annually in the United States is 0.5 billion dollars. About 1 million troy ounces of gold are used in these devices and on the contacts of printed circuit boards. The manufacture and servicing of modern telecommunications, computer, and electronic instruments would be impossible without connectors.

Design Factors Connectors typically have several to 100 or more contacts separated by dielectric material, each joined at their back ends to a conductor by solder, wire wrapping, crimping, or welding. They usually are engaged by a wiping action, although butt (nonsliding) contacts are also used. Typical designs include the pin in split tine socket, the printed circuit board edge connector having cantilever contacts which deflect when pushed over the board contacts, and forked contacts that spread during engagement by flat blade members. Substrates must be good conductors, and some of them that also are spring materials include copper-nickel-tin alloys, phosphor bronze, and beryllium copper. Copper, brass, and nickel are other widely used substrate metals.

Design normal loads for connector contacts range from ca. 50-300g. Contact geometries usually have single- or multi-point or line configurations. These devices are required to carry current with low and stable resistance, often limited to a few milliohms, for 5-40 years. The required numbers of engagements and rematings is usually in the range, 50-500. Service environments can be benign, as in air conditioned offices, or aggressive, such as in equipment that serves in sheltered out-of-doors locations, e.g., in aircraft. Ambient temperatures may range from subzero to 150°C or more, depending on the application. Above all, high reliability is necessary, with contact failure rates often having to be no greater than 10, or even 1, contact in 10^9 operating hours (1140 years). Connectors have more than 1 contact, and, therefore, would experience higher failure rates than this. A failure is an exceedance of contact resistance beyond some value dependent on the circuit in which the connector is used.

Contact Materials The popularity of gold, the most common contact material, originates in its nobility, for if insulating surface films form, contact resistance could increase. Gold is used mainly as electrodeposits on both members, or as a plating vs. wrought gold weldments or claddings on the opposite member. Wrought golds may be pure or be alloyed with other metals, such as silver.

Pure gold electrodeposits are unsatisfactory because of poor wearing characteristics and high friction on engagement. In practice, from ca. 0.1-0.5% of cobalt or nickel, is codeposited with gold to give a two to four fold increase in hardness, to ca. 140-225 kg/mm^2, and improved durability. Deposit thicknesses range from 0.5-5 micrometers.

Structure and Composition of Hard Gold Electrodeposits In the past few years it has been found that gold electrodeposits are complex materials, containing (a) C, N, and O polymeric substances[2,3] that originate in $KAu(CN)_2$ from the plating bath, (b) usually potassium in unknown form, but conjectured to be occluded plating solution and (c) hydrogen in minute voids, a few tens of angstroms across. The density of these golds may be 90% or less than that of pure gold. The hardener metal, Co or Ni, is mainly in solid solution and is believed by some to be partly combined with the organic polymers. Typical golds have ca. 0.2% each of Co or Ni, C, and K[4]. Metallographic examination reveals that hard gold deposits have laminar structures. The deposits are brittle, with elongations below 1%, and may be so internally stressed that when thick, i.e., 10 micrometers, they may spontaneously crack. Observation[4] of fracture edges of gold electrodeposits with the scanning electron microscope reveals the occluded polymer. On dissolving the gold in aqua regia, the polymer (or reaction product of polymer with aqua regia) can be isolated as a porous film. Transmission electron microscopic examination[5] of thinned gold shows them to have a fine structure with polymer "molecules" about 25 Å in size. Secondary ion mass spectrometric analysis[6] of a polymer-containing gold identified fragments of $AuNCN^+$, Au^+, AuC^+, AuN_2^+, $Au(CN)_2^-$, Au^-, $AuCN^-$, AuC_2N^-, and CN^-.

Undoubtedly, the unique compositions, structures, and properties of gold platings contribute to their good wear resistance, better than that of wrought golds having the same hardness. But rigorously cleaned hard gold electrodeposits are still poor wearing, for the codeposited substances are not solid lubricants.[7]

Porosity in Gold The chief determinant of the thickness of gold which is selected for contact use is its porosity. It is impossible to plate gold on practical substrates much less than 1-3 micrometers thick without it having a large number of submicroscopic voids that expose the substrate to the atmosphere. Because of the galvanic activity of the large area of gold in contact with exposed base metal, corrosion of the latter can occur at pore sites in humid, polluted atmospheres to produce surfaces spotted with corrosion product. The significance of porosity in electrodeposits on contacts is controversial. On the one hand, the high cost of gold makes it imperative to keep to a minimum the amount that is used, and thin gold tends to be porous. The cost trade-offs between having a thick deposit which can provide corrosion resistance, and the cost of a failure because of the susceptibility of the contact to degrade by film formation in the particular environment in which the connector serves are largely unknown. Resistance changes attributable to porosity are difficult to determine in the field because of their statistical nature, and there is little confidence that they can be realistically simulated in the laboratory by accelerated environmental testing.

A more positive approach is to learn how to reduce porosity by improved substrate preparation and gold plating techniques, and toward this end it has been shown that smooth substrates and underplatings may permit thinner deposits to be used. Other ways to reduce the susceptibility of porous golds to corrode in severe atmospheres are the use of post plating corrosion inhibiting treatments, such as coating with very thin films of alkoyl sarcosinates, and galvanically inert underplatings, like tin nickel alloy.

Wear of Gold The limited durability of gold is a restriction to its use. Gold wears by prow formation. Many gold contacts are unlubricated, but apparently are successful because adventitious contaminants from the atmosphere collect on the surface in sufficient amount to provide a lubricating function.[7] Conservative practice, however, involves the application of these lubricant films to contacts, either liquids or plastic solids. A widely used liquid lubricant is a mixture of 5-ring polyphenylethers, and a common solid lubricant is microcrystalline wax. These are applied at coverages of ca. 10-30 µg per cm^2 of surface. Liquids are less dependent than solids on surface roughness for effectiveness. Roughness provides a reservoir for the solid which is replenished as the surface becomes burnished during use. The polyphenylethers do not wet gold well, having contact angles of 20-25°, and thus their good lubricity is surprising. Nonwetting is desirable to minimize creep with subsequent lubricant starvation.

Diffusion Degradation Another consideration in the use of gold platings is the possibility of film formation due to diffusion to the surface of codeposited base hardener metals or of substrate elements where they can form insulating films. These processes occur slowly at room temperature, and it is unclear whether they are significant in degrading the contact. But at elevated temperature, say at 125°C, diffusion processes are rapid. Nickel underplate is an effective diffusion barrier for substrate metals. The use of minimal amounts of the hardener and care in maintaining low levels of metal impurities in the gold is an effective way to minimize this failure process.

Alternate Materials[8] There is considerable interest in finding alternate materials for gold. This work parallels the growing use of selective coating techniques for cost reduction which apply gold locally to the contact site, i.e., not to nonfunctional adjacent surfaces. Palladium has proven itself to be a viable alternative in some applications. The contact must be designed to not permit small movements of the mated contacts, because this would allow palladium to form insulating friction polymers. An opposing member of gold also reduces the amount of polymer that is formed. Palladium tarnishes at high relative humidity in atmospheres polluted with sulfur dioxide. Otherwise, considerations of porosity and contact lubrication apply to palladium as with gold.

The other materials which are making some inroad into gold as a contact material are the soft base metals, tin and solder plate. They are relatively corrosion resistant, but, more importantly, can tolerate some film formation since their plasticity allows the films to be easily fractured on making contact and low resistance to be attained. On the other hand, they have numerous deficiencies, listed below:

Problem	Possible Solution
1.. Whiskering (for tin).	1. Alloy the tin with another metal; reflowing the tin.
2. Excessive wear.	2. Lubricate; avoid applications requiring many cycles of mating.
3. Fretting corrosion due to vibration or differential thermal expansion of the contacts.	3. Design for rigid contact; coat contact with lubricant sealants.
4. Creep.	4. Restrict use to room temperature or below; avoid thick platings and sharp contacts.
5. Cold welding.	5. Lubricate; restrict use to room temperature or below.
6. Intermetallic compound formation at the interface with copper or nickel substrates.	6. Restrict use to room temperature or less.
7. Formation of insulating films by corrosion.	7. Design for contact loads above 200g (with blunt contact geometries); use corrosion inhibiting surface treatments.

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DISCUSSION

A. J. Babecki, NASA, Goddard Space Flight Center: How does the ductility of the tin-nickel compound compare with that of electroless nickel?

M. Antler: It is just as brittle.

S. Jahanmir, Massachusetts Institute of Technology: Has any work been done to relate porosity to thickness in various platings such as nickel, silver, cadmium, etc.?

M. Antler: You can get any porosity you want. Porosity is caused by occluded nonmetallic impurities that usually cannot be removed from substrate surfaces. These are called pore precursors. It is the quality of the substrate surface more than anything else which determines the porosity of a plating.

S. Jahanmir: With the same substrate and the same plating process, would the porosity increase with the plate thickness, say for nickel?

M. Antler: We would expect that the porosity would decrease with increasing thickness of nickel on a given substrate.

H. Ravner, Naval Research Laboratory: Have you noticed any chemical degradation of the polyphenyl ethers after use on these contacts?

M. Antler: I have not noticed any. The reason they were chosen for contact application, apart from the fact that they are good lubricants, is that they have low volatility and they are chemically stable.

COMPATIBILITY EFFECTS WHEN SOFT METALS ARE USED AS SOLID LUBRICANTS

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Abstract

The purpose of this study has been to test, mainly by means of metal cutting experiments, the extent to which the wear life of electroplated soft metal film coatings is governed by the metallurgical compatibility between the coating and the other sliding surface. Experiments have been carried out using hard steel tools coated with various soft metals, and cutting a number of different workpiece metals. Two different configurations were used, namely milling and shaping, and in some cases the lubricant was only applied once at the beginning of the test, while in other cases it was reapplied continuously. It was found that long tool life resulted when the soft metal had low metallurgical compatibility with the workpiece material but not otherwise. The other parameter investigated, namely relative mechanical strength between film and substrate was found to be much less significant. This is in contrast to the case of the friction coefficient, which has been found to be greatly influenced by the mechanical strength ratio.

Introduction

Soft metals are among the oldest and best established types of solid lubricants. As it happens, they do not at present enjoy wide usage as solid lubricants, since the friction and wear tend to be relatively high in comparison to the layer lattice substances (1). However, they are used to some extent in high vacuum applications, in which case many layer lattice lubricants are unsuitable (2). Furthermore, they have been found to be promising in certain metal cutting situations, in which case good performance at high temperatures and pressures and the ability to re-form the solid lubricant continuously during sliding are important assets (3). The recently developed technique of ion plating, which allows soft metals to be deposited in such a way as to avoid a sharp interface between the soft metal and its substrate, has also stimulated interest in the tribological behavior of soft metal films (4, 5).

It is generally realized that, in order to function as a solid lubricant, a metal film should be softer than the substrate on which it is deposited, should have a suitable thickness, and adhere well to the substrate (6). In this paper, we hope to examine one additional factor which makes one soft metal more suitable than another, when used as a solid lubricant, namely the factor of compatibility. The experimental testing has been confined almost exclusively to the use of the lubricants in metal cutting applications, but it is believed that the results are also applicable to other sliding situations.

The concept of compatibility assumes that if two metals sliding against each other have low metallurgical compatibility against each other, as evidenced by low solid solubility and poor liquid miscibility, the sliding characteristics will be good, (i.e. low friction, low wear, and good resistance to seizure will prevail). If on the other hand the surfaces have high metallurgical compatibility the sliding will be poor. This compatibility expresses the basic attraction between atoms of the sliding materials, and is best determined by a systematic evaluation of binary phase diagrams (7).

To show the application of these compatibility ratings to a metal cutting operation, consider the case of a nickel workpiece being cut by a steel tool, which may be assumed to be essentially iron. Examination of a compatibility chart (7) indicates that nickel is fully compatible against iron, and thus the nickel-steel combination is expected to give high friction and wear. Now consider some common soft metals, for example, lead, tin, cadmium, zinc, copper and silver which might be considered for application to the steel tool in order to function as solid lubricants. Assuming that the soft metal adheres to the steel tool, the sliding interface will consist of the soft metal sliding against nickel, and the compatibilities of these combinations become relevant.

On looking at a compatibility chart (7) it may be seen that copper and zinc are fully compatible against nickel, while lead and silver are incompatible, and tin and cadmium are partially compatible. Thus, the compatibility factors suggest that silver and lead are specially good soft metal coatings for a steel tool to be used against nickel because they greatly improve the compatibility rating of the sliding combination, while copper and zinc are less suitable, because they maintain the original unsatisfactory compatibility rating. The other two metals should fall somewhere in between.

Based on published data in the literature, the above argument should be regarded as a theoretical speculation, because there has been no systematic evaluation of soft metal coatings to see if indeed their wear properties are governed by compatibility relationships. Accordingly, a series of studies of various metal cutting operations has been undertaken in which soft metal coatings were used, and their influence on the cutting process was measured.

Apparatus

The experiments to assess the soft metal lubricants were carried out using two different cutting geometries, namely milling and shaping. Both continuously formed metal films, and films applied only once at the beginning of the tests were used. Fortunately, the results obtained with the two tests agreed quite well with each other and thus proved to be alternative ways of studying the lubricating ability of thin metal films.

The milling experiments were carried out in a milling machine using a standard end mill. A continuous jet of electrolyte from a positively charged nozzle was directed at the flutes of the negatively charged end mill as they emerged from the cutting zone and in this way the soft metal lubricant film was continuously replated (3).

The shaping tests were carried out in a horizontal milling machine, using a high-speed-steel tool. The tool was fixed to the machine overarms and the workpiece was mounted in a dynamometer bolted to the milling machine table. The horizontal feed was used to pass the workpiece under the tool, thus making a cut. Horizontal and vertical cutting forces were recorded, and wearing out of the lubricating film was detected by an increase in the cutting forces and by a reduction in curl of the chips formed.

Materials used

Besides testing the compatibility criterion, one of the purposes of the study was to find suitable lubricants for machining difficult to machine materials, such as titanium alloys and nickel-based turbine alloys and hence these materials were included in the testing program. Another purpose was to see if the performance of the soft metal coatings was determined by other criteria such as relative mechanical strength, and in order to extend the hardness range of the materials used some tests were also carried out with pure nickel and with an aluminum alloy.

The soft metal lubricants used were lead, tin, cadmium, zinc, silver and copper, and in addition a few tests were carried out using iron and cobalt films. All these metals were deposited by electroplating techniques. For most of the workpiece materials, the plated metals covered a wide range of compatibilities, ranging all the way from fully compatible to fully incompatible. However, in the case of the titanium the range of compatibilities tested was narrower, since no metal is fully incompatible against titanium.

In all the experimental tests, an attempt was made to keep the thickness of the electroplated soft metal layer constant for all the tests in that series, and reasonably close (within a factor of three) to a thickness value of 10^{-3} mm. This 10^{-3} mm represents the thickness value which is generally found to give the lowest value of friction coefficient (1).

Results

A. Lubricant reapplied continuously

In these tests, the performance of the lubricant was determined by the length of cut which could be undertaken before a sufficiently large wear land was found on the tool. Thus, figure 1 shows the results obtained in machining a nickel-based turbine alloy. On the horizontal axis is plotted the length of cutting required to wear out each tool (wear out being defined as the formation of a wear land of length .023 mm), while on the vertical axis the degree of compatibility of the soft metal lubricant against nickel is indicated. As will be seen there is a very good correlation between length of cut and degree of incompatibility.

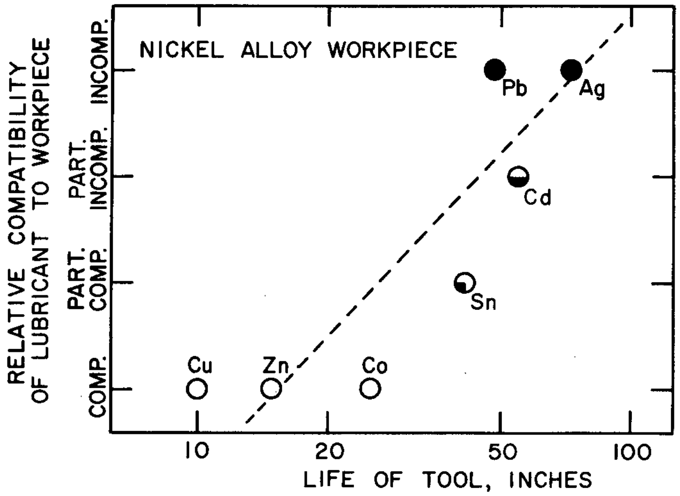

Fig. 1 Life of tool plotted against relative compatibility of the soft metal lubricant against nickel. The rank correlation coefficient for these data is +0.88.

Perhaps the best way of reducing this diagram to a single number is by computing the rank correlation coefficient r_{rank} between life and compatibility, as has been done in an earlier study (7). For the data shown in figure 1, r_{rank} is found to be +0.88 (on a scale in which a perfect rank correlation is 1.0, and a complete lack of correlation is 0).

Similar data were obtained for titanium with a number of different titanium alloys (3), and averaged life values have been computed (figure 2). In this case the r_{rank} value is much lower, namely +0.42, and for the limited number of tests run this figure is probably not significant. The reason for the poorer correlation in the case of titanium may lie in the fact that only a limited range of compatibility could be tested.

B. Lubricant applied once at the beginning of the test

In these experiments the friction during the cutting was monitored, and it was found that initially friction was low and the cutting chips were well curled, but as cutting proceeded the lubricant wore off and friction and chip radius of curvature increased. The length of cut required to wear off the solid lubricant was determined, and for each lubricant a relative life was determined, this being the length of cut obtained with the lubricant divided by the geometric mean length of cut with all the lubricants. Nickel and alumium workpieces were used, and the lubricants were the plated metals lead, tin, cadmium, copper and silver. A plot of relative life against compatibility for the ten combinations tested is shown in figure 3, and for these data the rank correlation coefficient was +0.80.

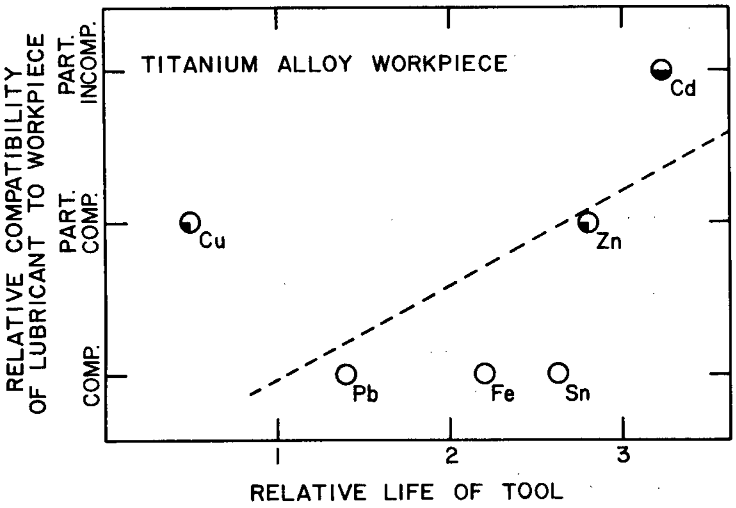

Fig. 2 Life of tool (relative to the life in the presence of a commercial cutting fluid) plotted against relative compatibility of the soft metal lubricant against titanium. The rank correlation coefficient is +0.42.

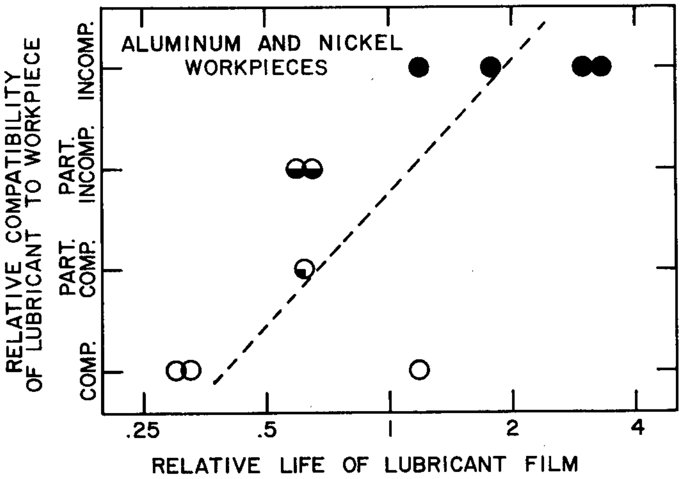

Fig. 3 Life of the lubricant film (relative to the average life for the whole series of shaping tests) plotted against relative compatibility of the soft metal lubricant against the workpiece metal. The rank correlation coefficient is +0.80.

Discussion

These experimental tests were undertaken to see if compatibility factors governed the performance of lubricating metallic coatings. It was found that, indeed, metallurgical compatibility has a strong influence on the performance of the coatings. The correlation coefficients between performance and the compatibility of the materials at the sliding interfaces were always positive, and if the three rank correlations coefficients values are averaged, the mean coefficient was found to be 0.70.

As it happens, in an earlier study of unlubricated sliding metals (8) it was found that in wear tests, (as opposed to friction tests which gave lower correlation values), a correlation coefficient of about +0.6 between wear and compatibility was generally observed. Thus the data obtained here for metals acting as solid film lubricants are right in line with those obtained earlier for unlubricated metals, and it is likely that the same factors influence the wear processes in both cases.

Why is the correlation coefficient not higher, more specifically, why does it not approach the theoretical maximum value of +1.0? The answer may lie in the fact that the real correlation is between wear and surface energy of adhesion, rather than between wear and compatibility. What is being measured then, in tests such as ours, is the correlation between surface energy and compatibility. This correlation is positive (8), but apparently does not approach the optimum value of 1.

Is there a correlation between life of a coating and its mechanical strength? In order to see if there is an effect of this type, we have for all our tests computed the ratio hardness of lubricant/hardness of workpiece. Figure 4 shows the result of plotting relative wear life, i.e. the ratio wear-life-of-film/median-wear-life, for all the data plotted in figures 1 to 3, against the hardness ratio. The compatibility rating for each point is indicated. The data indicate clearly the presence of a compatibility effect, as seen in the fact that most of the incompatible combinations give longer lives than the compatible ones. However, the effect of varying the hardness ratio is much less marked.

We may get a better idea of the hardness effect if we replot the data of figure 4, so as to try to eliminate the compatibility effect and reduce the experimental scatter. To do this it has been assumed that the lives for the incompatible combinations is higher by a factor of two, and thus to eliminate the effects of compatibility the lives should be reduced by a factor of two. Similarly, the lives of the fully compatible combinations must be raised by the same factor of two. The result of this adjustment is shown in figure 5, and now, with the experimental scatter approximately halved, it is quite clear that the hardness ratio has relatively little influence on the wear life of the coatings, but there is an optimum wear life when the hardness ratio is about 0.1.

The wear relationships shown in figure 5 are in some disagreement with the frictional relationships for soft metal films as a function of the (hardness lubricant/hardness substrate) ratio. Figure 6, based on earlier experiments (9,10), shows that in friction tests using a pin-on-disk tester, (using incompatible pin-film combinations throughout), the friction coefficient is reduced continuously and monotonically as the hardness ratio is reduced. The reason why this effect does not show up in the wear results must be that reducing the hardness of the soft metal film has two effects.

a) It leads to a lower friction coefficient, which, other things being equal should give a longer wear life.

b) The hardness of the surface layer is reduced, which for constant Archard wear coefficient, will give a greater wear volume and thus a shorter wear life.

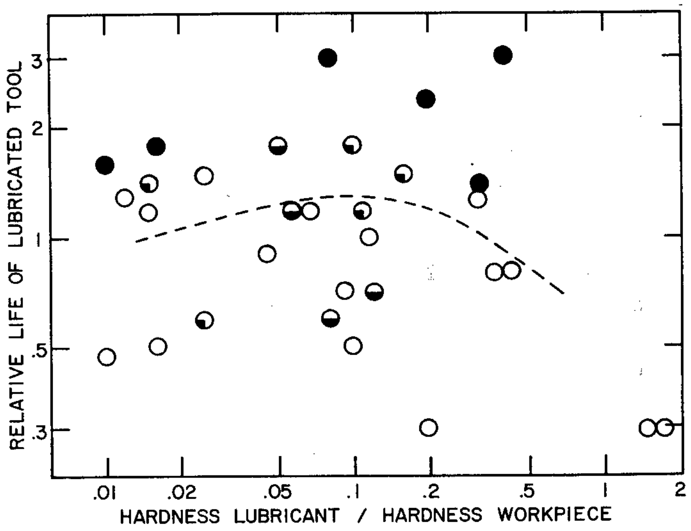

Fig. 4 Plot of life of lubricated tools against the ratio of lubricant hardness to workpiece hardness. There seems to be a very small influence of hardness ratio on wear life, but a strong influence on compatibility, since the films incompatible with the workpiece (full black circles) give exceptionally long life, while the compatible films (open circles) give very short lives.

Not surprisingly, the two factors tend to cancel out.

One of the purposes of the study was to determine the possible uses of soft metal lubricants. Past experience has suggested that the lowest friction coefficient is observed when the film thickness is very small (10^{-3} mm), but then the wear life is small. When much thicker films are used, there is a tendency for the whole film to be spalled off the surface and again the wear life can be very small (1). This suggests two main uses of soft films, first in situations in which a thin film can be replenished continuously, and second in situations in which a film resistant to spalling can be produced, as might be the case with techniques like ion plating. Assuming that reasonably long life can be achieved, then the concept of compatibility constitutes a useful tool for selecting the soft metal to be used with any specified workpiece material.

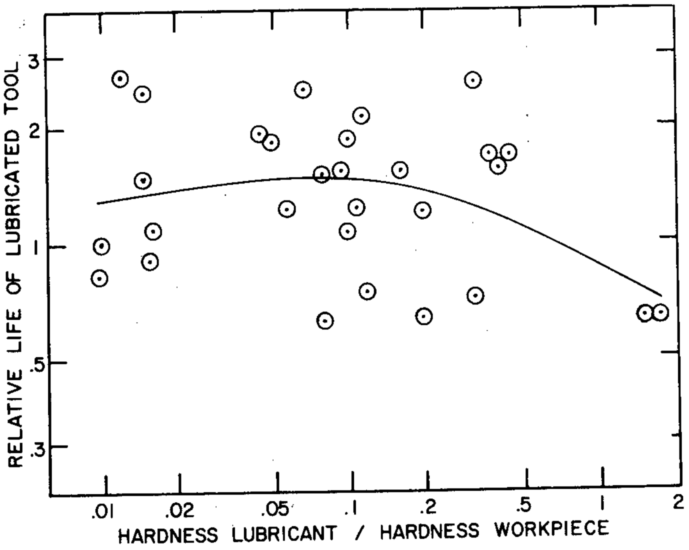

Fig. 5 Replot of the data of figure 4, but reducing the lives for the black circle combinations by a factor of two, and raising the lives for the open circles by the same amount. The experimental scatter is reduced considerably.

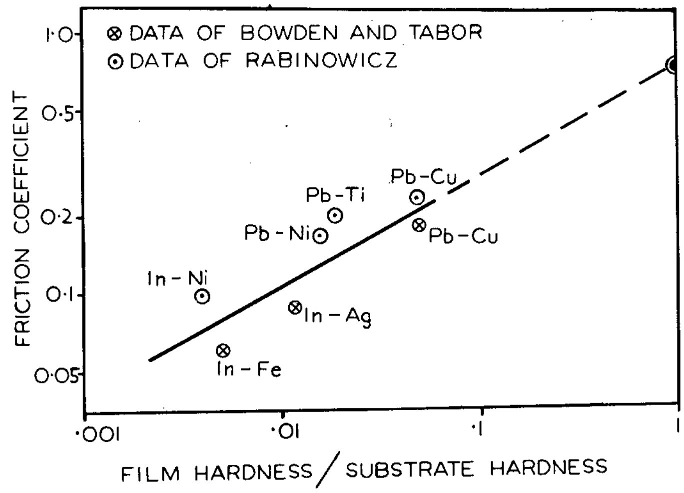

Fig. 6 Plot of friction coefficients for hard metals lubricated by soft metal film against the film/substrate hardness ratio. A hard steel rider was used for all the tests. The friction is reduced monotonically as the hardness ratio is reduced.

Acknowledgements

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DISCUSSION

R. M. Thomson, National Bureau of Standards: Could another reason for the scatter be the presence of voids in the interface? This may also be a random variable because the surface roughness is not necessarily given simply by looking at the compatability of the effects.

E. Rabinowicz: Yes, there are other reasons for scatter apart from the fact that the theory may not be correct. I would not have expected the correlation coefficient to be better than .85 under ideal conditions. I did expect a better coefficient than was obtained. I interpret the poorer coefficient as meaning that I was not correlating against the ideal parameter.

A. W. Ruff, National Bureau of Standards: Did you use the hardness value for the bulk material or did you actually measure the hardness of the thin films?

E. Rabinowicz: In one or two cases, we measured the thin film hardness. In the soft layers, like lead and tin, we did not make measurements.

A. W. Ruff: Perhaps the films would be somewhat harder than the bulk material. It might affect the scatter.

E. Rabinowicz: Yes.

A. W. Ruff: You commented on interactions between the cutting material and the film from the point of view of adhesive energy. Perhaps one should also consider the surface energy of the film material and some ratio of adhesive energy between the two dissimilar materials to the surface energy if you are pulling a fragment out of the film. I suppose both the new surface energy and the adhesive energy would be involved?

E. Rabinowicz: Yes. The expressions that are easiest to obtain mathematically involve the surface energy itself. In a dimensional analysis, it becomes very convenient to use the ratio of surface energy of adhesion to self energy of adhesion. This ratio does not, however, turn up in studies trying to produce a model of a process.

A. W. Ruff: I was thinking really of the physics of what is going on if you have two interfaces that are competing with one another; the dissimilar-metal interface and the like-metal interface. They are competing on an energetic basis in the simplest sense.

E. Rabinowicz: That is perhaps a new way of looking at it.

A. W. Ruff: There is not a single metal that is incompatible in some sense with, for example, titanium. I was wondering about ternary situations where one might consider a binary metal film interacting with titanium in such a way that the binary combination--lead, tin, or whatever--would be incompatible with titanium. Have you extended your ideas to ternary systems?

E. Rabinowicz: I have never looked at the three phase situation. In general, the indications are that when a binary system slides against another metal, it is either the higher compatability one that takes over or the softer of the components of the binary alloy that tends to take over.

R. M. Thomson: The definition of the surface of two materials that are diffusing into one another becomes a very complicated affair. It becomes time dependent, for example. I wonder if you are not using the right parameter after all instead of the surface energy.

E. Rabinowicz: That is true. I have seen that argument used the other way around against using compatability. Compatability theory tells what the equilibrium state will be, but it does not tell the rate at which the equilibrium is reached, and that is more significant. Possibly the diffusion coefficient would be the most logical parameter because that has rate built into it, whereas a phase diagram simply tells you what happens if you wait long enough. What you are really looking for is a parameter that tells you how the atoms at the surface are going to view each other.

J. Kruger, National Bureau of Standards: Just to introduce another complicating factor, we have been concerned for a number of years with the oxide films that form on a metal surface and their rate of reformation once a bare metal surface is produced. What effect would this have on evaluating compatability effects? For example, I notice with titanium, where you had problems, the rate of repassivation that we have measured is extremely rapid. It is in the order of microseconds. Would this have any effect on the process?

E. Rabinowicz: I think the only person who has studied the same material both in vacuum and in air in the same series of tests was Coffin in the early 1950's. Unfortunately he only used six combinations that are really comparable for this purpose. For his limited number of tests, it does turn out that the compatability effects correlate much better with performance in vacuum than in air. The metals seem to know whether they would be soluble in each other if they reach the melting point. They seem to be able to detect what the metals underneath the oxide layers are doing. So presumably there is enough cracking or breaking or puncturing of the oxide layer to permit some metallic interaction. The compatability relationship for oxides is also a significant factor. Compatabilities in oxides and other nonmetals are much smaller than in metals.

REDUCTION OF SLIDING WEAR BY METALLIC COATINGS

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Abstract

The role of soft metallic coatings in sliding wear has been examined experimentally. The results indicate that the tribological behavior of soft coatings is consistent with the delamination theory of wear, especially the critical nature of the plating thickness. It is shown that a reduction in wear rate of three orders of magnitude is possible when the coating material is softer than the substrate and thinner than a critical thickness. The optimum plate thickness was found to be less than 1 μm for cadmium, silver, gold or nickel plated on various steels. As the plate thickness is increased, wear by delamination within the plate occurs. Environmental effects are important in coating utilization.

Introduction

Soft metallic coatings have been used quite extensively in many applications (1-13) to reduce friction and wear of sliding surfaces. However, the exact nature and mechanism by which these coatings improve the tribological behavior has not been investigated completely. Previous attempts (12,13) have been made to determine the optimum thickness of these coatings, but the results and the theoretical considerations were insufficient and inadequate. Recently it has been shown that the delamination theory of wear (14) can be used effectively to predict the behavior of these coatings. This paper reviews some of our previously published (15-17) results on the role of metallic coatings.

A Brief Description of the Delamination Theory of Wear

According to the delamination theory of wear which was recently proposed by Suh (14), low speed sliding wear of metals occurs by delamination of sheet-like wear particles from the sliding contact, by the following mechanisms:

(1) plastic deformation and fracture of the original asperities (i.e. original machining marks)
(2) plastic deformation of the subsurface caused by the traction existing at the contact area
(3) void and crack formation in the deformed subsurface
(4) subsurface void growth and crack extension
(5) generation of long subsurface cracks nearly parallel to the surface
(6) crack extension to the surface to generate wear sheets.

The rate of delamination has been shown to be dependent upon such metallurgical variables as the type, size, and concentration of second phase particles, inclusions and voids (18). Previous investigations (18-21) have shown that delamination occurs in a wide range of different materials, from well annealed copper to fully hardened AISI 4340 steel.

In the original paper Suh (14) postulated the existance of a soft, low dislocation density zone at the outer surface of the wear track. It was believed that the dislocation image force coupled with the clean surface immediately behind the slider would allow dislocations very close to the surface to escape. Therefore, it was concluded that this layer could deform continuously without much workhardening and subsequent wear by delamination. For any metal, there would be some critical depth below which the image force would be too small to extract a significant number of dislocations.

A corollary of this argument is that if a composite surface is created by plating a thin layer of a softer metal (thinner than the softer metal's critical depth) on a harder substrate, large plastic deformation and delamination of the substrate may be prevented. This is based on the fact that dislocations are not stable in very thin layers of metals having a low flow stress, and most of them could be eliminated by the image forces. Therefore, the thin and soft plating could deform without workhardening and wear. The soft layer also reduces the frictional force which will delay substrate delamination.

Experimental Procedure

Wear tests were carried out with a cylinder-on-cylinder geometry. The specimens were rotated at a surface speed of 180 cm/min and the stationary pins were pushed against the specimens by a normal load of 2.25 kg. The wear tests were carried out dry, both in air and in argon gas. Some tests were also conducted under boundary lubrication in air. Gulflex 39 or a pure mineral oil (Nujol) was gravity-fed to the contact at a steady rate. All tests were performed at room temp. for 30 min.

The substrate materials used had a variety of hardnesses: AISI 1018 (84 kg/mm^2), AISI 1095 (170 kg/mm^2) and AISI 4140 (270, 370 and 460 kg/mm^2 — obtained by different heat treatments). In all cases the sliders were made of the same material as the specimen, heat treated, and plated in the same fashion. The plating thickness varied from .05 to 10 μm. The platings tested were gold, gold over a nickel flash, cadmium, nickel, and silver. Some of the gold plated specimens were plated with a flash of gold first and were then heated at 500°C for 2 hrs. in vacuum to obtain a diffused bonding between the plate and the substrate. Then the required thickness of gold was plated on the samples.

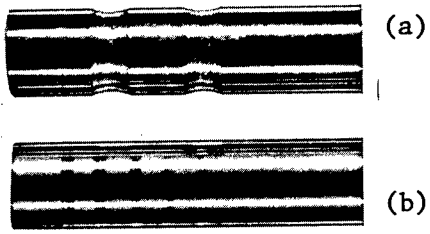

Fig. 1 Comparison between wear tracks of AISI 4140 steel (17)
(a) unplated
(b) 1.0 μm Ni plated

Selected wear tracks were observed with the scanning electron microscope. Some of the specimens were subsequently sectioned parallel to the wear track, metallographically polished and etched to reveal the structure below the wear tracks. The subsurface damage was then examined with the scanning electron microscope.

Experimental Results and Discussion

A. Effect of Plate Thickness

The effectiveness of plating in wear reduction is dramatically shown in Fig. 1 for unplated and 1 μm nickel plated AISI 4140 steel (17). The large difference in the wear track size between the unplated (Fig. 1a) and the plated sample (Fig. 1b) is clearly observed. The wear rate data of these two samples and other specimens with thicker nickel plates is presented in Fig. 2. The wear rate of the 1 μm nickel plated sample is three orders of magnitude lower than the unplated specimen. Fig. 2 also shows that as the nickel plate thickness is increased, wear rate increases. Similar dependence of the wear rate on the plate thickness is also shown in Fig. 3 for cadmium plated AISI 1020 steel (16).

The dependence of wear on the plate thickness can be explained in terms of the delamination theory of wear. In thin layers some of the dislocations can be eliminated by the action of image forces on the dislocations. Therefore dislocation accumulation and strain hardening does not occur, and the layers can deform substantially without wear by delamination. However, if the plate is thick, dislocation accumulation and strain hardening could take place within the plated layer and cause wear by crack formation and delamination of the plated layer. The existance of cracks in a thick plate (25 μm) of gold on AISI 1020 steel

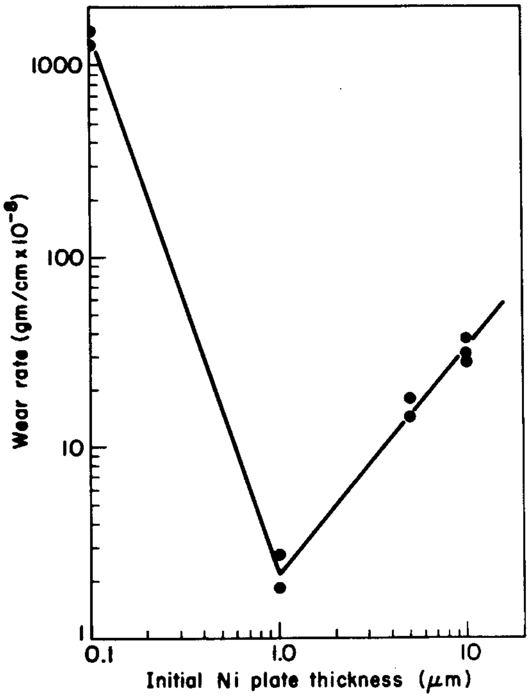

Fig. 2 The effect of Ni plate thickness on wear rate in argon(17)

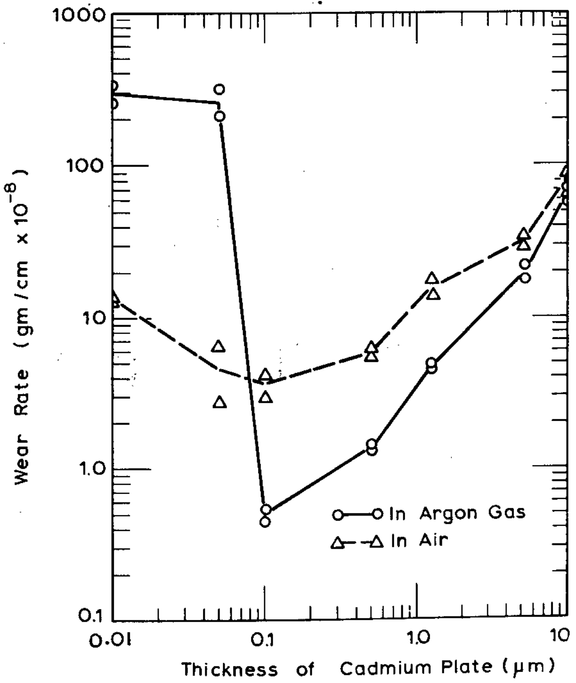

Fig. 3 The effect of Cd plate thickness on wear rate (16)

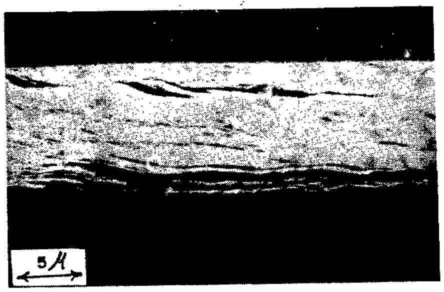

Fig. 4 Crack formation in 25 μm thick Au plate, after wear testing (17)

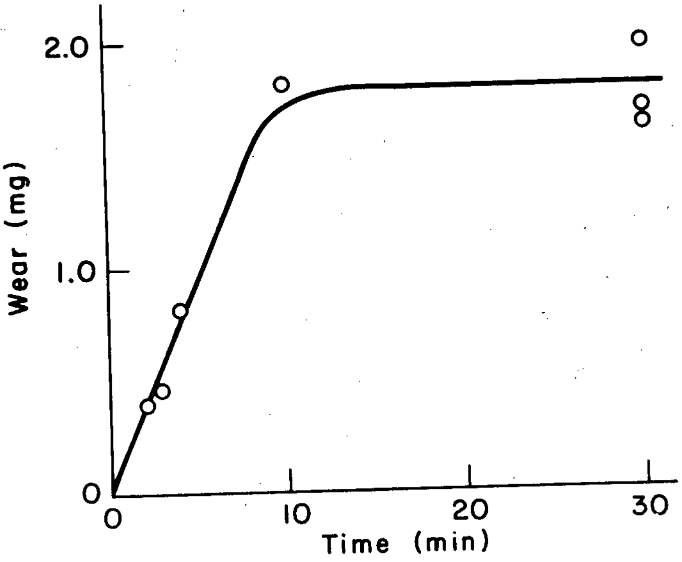

Fig. 5 Wear of initial thick plates vs. time (17)

is observed in Fig. 4 (17). The thick layers wear off by delamination until the thickness is reduced to a smaller thickness in which the dislocations are presumably unstable. At this point, the wear rate is reduced. The transient behavior of thick coatings is shown in Fig. 5 for an initial 10 μm nickel plate on AISI 4140 steel (17).

B. Surface and Subsurface Examination

The wear tracks of the unplated samples appeared to be very rough when compared with that of 0.1 μm cadmium plated steel tested in argon

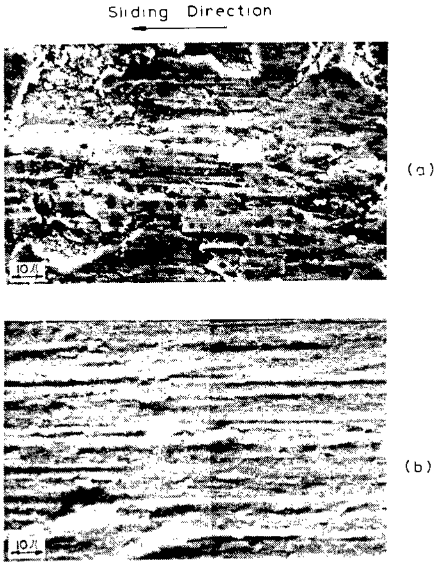

Fig. 6 Wear tracks of AISI 1020 steel tested in argon (16)
(a) unplated
(b) 0.1 μm Cd plated

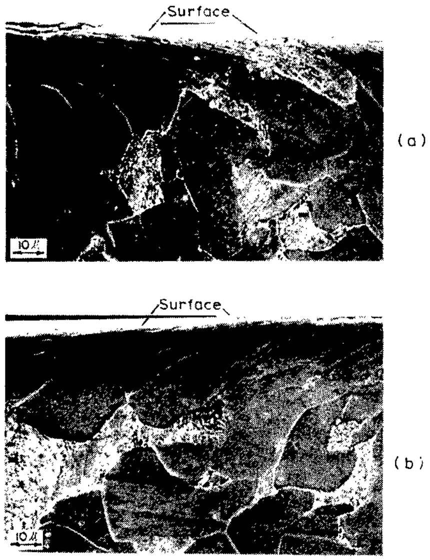

Fig. 7 Subsurface deformation of AISI 1020 steel tested in argon (16)
(a) unplated
(b) 0.1 μm Cd plated

(16), as shown in Figs. 6a and 6b, respectively. The cratered appearance of the unplated steel indicates that many wear sheets have been separated from the wear track. On the other hand, the wear track of the plated sample is much smoother, with parallel furrows in the sliding direction. Only a few indications of delamination were observed on the 0.1 μm Cd plated steel specimens.

Figure 7 compares the subsurface damage and deformation of the unplated steel (Fig. 7a) and the 0.1 μm Cd plated steel (Fig. 7b) tested in argon (16). The plated sample has undergone less deformation and contains a smaller number of subsurface voids and cracks. The depth of subsurface deformation in the unplated sample is 30 - 35 μm while the deformation depth in the plated steel is only 25 - 30 μm. The fact that the plated samples have some voids and cracks in the steel substrate indicates that the cadmium layer will eventually be removed when the steel subsurface delaminates. An extended test in argon with a 0.1 μm Cd plated specimen exhibited subsurface delamination after 86 m of sliding. The unplated steel specimen tested for the same distance of sliding had a weight loss greater than the Cd plated specimen by a factor of 5000.

C. Friction Coefficients

The coefficient of friction of the samples plated with the optimum thickness of cadmium (0.1 μm) and nickel (1.0 μm) were lower than the unplated samples. In the cadmium plating tests (16) the friction coefficient decreased from 0.85 to 0.25; whereas it decreased from 0.63 to 0.45 for nickel plating tests (17). This reduction of frictional force by plating an optimum thickness of material is partially responsible for lower subsurface deformation and retarded delamination, since

Table 1 Experimental results on the wear resistance of 1 μm plates on steel. Wear tested in argon. 2.25Kg normal load. 54m sliding distance.

Coating	Substrate and Hardness (Kg/mm^2)	Wear Rate ($mg/cm \times 10^{-8}$)	Coefficient of Friction
Cd	AISI 1018 (84)	3.6	0.35
Cd	1095 (170)	1.8	0.25
Cd	4140 (270)	3.6	0.35
Cd	4140 (370)	3.6	0.25
Ag	AISI 1095 (170)	1.8	0.33
Au (diffused)	AISI 1095 (170)	1.8	0.85
Au (Ni underlayer)	1095 (170)	-1.8	0.9
Ni	AISI 1019 (84)	immediate failure	-
Ni	1095 (170)	"	-
Ni	4140 (270)	"	-
Ni	4140 (370)	"	-
Ni	4140 (460)	1.8	0.45

it has been reported both experimentally and theoretically that wear coefficient is a very strong function of friction coefficient (20,22).

D. The Effect of Environment

The wear results in Fig. 3 indicate that a much smaller wear reduction was achieved by cadmium plating when the tests were carried out in air rather than argon. However, the lowest wear rate is still obtained with the 0.1 μm cadmium plating. This poor performance in air is caused by oxidation and abrasion of the plate by the hard oxide particles. A series of tests were conducted under boundary lubrication to minimize oxidation (16). It was found that wear reduction with 0.1 μm cadmium plated steel could only be obtained with the pure mineral oil (Nujol) and not with the Gulflex 39 lubricant. The poor performance of the latter oil was caused by the formation of new compounds on the wear track by chemical reaction.

E. The Hardness Match Between Plate and Substrate

The wear test results for 30 min (54 m sliding) for all coating materials and steel substrates with various hardnesses is summarized in Table 1 for the tests in argon (17). The 1 μm plate of gold exhibited low wear rate in air but other plates, i.e. nickel, silver and cadmium, did not last because of oxidation and abrasion. Table 1 indicates that nickel platings on steels softer than 460 kg/mm^2 failed immediately whereas cadmium platings showed low wear for all substrates tested. This experimentally observed phenomenon is in fact consistent with the predictions of the delamination theory of wear, that the thin plating must be softer than the substrate for major wear reduction. If the plated material is harder than the substrate, dislocations can accumulate below the plate and cause early failure of the specimen by substrate delamination. This fact was observed for most nickel plates on steel since nickel was harder than those substrates.

Soft metallic coatings have been used for wear reductions previously by others (1-11). These investigators assume that the soft metal layer melts during sliding and acts as a lubricant. This explanation can only be correct when the sliding speeds and the normal loads are high enough to cause a large flash temperature at the contact. However, the results on the coatings presented here for low speeds and loads and high melting point materials such as nickel (m.p. 1455°C), indicate that the so called "lubrication" mechanism is in general not correct. The role of thin metallic coatings can be explained better in terms of the delamination theory of wear.

Conclusions

(1) The delamination theory of wear provides a theoretical basis for reducing wear through the development of a coated metal surface.

(2) For major wear reduction the coating material must be softer than the substrate material.

(3) There exists a most effective thickness of soft coating for wear resistance. This thickness is less than 1 μm for steel plated with cadmium, silver, gold and nickel.

(4) Cadmium, silver and nickel plates are effective in wear reductions only under conditions where the formation of hard oxide layers or corrosion products are inhibited.

Acknowledgements

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DISCUSSION

L. Leonard, Franklin Institute: It seems to me that there is an alternate explanation for your data. You said that when the coating is too thick the maximum stress is within the coating. Then the low strength of the coating itself causes it to wear relatively rapidly. When the coating is thin, why isn't the lubricity or the coefficient of friction the major factor in wear?

S. Jahanmir: We are saying that the wear reduction or the wear retardation occurs because there is a low friction coefficient which leads to a low friction force on the surface which, in turn, causes a low amount of subsurface deformation.

L. Leonard: Have you looked at any of the pieces of wear sheet that have come off which supposedly have low dislocation densities in a transmission electron microscope?

S. Jahanmir: It is a very difficult process to observe the dislocation density of these thin films because the dislocations escape through very thin films.

L. Leonard: Yes, but if the dislocation density is high, this would counteract your argument.

S. Jahanmir: We have not found any direct evidence for the role of dislocations in the process of plating.

A. W. Ruff, National Bureau of Standards: Do you have any data on the variation of stress or some stress connected property with distance from the sliding surface in the bulk materials that you worked with?

S. Jahanmir: No, we do not have any definite results for that. One of the graduate students working in the group is using a finite element method to find the stresses and strains below the surface and, in fact, he is going to consider how the stress patterns or the displacement patterns change when there is a soft coating on the surface.

A. W. Ruff: Some work that I am doing now on iron surfaces in sliding is producing some results on the stress and strain distribution below the surface using electron channeling techniques. For iron, I find that the stress mounts steadily as one approaches the wearing surface. There is no decrease in residual stress and I think probably that same technique might be useful in monitoring the first 1 to 10 microns of material. We are hoping to get some data on some fcc materials such as nickel or aluminum to compare to some of the hardness data that were reported. Hardness measurements in thin films near free surfaces are sometimes difficult to do.

R. M. Thomson, National Bureau of Standards: One of the very important parameters in an experiment of this kind is the local temperature and, of course, this parameter is not directly measurable and must be inferred. Have you considered the effect of temperature in the whole process?

S. Jahanmir: All of our tests have been done at very low speeds (1.8 meters per minute) which will not cause a large temperature rise at the surface.

R. M. Thomson: In micron layers you could expect it.

S. Jahanmir: The flash temperature right at the contact depends on the sliding speed. If the speed is very low the flash temperature is not going to be large enough to affect the properties of the surface. Of course it would depend on the melting point of the material in question because the properties of each material differ. There is work in progress to look into the effect of speed on this whole process. Changes in the speed produce changes in temperature.

SESSION III

SOLID FILM LUBRICANTS

Chairman: H.Ravner
Naval Research Laboratory
(substituting for W.A.Glaeser)

THE SEARCH FOR FACTORS TO PREVENT MECHANICAL FAILURES DUE TO CORROSION WITH SOLID FILM LUBRICANTS

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The failure of mechanical components of contemporary flight vehicles has frequently been attributed to the corrosion characteristics of solid film lubricants. An ongoing program at the Naval Air Development Center is investigating how some parameters affect corrosion between solid film lubricants and various aircraft alloys. This paper will summarize some of the findings of this study.

Keywords: Corrosion; electro-chemical; lubricants; salt-spray

1. INTRODUCTION

Solid film lubricants have been in usage only about 25 years and it has only been in the last 15 years that they were found to cause corrosion. The controversy still exists as to whether these materials accelerate corrosion. In the early years of solid film lubricant technology, the general assumption was that the adhesion and thickness of the lubricant were the only determining factors for corrosion protection. Originally, these materials were formulated for usage on both parts of a two-component system, so that the corrosive effect on bare metal with this type of lubrication was not considered. However, in 1959, a study was instigated at our naval laboratory on the basis of field information which indicated that corrosion was induced when a dry-film-lubricated metal surface is in contact with an anodized aluminum surface(1).

A slight step forward was then made in the upgrading of the corrosion-resistant properties of these lubricants. However, due to insufficient knowledge of the mechanism of corrosion involving solid film lubricants and metals, this was found to be inadequate. Evidence appeared indicating graphite powder caused galvanic corrosion(2) and MoS_2 in powder pellet form set up a galvanic cell with Al and Mg(3). As yet, there appears to be no data in the literature on electrochemical tests of resin-bonded MoS_2 and graphite with metals. It would be interesting to determine if the resin binder changes the electrochemical nature of the powder and if applied pressure influences this effect.

During 1961 - 1965 period, another research center worked on factors influencing corrosion protection provided by solid film lubricant coatings(4). This work increased the corrosion protection provided with solid film lubrication (specification MIL-L-46010(MR)). For Army weapons' application, protection from the environmental combination of salt-spray and stack-gas emission is not necessary. It is, however, for naval aircraft applications.

Early in 1969, an investigation was conducted at our naval laboratory on the corrosion protection of solid film lubricants on steel in an environment with the combined effects of moisture, sea water and sulfurous acid (a product produced during combustion of fuel oil) for future upgrading of solid film lubricant specifications. A corrosion test was devised for ultra-thin preservative compounds (5,6). This was found, with a few changes, to adapt easily to solid film lubricant corrosion testing.

In 1971, the authors' interest and investigation into parameters affecting corrosion between aircraft alloys and solid film lubricants began as a result of findings (8) in a survey of these materials at the Naval Rework Facilities. A fastener corrosion problem was found at one facility (Figure 1). The only solution to the problem at that time resulted in high expenditures of money and man-hours. It seemed advisable not only to upgrade the corrosion resistance of these lubricants but also to determine the causes of corrosion when they were used. Thus the present program was initiated with the following three objectives:

Figure 1. Corrosion Noted on A-3 Stress Wing Spar

1. Static corrosion studies in a SO_2/salt spray environment of the corrosion resistance of solid film lubricants in conjunction with various inhibitors, metal pretreatment, etc., on aircraft alloys.

2. Dynamic testing under 20%, 40%, 60% and 80% relative humidity with electron diffraction analysis of the debris.

3. Electro-chemical investigation of the galvanic effects of dissimilar metals in combination with solid film lubricants.

These studies are described in the following paragraphs.

2. STATIC CORROSION STUDIES

Since many Navy planes on aircraft carriers are often stored on the flight deck, they are constantly exposed to an environment of stack gases and salt spray. The analysis of stack soot deposits taken from some carriers are shown in Table I (9). These results indicate the presence of acidic sulfur compounds. Therefore, a sulfurous-acid salt spray environment was selected for this phase of the study. The apparatus used is shown in Figure 2. The lubricant is applied to one side of the metal disk and inserted in the turntable above a SO_2-salt spray mist, rotating for a cycle consisting of two hour spraying and two hour drying at ambient temperatures of 77°F. The criteria for failure was the appearance of any evidence of corrosion. Using this test method the following systems were investigated:

TABLE I. STACK SOOT ANALYSIS

Carrier	pH	$SO_4^=$
1	2.7	21%
2	2.8	33
3	2.4	11
4	4.0	11

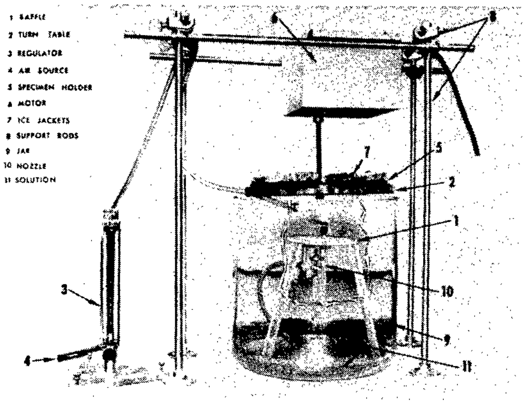

Fig. 2. SO_2/Salt Spray Apparatus

1. Conventional formulations of solid film lubricants on aircraft alloys and the effect of burnished surfaces.

2. Lubricating solids, individual and combined, in a binder on steel.

3. Formulations with different types of inhibitors on steel and aluminum.

4. Different surface pretreatments of steel and aluminum prior to lubricant application.

Initially the steel specimens were 1020 steel but when this became unobtainable, 1010 was substituted since the metallurgy of the two give similar corrosion characteristics. This was verified by duplicate tests with various lubricants on both 1020 and 1010 and obtaining correlating results. In the initial testing of conventional lubricants (results shown in reference (7)), it was found that none containing graphite passed this test. One film having no graphite in it, however, also exhibited rapid corrosion characteristics. Also presented in reference (7) are data indicating that MoS_2 in a phenolic binder resulted in corrosion sooner than was observed with an equal amount of graphite in a phenolic binder. These observations demonstrate that to provide a corrosion preventive solid film lubricant, synergistic effects of the solid contents of the film must be considered and that removing graphite does not result in a corrosion resistant film. For example, a film with MoS_2 and Sb_2O_3 in a phenolic binder will cause rapid corrosion on 1020 steel in the SO_2/salt spray environment when no corrosion inhibitor is present.

In reference (7) the results of adding various types of inhibitors showed, of the inhibitors studied, the acid acceptor and oxidizing passivator to be the most effective corrosion inhibitor for this type of lubricant on steel. When the solid film lubricant was applied to aluminum, only the organic hydrophobic inhibitor had any effect on the corrosion resistance.

Since the surfaces of these films become burnished when in actual use, it was considered necessary to study this effect on the corrosion protection properties of these materials. It is obvious from Table II that when burnished, these lubricants lose their corrosion protection by an enormous amount. However, it has been determined that even the burnished commercial lubricant protected the steel surface longer than an uncoated surface which shows severe corrosion in about ten minutes.

TABLE II. EFFECTS OF BURNISHING ON CORROSION

TEST METHOD - SO_2/SALT SPRAY CORROSION TEST

			ALLOYS		
Lubricant	Mg	Ti(4V)	Ti(6V)	Al	1010
* MoS_2, Sb_2O_3, phenolic-vinyl resin	3	7	>12	9	4
MoS_2, Sb_2O_3, phenolic-vinyl resin (b)	1	1		0	
** MoS_2, inh. epoxy-phenolic resin	3	6	>12	3	6
MoS_2, inh. epoxy-phenolic resin (b)	0	1		3	2
* MoS_2, inh. epoxy-phenolic resin	0	6	0	1	5
MoS_2, inh. epoxy-phenolic resin (b)	0	2		1	2
* MoS_2, Sb_2O_3, inh. phenolic	0	12	>12	3	4
MoS_2, Sb_2O_3, inh. phenolic (b)	0	3		0	
** MoS_2, thermo-plastic binder			>12		6
MoS_2, thermo-plastic binder (b)					4

* heat-cured
** air-dried
(b) burnished

Table III demonstrates the results obtained on steel and aluminum with the various types of pretreatments. The phosphating of the steel and anodizing the aluminum definitely affords these metals better corrosion protection. However, the iron-manganese phosphate did not enhance the corrosion protection of the solid film lubricant as much as would have been expected.

TABLE III. CORROSION RESULTS OF PRETREATED 1010 STEEL AND ALUMINUM

(Cycles to Failure)

Lubricant	Plain 1010	Sand Blast (1010) 100 OVB	Vapor Blast (1010)	Phosphate (1010)		Plain Al	Anodized Al
				FeMn	Zn		
None	0	0	0		3		
* MoS_2, Sb_2O_3, inh. modified resin	8	3	3	9	7	4	9
**MoS_2, graphite, phenolic	0	0	0	1			
* MoS_2 Sb_2O_3, phenolic-vinyl resin						6	11

* Heat-cured
** Air-dried

3. EFFECT OF HUMIDITY ON LIFE AND CORROSION

The corrosion behavior of solid film lubricants under stress and motion were investigated via a humidity-controlled wear configuration (LFW-1), using a stationary block (4130 steel) on a rotating steel ring (lubricant coated 4620 steel). A miniature hygrometer indicator gave the temperature and relative humidity readings. To effect various humidities glycerin/water mixtures, which should not affect the debris chemically, were employed. The speed of the rotating steel ring was 72 ± 2 rpm under a load of 630 pounds. The tests were run under 20, 40, 60 and 80% ± relative humidity. The lubricant was applied to a phosphated steel ring by normal spraying procedure.

The results indicated that humidity has little effect on the wear life of an improved corrosion-resistant film. This confirms previous studies where it has been noted that increased humidity had little effect of the wear life of solid film lubricants.

The wear debris generated from these investigations were examined by electron diffraction analysis in order to determine the corrosion mechanism of solid film lubricants in conjunction with humidity, stress and motion. Identification was made by "best fit" between the ASTM powder diffraction film and electron diffraction data. The composition of the wear particles appeared varied although the same set of test conditions on one lubricant was employed. Other patterns were observed but determination of the other compounds present was not possible by the above method. Some of the electron diffraction analysis results of the debris are listed in Table IV. These results are based on the average of three diffraction patterns per sample. The most significant fact drawn from this table is that the wear debris of the most corrosion protective lubricant was Fe_3O_4 which is less abrasive than Fe_2O_3.

TABLE IV. RESULTS OF ELECTRON DIFFRACTION ANALYSIS OF DEBRIS

Lubricant	Test No.	Average Relative Humidity 17%	 37%	 61%	 82%
A	1	$Fe_3O_4, Sb_2O_3, Fe_2O_3$	$MoS_2, MoO_3, \alpha Fe_2O_3, \epsilon Fe_2O_3$	αFe_2O_3	Fe_2O_3
	2	$Fe_3O_4, \alpha Fe, \alpha Fe_2O_3$	Fe_2O_3, Sb_2O_3	Fe_2O_3, Ni_xC	Fe_3O_4
	3	$\alpha Fe_2O_3, \beta Sb_2O_4, MoS_2$	$Fe_2O_3, Sb_2O_3, \alpha Fe_2O_3, NiS$	ϵFe_2O_3	$\alpha Fe_2O_3, MoO_3, Sb_2O_3$
	4	MoS_2, MoO_3	$Fe_2O_3, C, \alpha Fe_2O_3, Fe_3O_4$	Fe_2O_3, Fe_3O_4	$\alpha Fe_2O_3, Fe_2O_3$
B	1	$\alpha Fe_2O_3, MoO_3, Fe_2O_3$	MoS_2, Fe_2O_3	Fe_2O_3, NiS	Fe_2O_3
	2	Fe_2O_3	$MoS_2, \alpha Fe_2O_3$	$\alpha Fe_2O_3, NiS$	MoO_3, MoS_2, Fe_2O_3
	3	$\alpha Fe_2O_3, Fe_2O_3$	$Fe_2O_3, \alpha Fe_2O_3$	Fe_2O_3	$MoS_2, \alpha Fe_2O_3$
	4	$\alpha Fe_2O_3, Fe_2O_3$	$\alpha Fe_2O_3, NiS$	$Fe_2O_3, \alpha Fe_2O_3$	$Fe_2O_3, \alpha Fe_2O_3$
C	1	$\gamma Fe_2O_3, Fe_2O_3$	MoS_2, Fe_2O_3	$\alpha Fe_2O_3, Fe_2O_3, MoS_2$	$MoS_2, Fe_3O_4, \alpha Fe_2O_3$
	2	$\gamma Fe_2O_3, Fe_2O_3, MoS_2, Fe_3O_4$	$\alpha Fe_2O_3, NiS$	$\gamma Fe_2O_3, Fe_2O_3, MoS_2$	$\alpha Fe, FeO, \alpha Fe_2O_3, \epsilon Fe_2O_3, \gamma Fe_2O_3, \epsilon Fe_2O_3$
	3	$\alpha Fe_2O_3, Fe_2O_3, C, MoS_2$, Graphite	$Fe_2O_3, \alpha Fe_2O_3, MoS_2$	Fe_2O_3	$\alpha Fe_2O_3, Fe_2O_3, \epsilon Fe_2O_3$
	4	Fe_2O_3, MoS_2	$Fe_2O_3, \alpha Fe_2O_3$	$C, \alpha Fe_2O_3$	$\alpha Fe_2O_3, Fe_2O_3, MoS_2$

NOTE: A = MoS_2, Sb_2O_3, inhibitor and modified resin
B = MoS_2, graphite and modified resin
C = MoS_2, graphite and resin

4. ELECTRO-CHEMICAL INVESTIGATION

There rages quite a controversy about the effects of solid film lubricants when used with dissimilar metals, especially if graphite is present. For this reason, the electro-chemical nature of the solid film lubricated steel surface and aluminum couple was investigated. A simple experimental apparatus (Figure III) consisting of a cell with 3% synthetic sea salt solution, a 5" strip recorder, vacuum tube voltmeter and a resistance box were used to measure the potential and current density of our couples.

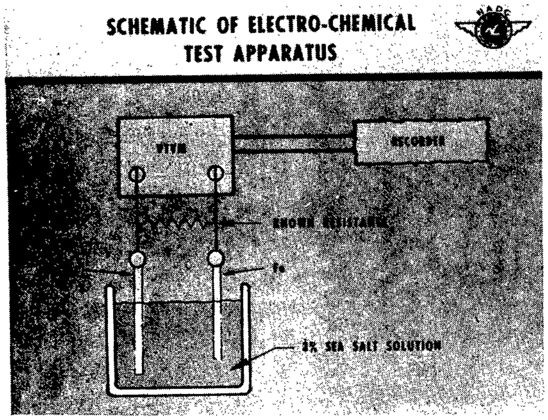

Fig. 3

The values given in the tables are usually those obtained during a four-hour test period in which steady state occurred. However, a few specimens were run overnight and one for a week, but the potentials were not appreciably different. The area of the aluminum specimens were set at twice the steel area since aircraft applications usually consist of a larger aluminum area than steel.

Baseline data was obtained of various combinations of aluminum and steel alloys commonly used on aircraft. Table V tabulates the results (average of three tests) which correlate with the order of metals and alloys in the galvanic series in sea water. The results indicate the corrosion potential between mild steel and aluminum to be less than a stainless steel/aluminum couple. Next, the lubricants with different corrosion protection properties were studied. They are the same lubricants used to determine effect of humidity in the second task area. These results are listed in Table VI. The current gives an indication of the rate of corrosion and so Lubricant A, which demonstrated the best corrosion protection in the SO_2/salt spray test, also exhibited an extremely low corrosion rate. The lower current can be caused by an inhibitor acting at the pores or by a more homogeneous porefree film. The latter is most likely since inhibition of the pores should give the same increase in potential difference for both steels. Lubricants B and C show very little difference in corrosion rate although B is slightly better than C in SO_2/salt spray corrosion test.

TABLE V. ELECTRO-CHEMICAL RESULTS OF DISSIMILAR METALS

Metal to Metal	(mV) Potential	(mA) Current	(ma/cm^2) Current Density Cathode
2024-T3 vs 304	-842	0.11	0.004
7075-T6 vs 304	-940	0.10	0.003
2024-T3 vs 4130	-397	0.04	0.001
7075-T6 vs 4130	-509	0.09	0.003

TABLE VI.

Metal to Metal + Lubricant	(mV) Potential	(mA) Current	(ma/cm^2) Current Density Cathode
2024-TS vs 304 + C	-987	0.06	0.002
7075-T6 vs 304 + C	-1105	0.08	0.003
2024-T3 vs 304 + B	-1000	0.03	0.001
7075-T6 vs 304 + B	-1110	0.04	0.001
2024-T3 vs 304 + A	-898	0.0004	0.00002
7075-T6 vs 304 + A	-1017	0.0005	0.00002
2024-T3 vs 4130 + C	-767	0.06	0.002
7075-T6 vs 4130 + C	-733	0.06	0.002
2024-T3 vs 4130 + B	-545	0.05	0.002
7075-T6 vs 4130 + B	-614	0.06	0.002
2024-T3 vs 4130 + A	-568	0.0004	0.00001
7075-T6 vs 4130 + A	-700	0.0002	0.00001

Lubricants: A - MoS_2, Sb_2O_3, inhibitor and modified resin
B - MoS_2, graphite, modified resin
C - MoS_2, graphite, resin

5. CONCLUSION

It has been found that burnishing the surface of a solid film lubricant causes rapid loss of corrosion protection. The reason for this could be that the MoS_2 particles are pressed closer together and become more of the conductor. If this is true, it would mean that a lubricant does not have to contain graphite to cause galvanic corrosion when involved in a dissimilar metal couple. Pretreatments were found to have less effect than expected on corrosion prevention. Humidity was found to have no effect on wear life or corrosion rate. A new method has shown promise in studying solid film lubricants electrochemically.

To find more answers, future investigations will be conducted to find the effect of new binders, inhibitors, porosity, conductivity, lubricating solids on corrosion protection by this type of material.

6. ACKNOWLEDGEMENTS

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DISCUSSION

A. J. Babecki, NASA, Goddard Space Flight Center: There has been a lot of test work done to show that MoS_2 is a good lubricant in vacuum and graphite is a good lubricant in non-vacuum conditions. Why is MoS_2 used in non-vacuum conditions when graphite should really be used?

M. K. Gabel: The Air Force and the Army are banning the use of any lubricant containing graphite because there are problems with what they call galvanic corrosion. I feel they are going a little too far in banning all of these lubricants. However, I have found that the new films that do not contain graphite seem to have as good an endurance life as those that do contain graphite. They also provide adequate corrosion protection.

A. J. Babecki: Maybe the lubrication and wear life is being provided by something else. What is the binder in these films?

M. K. Gabel: Most of the commercial lubricants that I studied have thermosetting binders. The formulations that I made in the laboratory contained phenolic resin type binders which are also thermosetting.

G. E. DeLong, Naval Air Systems Command Representative, Pacific: Most of the materials for inhibiting corrosion assume that a material is going to go into solution in the presence of moisture, which also assumes by definition that the inhibitor is a consumable part of that particular formulation. In the case of a burnished material, it would be rather difficult for this to occur. Is it a valid assumption, with dry film lubricants, that the inhibitors only work by going into solution, and therefore the dry film lubricant is time limited in its application in a damp environment?

M. K. Gabel: I don't think that all of the inhibitor would go into solution. It is distributed evenly throughout the film and as long as the film is there, some inhibitor is probably still present.

RUST-INHIBITED NONREACTIVE PERFLUORINATED POLYMER GREASES

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ABSTRACT

Perfluoroalkylpolyether fluids thickened with polytetrafluoroethylene were studied in connection with the development of rust-inhibited chemically inert greases for liquid-fueled rocket engines. It was found that 1.0 to 3.0 wt. percent of a physically and chemically modified organophilic dimethyloctadecylbenzyl ammonium bentonite + sodium nitrite imparts very effective rust-preventive properties to perfluoro polymer grease mixtures. Data are given which show that the rust-inhibited greases are nonreactive on contact with conventional fuels and oxidizers, exhibit lubricating properties comparable to soap-thickened greases with a significant improvement in extreme pressure properties, and are nonreactive at high impact energies in the presence of LOX. The results of this work are applicable to all liquid-fueled rocket engines for missiles and space vehicles.

KEYWORDS: Chemisorption; Corrosion preventives; Inhibitor additives; LOX compatible greases; Nonreactive lubricants; Rust inhibited perfluoro greases; Surface chemistry lubrication.

INTRODUCTION

Perfluorinated alkylpolyether fluids prepared either by photooxidation of perfluoroolefins at -30C (1,2) or by the anionic polymerization at temperatures below -27.5C of hexafluoropropylene epoxide in the presence of solvents using cesium fluoride (3) have recently been made commercially available. These fluids have considerably lower vapor pressures than the perfluorotrialkylamines which had previously been utilized as components of liquid-fueled rocket engine lubricants (4,5). A recent study of the physical and chemical properties of the alkylpolyether fluids thickened with polytetrafluoroethylene have indicated that the resultant grease mixtures are suitable as inert lubricants for rocket engines powered by liquid propellants such as ethyl alcohol aniline, hydrocarbon fuels (JP-4, JP-5, RP-1), diethylenetriamine (DETA), unsymmetrical dimethylhydrazine (UDMH), hydrazine, hydrogen peroxide, inhibited red fuming nitric acid (IRFNA), nitrogen tetroxide and liquid oxygen (LOX) (6). It was found that the polytetrafluoroethylene-perfluoroalkylpolyether grease mixtures exhibited effective lubricating properties, thermal, hydrolytic and oxidative stabilities, wide temperature range, extreme pressure properties, nonreactivity with fuels and oxidizers and shear stability. These lubricants are now extensively used on crew compartment (APOLLO) and launch components (Saturn boosters) of manned and unmanned space vehicles (7). While these uses indicate significant progress in the development of chemically inert lubricants for liquid-fueled rocket engines, it has been observed that the polytetrafluoroethylene-perfluoroalkylpolyether grease mixtures do not provide effective protection of ferrous alloys against rust. Using ASTM D1743-64, it was found that lubricated tapered roller bearings, SAE 4620 or SAE 8720 with 1010 mild steel roller retainer, rusted badly after fourteen days exposure at 100 percent relative humidity. A typical illustration is given in Fig. 1.

Further, recent tests (8) conducted on a 440C stainless steel R-4 bearing rotating at 3,000 rpm at 5-psi pure oxygen at 70 percent relative humidity lubricated with perfluoroalkylpolyether-polytetrafluoroethylene grease was found to be inoperable after approximately 1,000 hours due to extreme pitting and rusting. (This bearing is a component of the fan proposed for use for a minimum of 5,000 hours on the astronauts' orbital workshop.)

To overcome this deficiency, work was initiated at the author's laboratory toward the modification of the perfluoro polymer greases with commercially and experimentally available rust inhibitors. Initial exploratory tests (ASTM D 1743-64) indicated that adequate rust prevention could not be achieved through the addition of up to 3.0 wt. percent of rust inhibitors such as sorbitan mono-oleate, sorbitan trioleate, barium petroleum sulfonate, fatty amido phosphate and barium dinonylnaphthalene sulfonate. Also, contact compatibility tests with fuels and oxidizers showed evidence of reactivity, and, as a result, such inhibitors could not be considered satisfactory for liquid-fueled systems. In the work described here, a commercially available modified bentonite consisting of dimethyloctadecylbenzyl ammonium bentonite with sodium nitrite (9) was found to have rust inhibiting properties with perfluoroalkylpolyether-polytetrafluoroethylene grease mixtures. This paper describes the preparation and properties of a series of rust-inhibited nonreactive perfluoro polymer greases for liquid-fueled rocket motors.

EXPERIMENTAL

Grease Preparation

Materials. The thickener was a low molecular weight tetrafluoroethylene polymer having the following properties: softening point 321.1 C; mol. wt. 20,000-30,000; particle size 100 percent less than 30 microns. The product was supplied as a 7.5 percent suspension in trichlorotrifluoroethane.

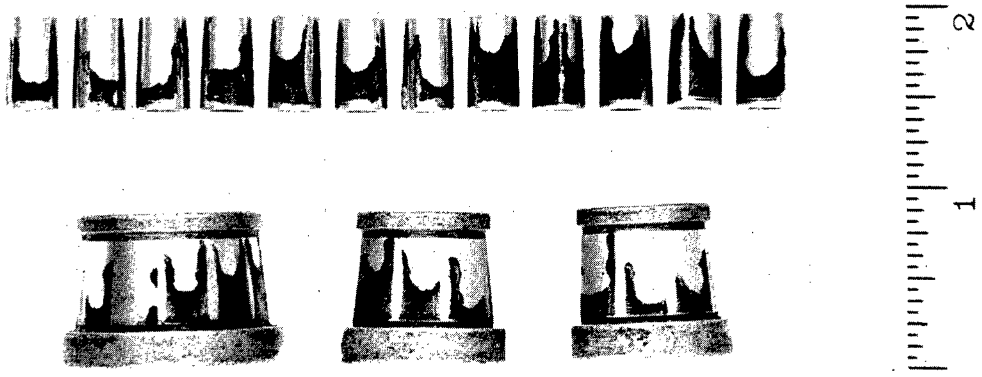

Fig. 1. Uninhibited Perfluoroalkylpolyether Grease (ASTM D 1743-64)

The fluids used were fluorinated alkylpolyethers (Table 1). The preparations and properties of these fluids were described previously (1,2,3,7,10).

The additive was a chemically and physically modified organophilic bentonite (dimethyloctadecylbenzyl ammonium bentonite + sodium nitrite) (9).

Composition. The compositions of the greases are given in Table 2. All greases were prepared to NLGI Number 2 Grade (265-295 worked penetration).

Table 1. PERFLUOROALKYLPOLYETHER FLUIDS

Fluid	Viscosity, cSt. at 37.78 C	Pour Point, C	Density at 23.8 C
PD-1023........	96.3[a]	-26.1	1.91[c]
PD-1024........	153.0[a]	-29.0	1.91[c]
PD-1025........	424.0[a]	-17.7	1.92
PD-1026........	18.0[b]	-56.2	1.86
PD-1027........	85.0[b]	-42.2	1.89
PD-1028........	270.0[b]	-34.5	1.90
PD-1029........	495.0[b]	-28.8	1.91

[a]Ref. (1,2,10). [b]Ref. (3,7). [c]at 15.5C.

Table 2. GREASE COMPOSITION (WT., PERCENT)

Grease	Perfluoroalkyl-polyether	Thickener[c]	Rust Inhibitor[d]
PD-1030........	85.1(96.3 cSt)[a]	13.9	1.0
PD-1031........	85.3(153.0 cSt)[a]	13.7	1.0
PD-1032........	84.7(424.0 cSt)[a]	14.3	1.0
PD-1033........	85.0(18.0 cSt)[b]	14.0	1.0
PD-1034........	84.7(85.0 cSt)[b]	12.3	3.0
PD-1035........	82.3(270.0 cSt)[b]	15.5	2.2
PD-1036........	87.4(495.0 cSt)[b]	11.6	1.0

[a]Ref. (1,2,10); [b]Ref. (3,7); [c]polytetrafluoroethylene, mol wt, 20,000-30,000, (7); [d]dimethyloctadecylbenzyl ammonium bentonite + sodium nitrite (9).

Dispersion Procedure. Each grease mixture was prepared as follows: The dispersion of PTFE in trichlorotrifluoroethane was heated on a steam bath until ∿50 percent of the solvent evaporated. Approximately 75 percent of the required quantity of base oil was then added, the mixture was stirred and heating continued until all of the trichlorotrifluoroethane had evaporated. (The absence of trichlorotrifluoroethane was determined by gas chromatography using the following technique. A sample of the grease mixture was extracted using C.P. benzene. Gas chromatography was used to show (absence of a retention peak after 3.3 minutes) that all the trichlorotrifluoroethane had evaporated (20-ft carbowax 20M column at 50 C, helium flow, 10 ml per minute).

The remainder of the base oil was then added while stirring, and stirring continued until a homogenous grease-like product was obtained. The mixture was cooled to room temperature. The rust inhibitor was then added, thoroughly mixed into the grease, the mixing being completed by passing the grease twice through a colloid mill with a stator-to-rotor clearance set at 0.001 inch. The homogenized mixture was permitted to remain at room temperature for 24 hours prior to use. Greases were prepared in 200-g batches (Table 2).

Rust Preparation

Initial studies were directed toward establishing the minimum quantity of rust inhibitor required for each grease to pass the rust test using the tapered roller bearing described in ASTM D1743-64. (This test was used since it is currently specified in numerous specifications, e.g., MIL-G-23827, MIL-G-25013, MIL-G-21164 and MIL-G-81322). The minimum quantity of rust inhibitor required for rust prevention is given in Table 2. The same test was run on grease samples prepared without the inhibitor and also on uninhibited commercial greases (7,10). Figures 1 and 2 are typical of the test results; all bearings lubricated with greases containing the rust inhibitor showed no corrosion; all samples without the inhibitor rusted badly. This was found to be so whether the viscosity of the fluid used to prepare the test grease was as low as 18.0 cSt or as high as 495.0 cSt at 37.78 C (Table 2).

Reactivity with Fuel and Oxidizers and Metals at High Shear

Contact Tests. Contact compatibility tests were run at 25 ± 1.0 C. One gram each of the material being tested (or 1 ml if fluid) was placed in a 5 ml graduated glass-stoppered cylinder and 1 ml of fuel or oxidizer added. Visual observations preceded by shaking were made after five minutes and 1, 24, 48 and 72 hours. The fuels and oxidizers used were EtOH, JP-4, UDMH, DETA, $C_6H_5NH_2$, N_2H_4, H_2O_2, IRFNA and N_2O_4. The tests using N_2O_4 were run in closed pressure glass jars 1 x 5 inches. The results (Tables 3,4) show that the low molecular weight polytetrafluoroethylene thickener was nonreactive and insoluble with

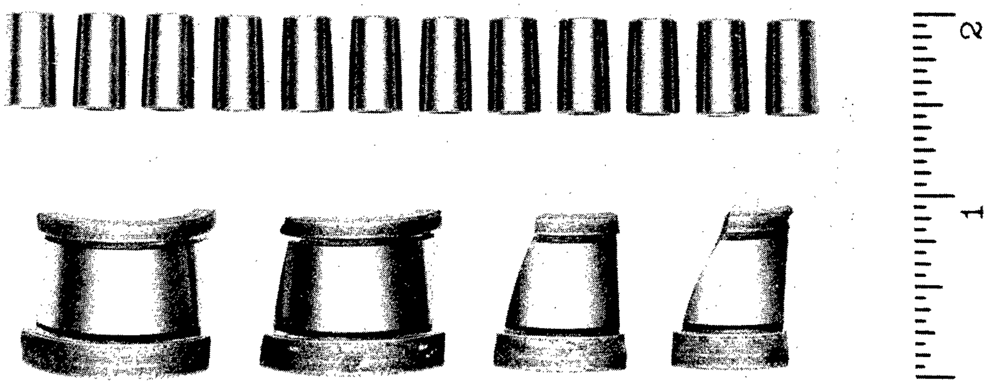

Fig. 2. Inhibited Perfluoroalkylpolyether
Grease (ASTM D 1743-64)

Table 3. CONTACT COMPATIBILITY OF THICKENER, RUST INHIBITOR AND BASE FLUIDS

Material	EtOH	JP-4	$C_6H_5NH_2$	UDMH	DETA	N_2H_4	H_2O_2	IRFNA	N_2O_4
PD-821[a].......	I	I	I	I	I	I	I	I	I
PD-1016[b].......	I	I	I	I	I	I	I	I	I
PD-1024[c].......	I	I	I	$\sim$10[e]	$\sim$10[e]	W	I	$\sim$10[e]	$\sim$20[e]
PD-1027[d].......	I	I	I	$\sim$ 5[e]	I	W	I	$\sim$ 5[e]	$\sim$15[e]
PD-1028[d].......	I	I	I	I	I	W	I	$\sim$ 5[e]	$\sim$10[e]

[a]Thickener; [b]rust inhibitor; [c]Ref. (1,2,10); [d]Ref. (3,7); [e]fuel or oxidizer soluble in base oil, vol, %; W. white emulsion; I, no apparent change.

Table 4. CONTACT COMPATIBILITY OF GREASES

Grease[a]	EtOH	JP-4	$C_6H_5NH_2$	UDMH	DETA	N_2H_4	H_2O_2	IRFNA	N_2O_4
PD-1030........	I	I	I	SS	SS	SS	SS	SS	SS
PD-1031........	I	I	I	I	I	I	I	SS	SS
PD-1032........	I	I	I	I	I	I	I	I	SS
PD-1033........	I	I	I	I	SS	SS	I	SS	SS
PD-1034........	I	I	I	SS	I	I	I	SS	SS
PD-1035........	I	I	I	I	I	I	I	SS	SS
PD-1036........	I	I	I	I	I	I	SS	SS	SS

[a]Composition given in Table 2; I, no apparent change, SS, slightly soluble (< 5.0 percent by volume).

all of the test fuels and oxidizers. The dimethyloctadecylbenzyl ammonium bentonite + sodium nitrite rust inhibitor swelled but showed no reactivity. The data in Tables 3 and 4 indicate no reactivity of the test materials with the fuels and oxidizers. Although some of the fuels and oxidizers were somewhat soluble in the perfluoroalkylpolyether fluids, the degree of solubility was less on the greases made up with the same base oils. Only a slight solubility (<5 percent by volume) of the grease was noted. Evidently the structure of the grease dispersion is such that the fluid is not readily accessible for solution.

Impact Tests. Liquid oxygen impact compatibility tests were run at an impact level of 72.3 foot-pounds (11). The thickener, rust inhibitor, fluids and greases were considered nonreactive with LOX if they withstood 20 separate impact trials without reaction (flashes, explosions or other indications of sensitivity). Since none of the materials tested were found to be reactive with LOX, within the limits mentioned in Table 5, it appears that the thickener, the rust inhibitor, the fluorinated polymer fluids and greases made from these products may be useful for rocket motor systems which use LOX as the oxidizer. It is significant to note that the modified organophilic bentonite was not sensitive when tested alone (PD-1016) or as part of the grease mixtures (PD-1031, PD-1034 and PD-1035) when subjected to high-impact energy levels. PD numbers in text and tables are in-house code designations for experimental materials used by the author's laboratories.

Metals at High Shear. It has been reported that explosive reactivity occurs when aluminum surfaces are coated with polytetrafluoroethylene (12) or polymers of chlorotrifluoroethylene (13-16) when subjected to mutual shear at high loads. To determine whether similar reactivity is associated with the products described here, tests were run on the fluids and greases using proposed ASTM D-2 Method (17). Seven tenths ± 0.1 of a ml of materials was placed in a cylindrical hole (1/2 in dia x 1/2 in deep) in a block of 2024-T4 aluminum. A dowel of 2024-T4 aluminum (1/4 in diameter, rounded end (0.250 ± 0.001 inch radius tip) X 3.0 inches long) was rotated into the block at 1,760 rev per min under a load of 1,000 psi for one minute. The dowel mating surface in the specimen block was made using a fluted carbide-tipped ball-end mill 0.500 ± 0.001 in in diameter with 0.250 ± 0.001 in radius tip finished to 8 to 16 microinch rms. The load is weighted to provide a 1,000 psi at the dowel and specimen block mating surfaces. The data is given in Table 6. All of the lubricants tested were reactive to some degree; none appeared to be as sensitive as the polychlorotrifluoroethylene fluid (13-16). The addition of the rust inhibitor did not increase the reactivity of the lubricant with aluminum at the 1,000 psi load. However, since the data is important in the potential use of the lubricants for metallic connectors and thread fasteners in rocket motor systems, it would appear that as a precautionary measure this apparent deficiency of the lubricants should be checked on any batch contemplated for use.

Table 5. IMPACT COMPATIBILITY

Material	LOX[f]
PD-821[a]...............	Not reactive
PD-1016[b]..............	Not reactive
PD-1024[c]..............	Not reactive
PD-1027[d]..............	Not reactive
PD-1028[d]..............	Not reactive
PD-1031[e]..............	Not reactive
PD-1034[e]..............	Not reactive
PD-1035[e]..............	Not reactive

[a] Thickener; [b] rust inhibitor; [c] base oil Ref. (1,2,10); [d] base oil Ref. (3,7); [e] grease; [f] no reaction in 20 trials Ref. (11).

Table 6. REACTIVITY OF LUBRICANTS WITH ALUMINUM AT HIGH SHEAR[a]

Lubricant	Explosive Reactions/No. of Trials
Perfluoroalkylpolyether, (96.3 cSt)[b]..............	4/6
Perfluoroalkylpolyether, (96.3 cSt) + thickener....	1/6
Perfluoroalkylpolyether, (96.3 cSt) + thickener + rust inhibitor..............................	1/6
Perfluoroalkylpolyether, (85.0 cSt)[c]..............	2/6
Perfluoroalkylpolyether, (85.0 cSt) + thickener....	1/6
Perfluoroalkylpolyether, (85.0 cSt) + thickener + rust inhibitor..............................	1/6
Perfluoroalkylpolyether, (270.0 cSt)[c]	2/6
Perfluoroalkylpolyether, (270.0 cSt) + thickener...	1/6
Perfluoroalkylpolyether, (270.0 cSt) + thickener + rust inhibitor..............................	1/6
Polychlorotrifluoroethylene oil, 6.5 cSt at 37.78 C.	6/6

[a] Load, 1000 psi at 1760 rpm, dowel and block 2424-T4 Al, Ref. (17); [b] Ref. (1,2,10); [c] Ref. (3,7).

Lubricant Properties

Antiwear characteristics were determined on the four-ball wear tester, using ASTM D 2266-64T. Wear scar diameters were measured on the three stationary balls after one hour at 1200 rpm at 75 C with 10-kg and 40-kg loads using a travelling microscope at 40 X. The values are the average of the readings taken parallel and normal to the scuff marks. The data (Table 7) show that the addition of the rust inhibitor to each thickened oil lowers the scar diameter to slight degree.

Extreme Pressure (EP) properties of the test greases were determined using the four-ball method described in ASTM D 2596-69. It was found that the rust-inhibited perfluoro polymer greases did not weld under an applied load of 800 kg.

Comparisons were made with similar greases containing no rust inhibitor. The data (Table 7) show a marked improvement in EP properties due to the addition of the rust inhibitor. Further, the EP characteristics of the inhibited or uninhibited polytetrafluoroethylene-perfluoro-alkylpolyether greases are far superior to the currently used EP MIL SPEC greases, e.g., MIL-G-23827, MIL-G-21164, or MIL-G-81322.

It is also of interest to note that the scar diameters on the balls in the EP tests using ASTM D 2596-69 which did not weld at 800-kg loads were all below 4.0 mm. These data (no weld at 800-kg load or scar diameters below 4.0 mm) clearly suggest that the modified organophilic bentonite plays a major role in enhancing the EP properties of the test greases.

Other Lubricant Properties. The data (Table 8) show that the inhibited perfluoro polymer greases exhibit high dropping points, low water washout characteristics, low vapor pressures, and good mechanical stabilities. It is of interest to note that no adverse changes took place in these properties due to the addition of the rust inhibitor.

Limited tests were also conducted to determine the effect of the rust inhibitor on low temperature torque. It was found (Table 9) that the starting torques of the inhibited greases were higher than the uninhibited greases. It should be noted, however, that the torque values of the inhibited perfluoro polymer greases compared favorably with the products meeting MIL-G-27617 "Grease, Aircraft, Fuel and Oil Resistant." The latter specifies a 7,000 g-cm starting torque at -22.0 C.

SUMMARY OF RESULTS

The primary purpose of the work was to develop rust-inhibited nonreactive perfluoro polymer greases for liquid-fueled rocket motors. Based on the test data given, it must be concluded that the modified ammonium bentonite imparts effective rust-prevention properties to perfluoroalkylpolyethers fluids thickened with polytetrafluoroethylene. It is

Table 7. ANTIWEAR AND EXTREME PRESSURE PROPERTIES

	Antiwear^{a} Wear Scar Diam, mm		Extreme Pressure^{b}	
	10-Kg Load	40-Kg Load	Weld, Kg	Scar Diam, mm
Base Oil, 96.3 cSt^{c} + thickener	0.418	1.235	400	...
Base Oil, 96.3 cSt + thickener + rust inhibitor.	0.275	1.095	>800	2.383
Base Oil, 85 cSt^{d} + thickener	0.462	0.796	800	3.533
Base Oil, 85 cSt + thickener + rust inhibitor...	0.297	0.603	>800	2.218
Base Oil, 270.0 cst^{d} + thickener	0.502	0.943	600	...
Base Oil, 270.0 cSt + thickener + rust inhibitor	0.301	0.632	>800	2.761
MIL-G-23827	...	...	<300	...
MIL-G-21164	...	...	<400	...
MIL-G-81322	...	...	<300	...

[a] ASTM D 2266-64T; [b] ASTM D 2596-69; [c] Ref. (1,2,10); [d] Ref. (3,7).

Table 8. Lubricant Properties

					Shear Stability^{e}		
Grease	Dropping Point, C^{a}	Bleeding wt, %^{b}	Water Washout, wt. %^{c}	Evaporation wt, %^{d}	Unworked, No Stroke	10,000 Strokes	100,000 Strokes
PD-1031	318(281)^{c}	4.5(4.8)	1.5(1.3)	0.21(0.36)	269	324	312
PD-1034	280(281)	3.1(2.4)	2.2(3.7)	0.03(0.03)	271	305	305
PD-1035	272(275)	2.4(2.6)	2.3(3.9)	0.07(0.06)	296	317	324

[a] ASTM D 2265-67; [b] Fed. Std. Test Method 321.2 (100 C for 30 hr); [c] ASTM D 1264-63 at test temperature of 38.0 ± 3.0 C; [d] ASTM D 972-56; [e] ASTM D 1403-62; # Data in parentheses are values on greases without the rust inhibitor.

Table 9. TORQUES (G-CM) ON PERFLUORO GREASES[a]

Grease	Inhibited		Uninhibited	
	Starting	Running	Starting	Running
PD-1031 (1.0)[b]..	5074[c]	1770[c]	3540[c]	1925[c]
PD-1034 (3.0)[b]..	4307[d]	1032[d]	4071[d]	2478[d]
PD-1035 (2.2)[b]..	8053[c]	2212[c]	5768[c]	1667[c]

[a]ASTM D 1478-63; [b]rust inhibitor, wt, %; [c]test temperature, -22 C; [d]test temperature, -40 C.

further concluded that the rust inhibitor is nonreactive (alone or in grease mixtures) on contact with the fuels and oxidizers (Tables 3,4) and under impact with LOX at high energy levels (Table 5). The lubricating properties of the inhibited polytetrafluoroethylene-perfluoroalkylpolyether greases are comparable to soap-thickened greases with a marked improvement in extreme pressure properties (Tables 7-9). The lubricants reported here are applicable to all liquid-fueled rocket engines for missiles and space vehicles.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to F. Key, George C. Marshall Space Flight Center, for conducting the LOX impact compatibility tests.

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DISCUSSION

A. J. Babecki, NASA, Goddard Space Flight Center: We use the Krytox oils and greases in a lot of spacecraft applications, such as in instrument bearings, because it has such good lubricating properties, not only with the conventional bearing steels, but also with the various gear materials such as aluminum and austenitic stainless steel. I am a little perturbed by your statement that it causes corrosion. We have had 52100 and 440C steel samples partly submerged in Krytox 143AB for almost two years now and we don't see any evidence of corrosion. Under what conditions does the Krytox fluid cause corrosion and, secondly, since it is supposed to be an inert material, is it the fluid or is it moisture in the fluid that might cause the corrosion?

J. Messina: The fact that you haven't experienced corrosion is puzzling to me. Unless there is an inhibitor in the system, there will be a tendency for water to seep into the metal. Our laboratory tests indicate that Krytox grease will not keep moisture out.

J. E. Stern, NASA, Goddard Space Flight Center: In Al Babecki's tests, the Krytox has probably been dehydrated. The bearing has been submerged in a significant quantity of fluid which precludes attack by oxygen or moisture in the air. Do you have any experience with the corrosiveness of the Krytoxes or the Montecateni fluids in a vacuum environment?

J. Messina: No, we have done no work in that area.

N. Glassman, David Taylor Naval Ship Research and Development Center: What inhibitor are you using?

J. Messina: It's montmorillonite clay which is encapsulated by means of the dimethyloctadecylbenzyl ammonium compound and then to which sodium nitrite is added.

N. Glassman: Is the sodium nitrite a solid in this particular case?

J. Messina: Yes, so is the other component.

N. Glassman: What are the operating conditions of the bearings when this grease is used?

J. Messina: The bearings were run at 3,000 rpm under very low loads.

THE ROLE OF COATINGS IN THE PREVENTION OF EROSION DAMAGE

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ABSTRACT

Among the various methods available for protection against cavitation erosion, elastomeric coatings offer great potential. However, adhesion failures, tearing, and substrate mismatching are some of the problems to be solved for a successful application of protecting coatings. Basic studies in understanding this problem includes stress-wave interaction analysis, controlled experiments with a vibratory cavitation erosion apparatus and the generation of high strain data with the help of a Hopkinson pressure bar apparatus. It is hoped that such a coordinated approach would lead to the design and development of successful coating systems.

Keywords: Adhesion; cavitation; coatings; design charts; elastomers; erosion; Hopkinson pressure bar apparatus; impedances; mismatching; stress wave interactions; substrates; tearing; vibratory apparatus.

Cavitation erosion is a serious problem in high speed flow systems including high performance ships. It is characterized by the formation of vapor bubbles at low pressure regions. This is called inception of cavitation. Following the inception process, the cavitation bubbles grow to their maximum sizes in the low pressure regions and collapse violently when they are carried into high pressure regions. If these bubbles collapse on or near the solid surface, the collapse pressures may be strong enough to erode the material. Currently there are two theories of bubble collapse; both have some experimental and theoretical support. One is the spherical collapse mechanism in which the bubble is assumed to collapse symmetrically maintaining its spherical shape throughout the collapse time. The collapse energy is transmitted back to the material in the form of a short range shock wave causing damage. The other mechanism assumes that the bubble collapses unsymmetrically producing a high speed jet which impinges on the solid surface causing material erosion.

It has been observed both in laboratory experiments as well as in service that these bubbles erode even the strongest material in relatively short durations depending upon the intensity of bubble collapse. In a rotating disk screening test, common propeller materials such as manganese bronze, manganese-nickel bronze and nickel-aluminum bronze would erode at a rate of about one sixteenth of an inch in 72 hours. This corresponds to about 8 inches per year rate of erosion.

The material, at the same intensity of erosion, would erode one eighth of an inch in only 3 hours. Epoxy glasses possess at least two orders of magnitude less erosion resistance compared to other structural materials. Reinforcements would improve the resistance slightly. It is essential to develop suitable protection techniques for avoiding cavitation erosion problems in high speed systems. Elastomeric coatings offer good potential as protective coatings. An epoxy-glass disc coated with a neoprene coating exposed to cavitation erosion performed well for more than 72 hours; whereas it would have been eroded completely in less than 3 hours.

However, there are a few problems associated with the application of protective coatings to the substrate. For example, the response of a viscoelastic coating-adhesive-substrate system to the dynamic bubble collapse pressures is a fairly complex phenomenon. Several coating-substrate parameters enter into the analysis. Depending upon the specific bubble collapse intensities and coating systems, several failure modes are possible.

If the relaxation times are smaller than the bubble collapse durations and if the bubbles collapse violently enough, the coatings erode in a brittle manner. On the other hand, the coatings can fail by tearing. Even before tearing and/or erosion is initiated, the adhesive or the substrate might fail. Adhesion failure, crushing, spalling and scabbing have been observed in cavitation erosion as well as in rain erosion. In order to understand the conditions under which these failures are initiated, an elementary wave propagation model has been developed. With the help of this model, the stress-wave interactions may be calculated. Depending upon the complexity of the coating system, one may use a computer for calculating the stresses within the multi-layered system.

From such calculations, design charts have been developed for selecting the suitable coatings and adhesives for specific substrates and intensities of cavitation. In spite of the elementary nature of this theoretical model and of its assumptions and limitations, it offers some practical results that can be used by materials' engineers developing coating systems for erosive environments. A typical application of the analysis was demonstrated through the use of the vibratory cavitation erosion apparatus. A test specimen is vibrated at 20 KHz producing a stream of cavitation bubbles in a beaker of water. The coated substrates are exposed to this stream of bubbles. The intensity of erosion may be controlled through the amplitude of vibration and the test specimen distance.

One of the coating systems tested failed in brittle mode within 30 minutes. With the guidance of the analysis, another coating system was selected specifically for this application which lasted more than 32 hours. Judicious combination of theory and experiments led to a significant improvement in performance from 30 minutes to 32 hours. The same coating that performed well for 32 hours would fail in less than 3 hours if it were used on the wrong substrate as a result of wave reflections caused by impedance mismatching. Further research is needed to establish such practical approaches.

DISCUSSION

H. Ravner, Naval Research Laboratory: Did you use only water as a substrate?

A. P. Thiruvengadam: Yes, we used sea water and laboratory tap water.

P. Weinberg, Naval Air Systems Command: What is the effect of moisture on the polymer protective coatings on the composites?

A. P. Thiruvengadam: Just exposure to salt water may reduce the adhesion strength by 5 to 10 percent. Exposure to cavitation will further reduce the adhesion strength. These results are based on laboratory measurements.

SOLID FILM LUBRICANT TO PREVENT FRETTING DAMAGE IN TITANIUM ENGINE COMPONENTS

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ABSTRACT

An air drying solid film lubricant originally developed for applications in the field has been found to be an excellent coating for prevention of fretting damage in titanium-titanium mated parts. This film, designated AFSL-41, is composed of molybdenum disulfide (MoS_2) and antimony trioxide (Sb_2O_3) carried in a methyl phenyl silicone binder. The film air dries without heat through the use of a curing agent, an amino-alkyl alkoxy-silane. A brief description of the formulation is presented along with laboratory evaluation data comparing its anti-fretting performance with other candidate materials. The performance on titanium led to its consideration as a candidate anti fretting coating for titanium components. The various screening tests used to determine anti fretting properties are described along with results which led to AFSL-41 being selected for full scale engine tests. Current use of AFSL-41 by two gas turbine engine manufacturers on a production basis is discussed and the types of applications (over 100 in one engine) are described.

Key words: Curing agent; fretting; silicone resin; solid lubricants; titanium; wear.

Introduction

The development of an air drying solid film lubricant for application in the field has been described previously (Reference 1, 2, & 3). Early in the development it was found that this formulation exhibited excellent performance on titanium substrates. This led to its evaluation as an anti-fretting coating for titanium. The purpose of this paper is to briefly describe the formulation, its evaluation and use as an anti-fretting coating for gas turbine engine components.

Formulation

The composition of the film was based on a silicone resin system developed for air drying paints by Stout (Reference 4). This system possessed good thermal stability (over 500°F) and the ability to cure without heat. The solid lubricant materials selected for the film was an optimum mixture of one part MoS_2 and one part Sb_2O_3 by weight. This mixture was used in a lubricant to binder volume ratio of 70:30. The resin binder is a mixture of 90% by weight polymethyl phenyl-siloxane and 10% gama amino-propyltriethoxy silane. The amino-silane serves as the curing agent to cross link the siloxane resin. The film can be applied by brushing, dipping, or spraying and is effective in film thicknesses of 0.0002 to 0.0005 inches. The film air dries to the touch in 5-10 minutes and cures ready for use in six hours.

Evaluation

The laboratory screening tests used in developing and optimizing the formulation have been discussed in detail previously and will not be presented here (Reference 1). Initial fretting testing of AFSL-41 was conducted by an engine manufacturer in a bench fretting machine described in detail elsewhere (Reference 5). The contact is depicted graphically in Figure 1 and consists of a spherical tipped specimen (A) 0.5 inch in diameter with a ground spherical tip of 4.0 inch radius. This serves as one half the specimen combination and it rubs in a reciprocating motion against the flat, horizontal surface of a stationary specimen or platen (B). The platen is gripped in a holder (C) which is, in turn, clamped onto a heavy work table, which may be adjusted vertically for position. The spherical specimen is held rigid at one end of the holder rod (E) which is connected to a vibration exciter capable of 10 to 2000 cps vibration frequencies. The vibrator exciter of this arm is equipped with a flat spring, flexible joint which permits slight vertical movement of the arm for leveling purposes. A guided push rod assembly (H) aligned directly above the test sphere and platen combination allows the normal load to be varied over a wide range. The horizontal reciprocating motion of the spherical specimen on the platen surface produces a wear scar, the cross-sectional area of which, taken at the plane of maximum wear penetration relative to the unfretted surface is a reliable measure of material removal and thus of relative fretting wear. Figure 2 compares the fretting wear results of AFSL-41 using two different manufacturers silicone resins to that of unlubricated titanium and a silver film. These results were encouraging and prompted further tests more closely simulating the actual application. These tests were carried out on a coated compressor blade dovetail section of an actual compressor wheel. The blade was subjected to

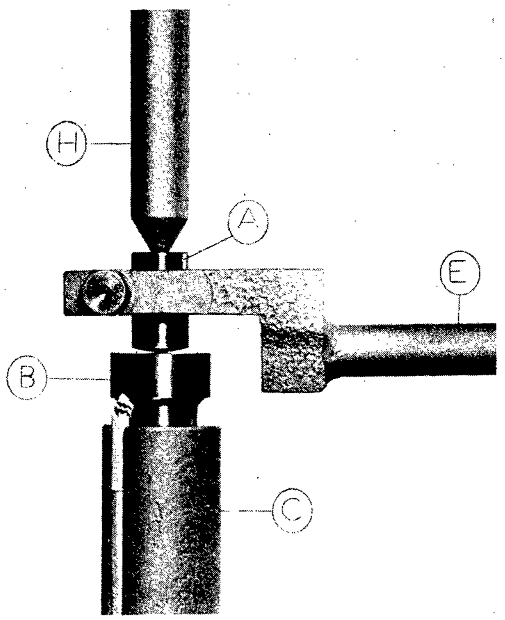

Figure I Fretting Test Geometry

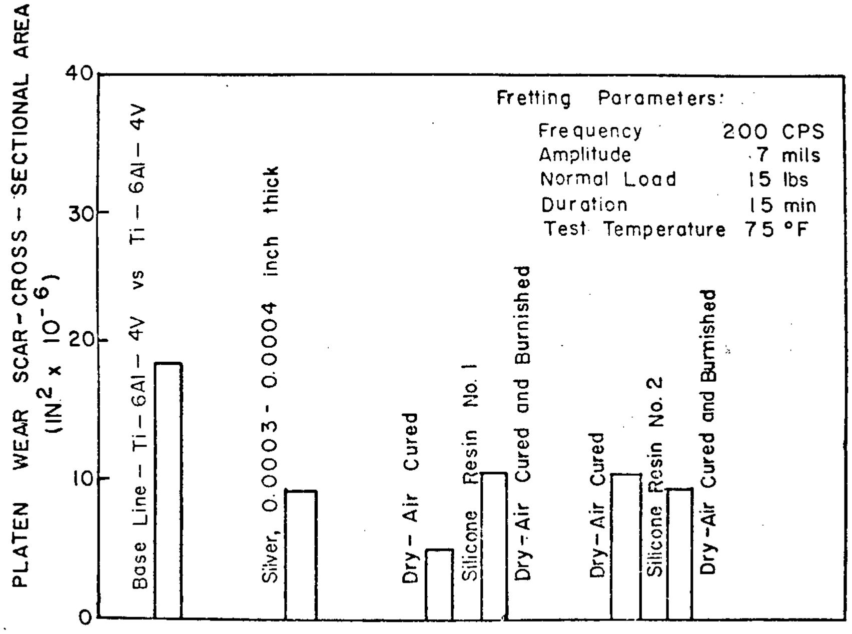

Figure 2 Fretting Wear Test Results

vibrational testing under a stress of ± 3700 psig in the 2nd bending mode. The condition of the coated dovetail section after 12,000,000 cycles is the criteria for these tests. Table I compares the performance of AFSL-41 to other coatings evaluated in this test.

Table I Compressor Blade Fretting Test

Material	Cycles	Fretting Resistance
AFSL-41 on Blade only	12×10^6	Excellent
Blade Silver Plated Over Nickel Flash	12×10^6	Good
Blade Silver Plated Only	12×10^6	Fair
Flame Sprayed Cu-Ni-In	12×10^6	Excellent
Graphite Varnish on Blade	4×10^6	Poor
Graphite Varnish on Blade and Slot	4×10^6	Poor

The final evaluation was conducted in full-scale engine tests with side by side comparison with silver coated compressor blades. A number of first and second stage compressor blades were coated with AFSL-41 and assembled into the wheel. The first engine test ran for 187 hours before shutdown for other causes. Upon teardown, inspection of the blades showed them to be in excellent condition and at least comparable to the silver coated blades. The only evidence of change was some initial burnishing of the bonded film and considerably longer operation could be expected. The blades were reinstalled in the engine and subjected to a second full scale engine test. This test ran for 202 hours giving almost 400 hours of total time on the coating. The blades were removed, examined, and found to be in excellent condition. The coating was intact and was well burnished. There was no evidence of film damage which indicated the loading was uniform. It was concluded that AFSL-41 was comparable to silver in preventing fretting damage to the dovetail surfaces of the compressor blades.

Another engine manufacturer became interested in AFSL-41 for its anti-fretting properties on titanium alloys. This manufacturer conducted fretting-fatigue tests on a combined bearing/vibratory load apparatus, shown schematically in Figure 3.

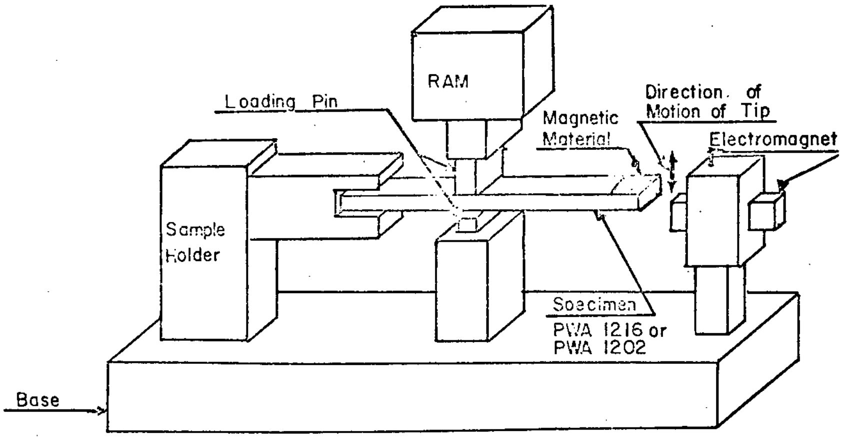

Figure 3 Bearing/Vibratory Load Tester

The test specimen is a bar which is clamped rigidly on one end and passes between two load bearing pins through which the test load is applied by means of a hydraulic ram. The free end of the test bar is vibrated with an electromagnet at a rate of 3000 to 5000 cycles per minute. The coating to be evaluated is applied normally to the test bar although both bar and bearing pins may be coated if desired. The normal test time is approximately 30 hours. Tests were conducted at 600°F and 50KSI bearing stress. Two titanium alloys, Ti-8-1-1 and Ti-6-2-4-6 were used in the evaluations. Many candidate coatings have been evaluated in this test and selected results are compared in Table II. Most of the coatings were able to attain 10^5 cycles before failure and in some cases achieved 10^7 cycles at the lower alternating stress levels.

The conclusions drawn from these tests allowed selection of coatings for further testing and eventual full scale engine testing. A

Table II Fretting Fatigue Tests - Ti-6-2-4-6 pins, 600°F, 50KSI Bearing Stress

Alloy	Coating	Alternating Stress, KSI	Cycles to Failure
Ti-8-1-1	Fel-Pro C-200	60	1.47 x 10^5
		55	1.8 x 10^5
		45	3.5 x 10^5
		35	7.66 x 10^5
Ti-8-1-1	Graphite Varnish	45	2.94 x 10^5
		30	5.1 x 10^5
		25	7.3 x 10^5
		20	DNF*
		20	DNF
Ti-8-1-1	AFSL-41	27.5	6.0 x 10^6
		25	DNF
Ti-6-2-4-6	Fel-Pro C-200	30	1.3 x 10^6
		27.5	DNF
		35	3.6 x 10^5
Ti-6-2-4-6	AFSL-41	30	3.26 x 10^5
		30	2.1 x 10^6
		25	DNF
		25	3.34 x 10^6
Ti-6-2-4-6	Cu-Ni-In	35	5.3 x 10^4
		25	2.8 x 10^5

*Did not fail

prime consideration in the final selection of coatings for production use was cost of the materials and cost of processing. Some of the coatings performed better in the above tests than AFSL-41 but due to higher costs of these coatings AFSL-41 was specified in those applications where it would meet the hardware requirements as determined by final engine testing.

Conclusions

Two gas turbine engine manufacturers have selected AFSL-41 for use on a production basis in their respective engines. Both have issued specifications covering the material and its use in their engine. The TF-41 engine utilizes AFSL-41 in a compressor wheel seal plate application while the F-100 engine now has over 100 different applications ranging from compressor blade roots, disks and hubs, shaft couplings, and ball socket seats to entire bearing assemblies. Further tests are being conducted to find other applications where AFSL-41 can be effectively utilized.

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DISCUSSION

A. W. Ruff, National Bureau of Standards: The behavior of titanium varies considerably with environment. Can you give any details as to the temperature, humidity, etc., in the vicinity of the fretting contact both in service and laboratory conditions?

B. D. McConnell: There were no precautions taken to exclude any moisture or provide any special environment for the laboratory tests.

G. Hurt, Detroit Diesel, Allison Division: Almost all of these engines currently use the technique of air blown seals which means that the engine is filled with atmospheric air. The engine that Bob McConnell is talking about is used by the Navy and the Air Force and is exposed to a salt water environment. The engine does have to be protected and lubricated with this solid film lubricant kind of material. The temperature in the front end is not high--about 100 to 120 F maximum--but further back in the compressor the temperature can get up to 200 to 300 degrees.

A. J. Babecki, NASA, Goddard Space Flight Center: Were the coating thicknesses the same regardless of the technique employed? It seems to me that the coating thickness would affect the performance of the material; that is, if the silicone rubber bonded coating was much thicker than the silver, I would think that that in itself would tend to make the silicone much better.

B. D. McConnell: I can't recall the thickness of the electroplated silver. Most of the other bonded films were in the 0.0002-0.0005 in thickness range.

A. J. Babecki: This may have use in other applications where we are not concerned about fretting, but perhaps with sliding friction or something where there is large amplitude motion. Has there been any testing to determine the quality of the adhesion of the silicone rubber bonded coatings?

B. D. McConnell: This is not a silicone rubber. This is a methyl phenyl silicone which is a fluid. We did not perform any adhesion tests, as such. We ran various formulations under some fairly high loads. How long a film will run under some of these conditions is a fair indication of how well it will adhere. We found that, although this formulation is air drying without any heat curing, the curing agent cross-links the polymer or the resin. The adhesion is equal to or, in many cases, better than a lot of the high temperature polyimide type resins or the epoxy resins. We ran these at temperatures up to 800 F and we got much better high temperature performance.

A. J. Babecki: Would the performance of the coating be similar to or better than MLR-2 or the MLF-5?

B. D. McConnell: Equal to in most cases.

G. Hurt: We had blade failures due to fretting. These failures were eliminated by applying a multilayer coating to the fretting areas. We also use your coating in other locations to prevent galvanic corrosion in the compressor of the engine.

G. E. DeLong, Naval Air Systems Command Representative, Pacific: You said something about 800 F for a turbine blade. The temperature would be a lot higher than that for a turbine blade.

B. D. McConnell: I said that we had evaluated the films in laboratory bench tests up to 800 F and found that this film, although it air drys without any heat cure, has performance equal to or better than many of the heat cured films such as the polyimides, the epoxies and other types of binders.

A STUDY OF SOLID LUBRICATED GEARS AT ELEVATED TEMPERATURES

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ABSTRACT:

An experimental study has been made of the performance of advanced, state-of-the-art solid lubricants applied to spur gears expected to operate to high temperatures in reusable space vehicles (space shuttle). Tests of Inconel 718 gears covered the range 25-482°C in air, and the lubricants studied included MoS_2 in several binders (glass, metal matrix, polyimide, and polyphenylene) and mixed fluoride compositions. All of the combinations demonstrated acceptable wear over portions of the temperature range, but the glass bonded films showed the most promise--particularly at higher temperatures.

Keywords: Fluoride Films; Gears; Molybdenum Disulfide; Solid Lubricants; Wear

INTRODUCTION:

The design of lubrication systems for space shuttle machine elements presents a unique set of problems due to the mission profile of this class of vehicle. The shuttle will be launched in a manner similar to today's spacecraft, and will spend some period of time in an orbital environment. It must then reenter the earth's atmosphere in a configuration that will permit it to maneuver and land as a conventional, though unpowered, aircraft.

The shuttle will thus be subjected to a series of environmental conditions which, taken individually, can be addressed by current technologies, but in combination will make lubrication by conventional means improbable. In particular, several mission-critical mechanisms will be located in areas on the shuttle that can be exposed to extremely high temperatures during reentry. Very high temperature regions will include wing leading edges and the area of the nose ablator. It is clear that special design provisions must be made for nearby mechanisms such as control-surface and landing-gear-door hinges and actuators.

An additional requirement is that the shuttle operate with a high degree of reliability, and be reusable with a minimum of maintenance.

It is particularly important to note that space shuttle machine elements must operate in an environmental regime where considerations of material selection and application are inseparable. It will no longer be possible to design a machine element, then select an appropriate material. On the contrary, the design configuration will be defined to a large degree by the materials available; and because the final design is dependent upon satisfactorily matching such factors as strength, friction/wear characteristics, oxidation resistance, and thermal properties, the choices available to today's designer are severely limited. (For many candidate materials, the necessary information does not exist in the literature and must be generated.) Space shuttle environments require that machine elements and their lubricants be treated as integral parts of a lubrication system, and not be dealt with separately.

It is obvious that reusable space vehicles place unique demands on lubricant systems in terms of environment, life, and reliability. Machine elements such as gears will be repeatedly subjected to an environment which is unique in spacecraft applications: exposure to an oxidizing atmosphere over a wide temperature range. In the past decade, a significant amount of research has been devoted to the development of advanced solid lubricants for use at elevated temperatures. (For a review of the current literature, see Reference 1). While these lubricant systems are, in many cases, highly developed, there is little information on the application to actual machine elements. Thus, the designer of machine elements and lubricant systems for reusable space vehicles is hindered by the lack of knowledge of the limitations of these advanced lubricants when applied to typical machine elements such as gears.

PROGRAM OBJECTIVES:

The purpose of this experimental program was to provide the designer of reusable space vehicles with the data necessary to design critical machine elements and to carry out valid trade-offs in terms of life, weight, reliability, maintainability, power requirements, etc. The air has been to provide data sufficiently general to be useful in the design of machine elements that may not yet be defined, while providing sufficient depth to allow direct use by the designer.

A considerable amount of research and development effort has gone into the areas of high-temperature lubricants and machine-element design. (See, for example, References 2, 3, and 4.) While these prior studies have provided a good baseline, or point of departure, for the present program, they represent the materials state-of-the-art of the mid-1960's. Also, much of the earlier work was not addressed to the unique characteristics of the shuttle environment -- in particular, that certain machine elements must function both at elevated (i.e., reentry) and ambient temperatures, and under pressures ranging from orbital vacuum to sea level atmospheric.

The objectives of this research were to identify and develop lubrication systems for machine elements operating in space shuttle environments, and to characterize those systems to the degree necessary to provide vehicle designers with valid trade-off data, particularly with respect to limiting conditions of wear-life, friction, and material interfaces.

Several advanced solid lubricant systems were evaluated for performance and life when applied to spur gears operated at various temperature levels varying from room ambient to 500° C. Endurance, wear debris-quantity and morphology and failure mode were determined. Based on the selection of the most promising candidate lubricants, a test matrix for gears was set-up and carried out. The gears were fabricated from Inconel 718, chosen for its hot strength and compatibility with some of the solid lubricants. To carry out the gear test program, a new gear tester of four-square design was designed and constructed with high temperature capability. New techniques were devised for determining lubricant film failure in gears.

THE FOUR-SQUARE GEAR TESTER:

The major problem in the design of a gear test machine is in the method of loading the gear teeth with a well-characterized, constant load. In general, there are two methods of accomplishing the task; (1) loading gears against a dynamic load or (2) against themselves. The four-square gear test machine, which was used for the majority of tests on this program, represents the second concept. This configuration offers the advantages of low driving torque, flexibility, simplicity, and capability of running two sets of gears at once. The test machine program requirements and design goals are summarized in Table 1.

TABLE 1. GEAR TEST MACHINE REQUIREMENTS

	Test Requirements	Design Goals
Gear Sample Diameter	.0508 meters	.0508 - .1016 Meters
Tooth Load	5.65 NT-M	1.13-113 NT-M
Speed	100 rpm	0-300 rpm
Temperature Range	21° - 482°C	21° - 927°C
Number of Test Specimens	1 mesh at a time	---
Failure Detection	Yes	Yes

The test machine functions in the following manner (see Figure 1). After installation of the four gears, two on either end, the system is locked to prevent the rotation of the gears using a pin. Then the spring side of the adjustable coupling is released, adjusted to a torque corresponding to the desired tooth load, and relocked to maintain the spring torsion. The system is then released by removing the locking pin and the required tooth load is placed on the gear teeth in both meshes.

The greatest advantage of this system stems from the fact that the spring torque cancels itself through the system and thus the drive motor must work against friction forces only.

Figure 2 shows the layout of the four square tester developed for this program. The gears are attached to a stub shaft and heat dam made from Inconel 718. This material was chosen because of its high temperature strength and corrosion properties. The stub shaft is fastened with eighth-inch spiral pins to a 316 stainless steel drive shaft which is hollowed to provide a heat dam for additional resistance to the flow of heat from the gear face to the shaft bearing.

The shaft support bearings, packed with Andok-C grease, are aircraft-type full complement, thin section ball bearings capable of withstanding 2240 NT radial loads. They are fitted with a face seal on the specimen (hot) side to prevent the lubricant from bleeding and creeping into the hot zone. Each set of shaft bearings is supported by a carbon steel trunnion block. These blocks can be heated to relieve thermal stresses due to radial gradients across the bearing, should these stresses become excessive.

One set of half-shafts is joined by a Thomas Coupling which makes use of stainless steel flex members to provide for angular and parallel misalignment. The coupling also provides a small preload to position the shafts in their trunnion blocks and allow for thermal expansion.

The torsion spring is made from a chrome-vanadium steel alloy. This spring provides the torque load, a light bearing preload, and acts as a flexible coupling. While many four square systems use a torsion bar, this design makes use of a coil spring because of space requirements and the flatter spring rate characteristic of such springs, making control of torque simpler and more reliable.

The adjustable coupling is made from 316 stainless and it serves to lock the gears and provide a means of deflecting the spring by hanging weights from its grooved member. The two members of the coupling are free to rotate relative to each other after the loosening of locking screws. After deflecting the spring, the parts are locked together and that torque is maintained on the test gears.

The gears on the test machine are covered with a transite insulation box that acts as a heat shield to contain radiant energy and provides a housing for the quartz lamps and their reflectors. The temperature of the lamps is controlled with variable transformers.

A failure detection system for lubricant films on the gears is based on electrical conductivity across the gear mesh. To achieve this purpose, the trunnion blocks and the adjustable coupling are electrically isolated with Kapton sheets and with Teflon sleeves around their fasteners.

Shaft stresses due to mechanical and thermal loading are within recommended values for the chosen materials. The heat dams are designed to provide a 380°C gradient when the gear boxes reach 500°C. This is important in maintaining very low radial thermal gradients across the support bearings. Such gradients can bring about closure of the bearing radial play and greatly increased ball loads. Piece parts such as the sprocket, spring, and coupling have safety factors greater than 2. Design goals in general exceeded the test requirements in order to allow for unexpected problems and potential future applications to more severe test conditions.

Figure 2 shows a drawing of the involute, 24-pitch spur gear test specimen used in these tests. All gears lubricated with bonded films are fabricated from Inconel 718, a material chosen for its high temperature strength and compatibility with the AFSL-Class lubricants.

The gear test conditions are as follows:

Stress	684×10^6 N/m^2, Hertzian mean stress
Speed	100 rpm
Atmosphere	Air, ~40 percent R.H.

TEST PROCEDURES:
The gear test specimens were coated with the various lubricant films by the lubricant suppliers according to their procedures (Reference 5). Prior to coating, the gears had been serialized and the run-out maxima marked and indexed with respect to red-line plots. After coating, the gears were inspected visually and stored until use.

The following procedure was followed for all gear tests.

(1) The appropriate pair of gears was mounted on the machine with the run-out maxima properly aligned.
(2) The thermocouple was placed in the shaft of the driven gear.
(3) The mesh was heated to the test temperature. Typically, this took from 5 minutes for 149°C tests to 30 minutes for 482°C tests.
(4) Upon reaching temperature, the test gears were loaded. This was accomplished by deflecting the torsional spring to an equivalent of 40 pounds force by deadweight loading a lever arm attached to the shaft. Once loaded, the coupling was locked and the weights removed. A line was drawn across the coupling interface to aid in detecting any slippage (and hence load relaxation) at the interface.

(5) The wear debris pan was put in place and the electrical conductivity circuitry checked.
(6) The machine was turned on and the 100 ± 5 rpm speed checked with a chronometric tachometer.

(7) During the course of the test, up to three critical parameters were monitored as evidence of failure:

(a) Electrical conductivity
(b) Wear debris-generation rate and morphology
(c) Visual inspection during periodic slow-downs.

FAILURE CRITERIA, THE ELECTRICAL CONDUCTIVITY METHOD:
A major problem in the evaluation of lubricants on gears is the determination of the point of lubricant failure. Solid film lubricant failure and the onset of substrate wear cannot be easily detected by monitoring performance parameters such as torque or by acoustic means. Substrate wear may be measured by the use of master gears or pins and micrometers; however, these methods require that the test be stopped and the specimens cooled to room temperature. The visual inspection of the gears during a brief slow-down is effective but does not lend itself to long-term, unattended operation.

A new method, based upon the electrical conductivity across the mesh, has been developed. This method makes use of the fact that dry lubricant films form insulating or semi-conducting films. If a very low potential, approximately 100 mv, is imposed across a gear mesh coated with an intact film, the circuit resistance remains high and virtually no current flows. When the film wears, allowing metal-to-metal contact, the circuit resistance drops to allow a large increase in current flow.

Figure 3 shows a diagram of the circuit used for these tests. The four-square gear test machine was designed such that each mesh could be electrically isolated. Electrical contact to the machine shafting was made by slip rings. In a typical test, oscillograph traces show a transient run-in condition followed by a period of smooth operation. (Figure 4) When a thin spot in the coating develops, a spike appears--1/revolution (Trace D). Single spikes have been correlated visually with a bare spot on the tooth predicted by the position of the spike in the time domain.

More spikes appear as other teeth degrade, until several dead shorts per revolution are observed. Failure is defined as two or more total shorts accompanied by a generally high level of noise. The test is then continued for 5 to 10 minutes to make certain that lubricant failure has taken place. (AFSL-28 at 482^{o}C repaired itself from a seemingly terminal condition twice before finally failing several hours later.)

Gear lubricant failure detection by this method has two drawbacks. First, the thin or bare spot responsible for the short can be extremely subtle and localized. This technique must be accompanied by careful post-test visual inspection to ensure that a general failure has occurred rather than just an anomalous isolated event on a single tooth resulting from factors not related to lubricant performance. Furthermore, the damage is often difficult to detect and characterize. A second drawback is that MLR-2 and MLR-66 both conduct electricity at temperatures >350°C and, hence, the method may not be applied.

The conductivity method for detecting the failure of dry film lubricants on gears is extremely promising. By determining when the lubricant itself has failed, the method allows the testing of lubricant properties uncomplicated by differences in the wear resistance of the substrate. Thus, much test time is saved and data are obtained that are directly related to the lubricant itself.

TEST RESULTS:

Inconel 718 gears were used lubricated according to the test matrix given in Table 2.

TABLE 2. GEAR TEST MATRIX

Lubricant	Substrate	Temperature			
		70°F	300°F	600°F	900°F
Clevite 300	--				
MLR-2	Inconel 718				
MLR-40					
NPI-425					
AFSL-28					
AFSL-29					

Load = 100 ksi mean Hertz stress; speed = 100 rpm.

Wherever possible in these tests, the failure point of the lubricant film was established by the electrical conductivity technique previously discussed.

Table 3 summarizes the results of the gear tests. Figure 5 shows the comparative times-to-failure for the various lubricants at the three temperature levels.

DISCUSSION:

Gears coated with MLR-2 and MLR-66 at 482° and 316°C, showed a distinct gray appearance at the elevated temperature indicating widespread oxidation. This oxidation was accompanied by a rapid breakdown of the lubricant film. At the higher temperature, AFSL-28 showed a "healing" property not noted in the other lubricants at any temperature. This system made two complete recoveries from what appeared to be a condition of terminal degradation: multiple electrical shorts on several teeth and increased acoustic noise. In general, failure was a rather long process comprising ~25 percent of the life of a gear. It usually began with a short on one tooth that was often due to degradation on

TABLE 3. RESULTS OF GEAR TESTS (100 RPM in Air-684 x 10^6 N /m^2 - Mean Hertzian Contact Stress)

Lubricant	Lubricant Description	Mesh Temp (°C)	Time to Failure (min)	Failure Criterion
MLR-2	0.55 MoS_2, 0.45 Sb_2O_3, Polyimide binder (Ref. 5)	482	13	Visual
		316	195	Conductivity
		149	975	Conductivity
		25	42	Conductivity
MLR-66	MoS_2/Sb_2O_3, Polyphenylene binder (Ref. 6)	482	15	Visual
		316	302	Conductivity
		149	1322	Conductivity
		25	66	Conductivity
AFSL-28	Fused calcium and Barium fluoride mixture, aluminum phosphate (Ref. 7)	482	150	Conductivity
		316	78	Conductivity
		149	43	Conductivity
		25	19	Conductivity
AFSL-29	Fused calcium, barium and magnesium fluoride mixture (Ref. 7)	482	216	Conductivity
		316	93	Conductivity
		149	56	Conductivity
		25	14	Conductivity
Vitrolube	MoS_2, C + glass binder	482	189	Visual
		316	428	Visual
		149	752	Visual
		25	882	Visual

a tooth face that was visible. As the test continued, other failure spots usually remote from the original appeared. Failure did not generally propagate from tooth-to-tooth, as one might expect if failure were due to a geometric anomaly such as excessive run-out.

MLR-66 consistently produced copious quantities of wear debris, at all test temperatures. AFSL-28 and AFSL-29 both produced very little, even at failure. In fact, none of the tests was accompanied by any change in debris generation rate at failure. Only MLR-66 at 316°C showed any evidence of peeling. In this case, peeling took place early in the test and seemed to involve excess lubricant.

The Vitrolube coating appears to yield somewhat better wear results over the temperature range than the other four coatings tested on this program. The coating had a superior wear life at room temperature, and though there was a progressive deterioration in wear life as the test temperature was raised, the wear life at high temperature was at least comparable to the wear life for the fused fluoride films. The wear debris was powdery and particularly voluminous at room temperature with about three or four times as much debris volume as was observed at other temperatures. The wear debris at 149° and 316°C was also powdery but at 482°C, the debris was in the form of flakes. The qualitative wear observations would at first appear to be inconsistent with the data on coating life. However, it is possible that the wear mechanism is changing as the temperature rises. At the lower temperatures, the debris is formed at a much higher degree of subdivision which would make it appear to be formed in greater quantities. It is possibly the agglomeration of very small particles. At elevated temperature, the wear particles resemble the physical state of the material in the lubricant coating. Although some quantity of metal was observed in the debris at 25°C and 149°C, it was more prominent at 316°C and a significant constituent at 482°C .

Failure of the lubricant coating in all of the tests was observed to proceed according to the sequence.

(1) Appearance of evidence of wear at or near the pitch line. This resembles a score mark. Since, ideally, pure rolling occurs at the pitch line, it is difficult to associate this with adhesive or abrasive wear phenomena. It is possible that particles are leaving the coating as a result of cyclic stress (fatigue). At room temperature, the phenomenon is evident after 40,000-50,000 stress cycles.
(2) The occurrence of a dull coloration on the teeth (possibly related to metal oxide formation).
(3) The appearance of bare metal spots on individual teeth.

CONCLUSION:
These fairly limited tests indicate that none of the lubricating films studied are completely satisfactory over the entire temperature range from 25° to 482°C. The maximum cycle life observed at any temperature was about 10^5. The Vitrolube was apparently the best performer at room temperature and at the highest temperature its wear life was comparable to the fused fluoride films. On this basis, it is the most promising candidate gear lubricant studied. It is quite possible that these results could be significantly influenced by more careful control of such variables as film processing, substrate physical and chemical properties, film thickness, and a more elaborate process of film run-in and conditioning.

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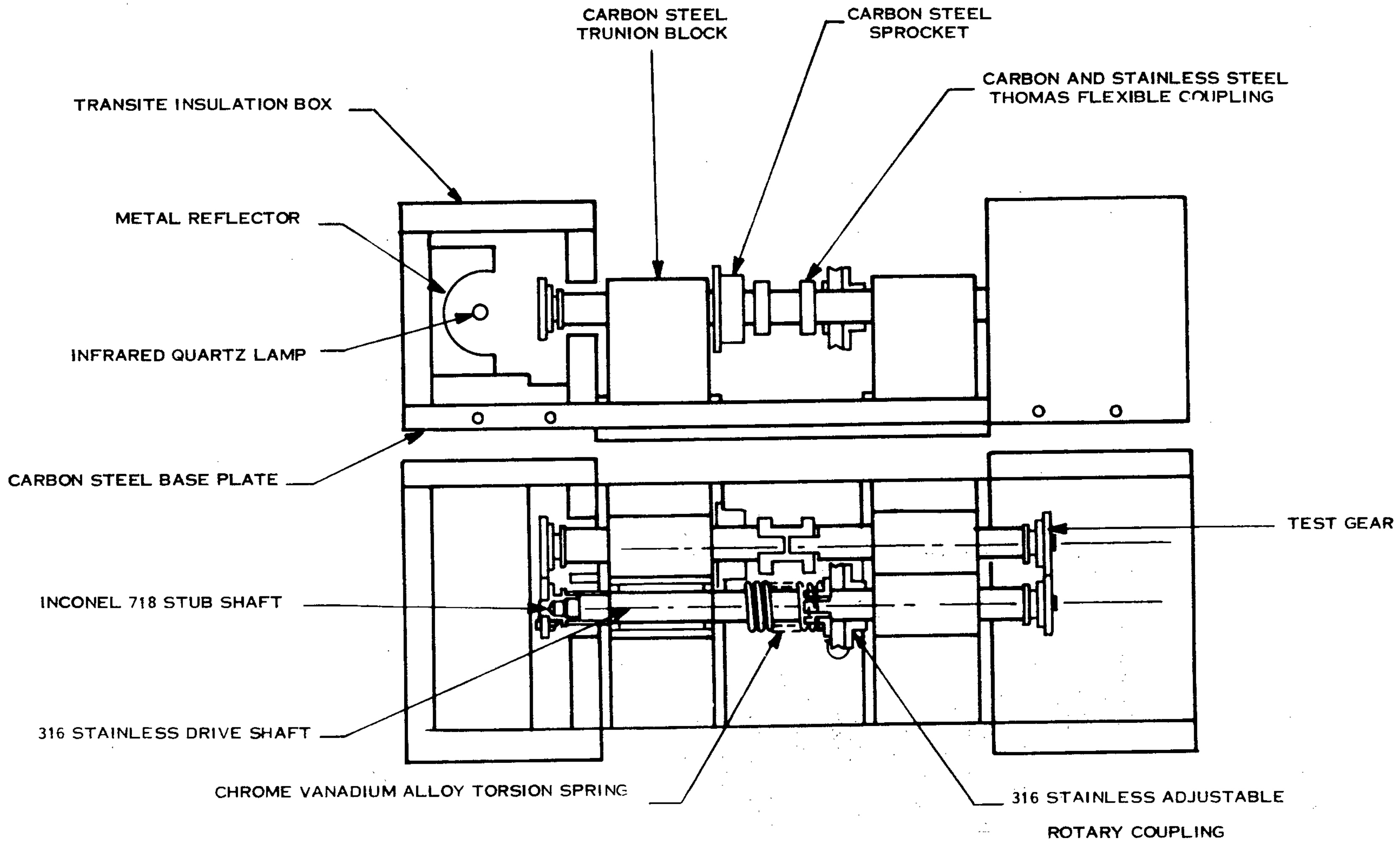
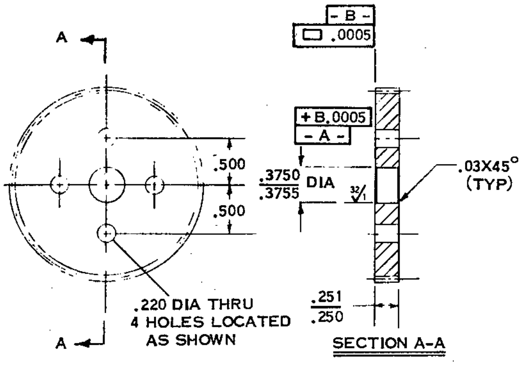


FIGURE 1. FOUR SQUARE GEAR TEST MACHINE LAYOUT

SPUR GEAR DATA	
NUMBER OF TEETH	48
DIAMETRAL PITCH	24
PITCH DIAMETER	2.00
PRESSURE ANGLE (CUTTER)	20°
TOOTH THICKNESS ARC	.06545
BASE CIRCLE DIAMETER	1.8793852
FORM DIAMETER	1.9367
ADDENDUM	.0417
ROOT DIAMETER	1.896 1.884
OUTSIDE DIAMETER	2.083 2.080
MASTER GEAR TOOTH THICKNESS	.06545
TESTING RADIUS	.9999 .9969
TOTAL COMPOSITE ERROR	.0030
TOOTH-TO-TOOTH COMPOSITE ERROR	.0015
MEASURING PIN DIAMETER	.0720
MEASUREMENT OVER (2) PINS	2.1011 2.0982
AGMA QUALITY NUMBER	88



NOTE:
1. BREAK SHARP CORNERS .005
2. REMOVE BURRS .015

FIGURE 2. DRAWING OF INCONEL 718 AND CLEVITE 300 TEST GEAR

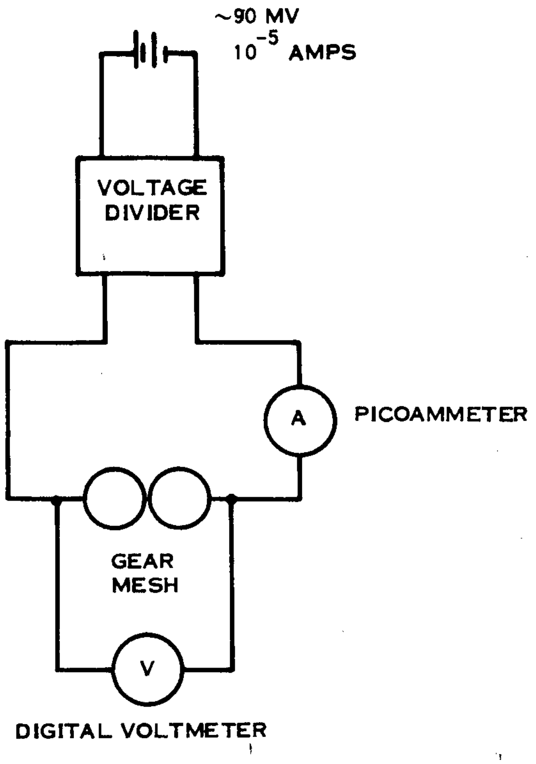


FIGURE 3. CIRCUIT DIAGRAM FOR CONDUCTIVITY MEASUREMENTS

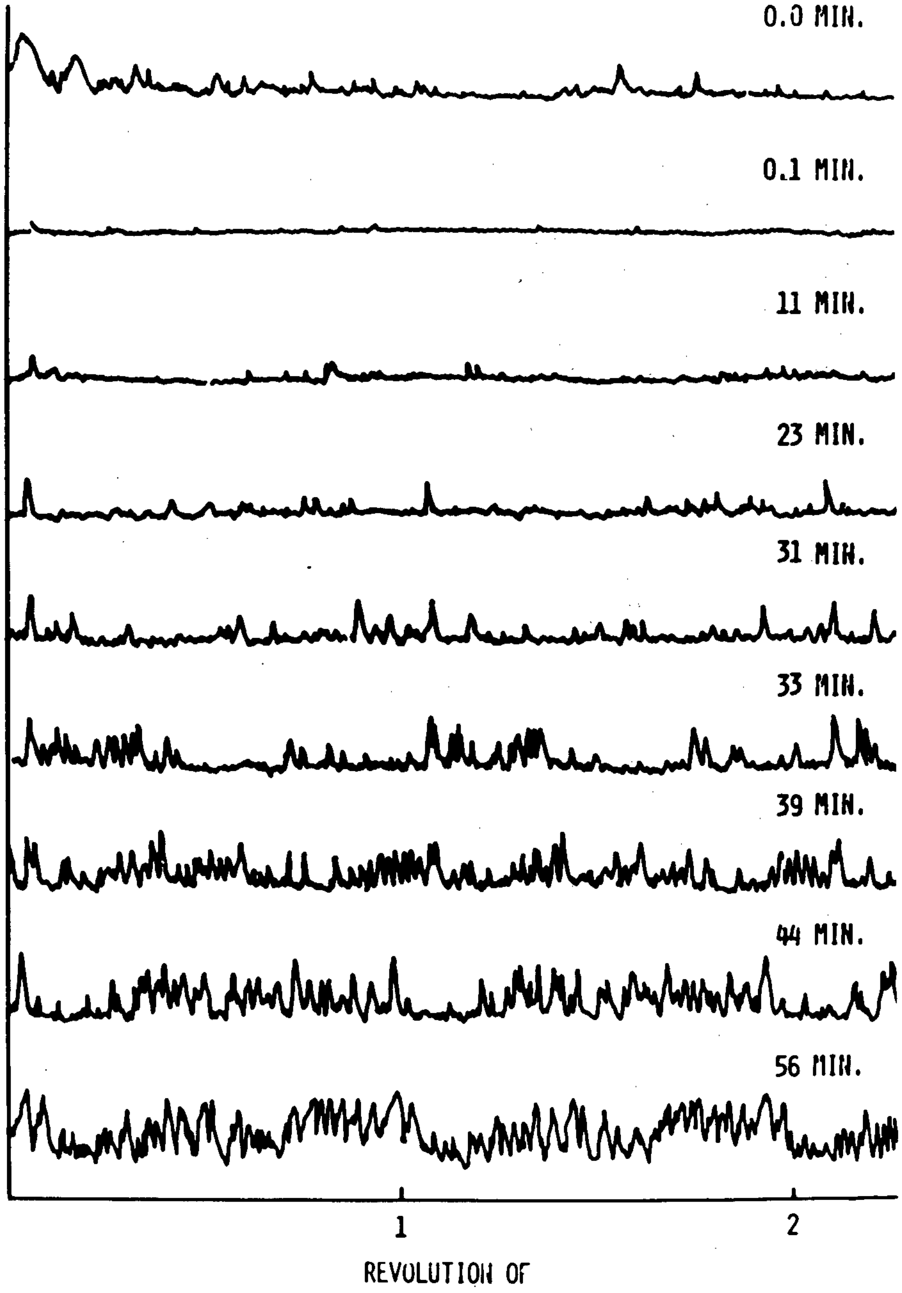


FIGURE 4. PLOTS OF THE ELECTRICAL CONDUCTIVITY ACROSS A SOLID LUBRICATED GEAR MESH AS A FUNCTION OF ELAPSED TEST TIME

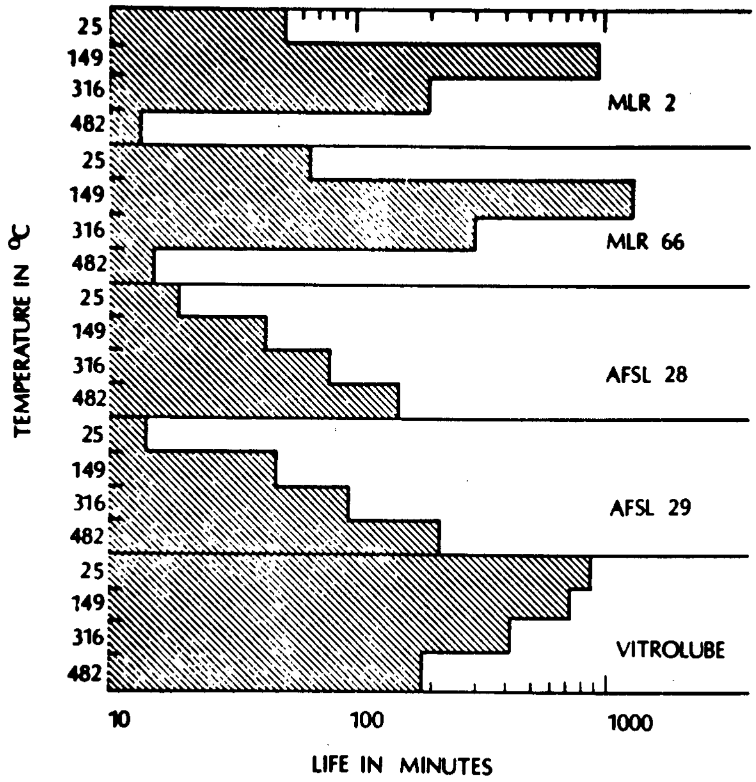


FIGURE 5. TIME TO FAILURE AS A FUNCTION OF TEMPERATURE

DISCUSSION

J. E. Stern, NASA, Goddard Space Flight Center: Did you take the gears apart to examine them?

D. K. Snediker: No, we had a hole in the top of the heat shield. We looked down through the hole and rotated the two axes of the four-square machine. We watched the teeth go by and the positioning of the quartz lamp was such that we got a very good definition of the surface geometry, with shadowing of any irregularities. It turned out to be a pretty good method of visual inspection.

J. E. Stern: You couldn't then identify the cause of recovery?

D. K. Snediker: No, we could not, although I suspect it was probably due to a reburnishing of the lubricant. In all of these gears, there was a lot of solid lubricant powder, a wear debris, that was moved from the area around the pitch line and the areas on the adendum and dedendum immediately adjacent to the pitch line down into the dedendum and up onto the adendum of the tooth. Therefore, there was plenty of lubricant around all of the time, and there was the shower of debris raining down in most cases. There may be a favorable relationship between the oxidation products of Inconel 718 in air and this particular lubricant system that produced a good lubricating film.

J. E. Stern: Did you make any chemical analyses of the wear debris?

D. K. Snediker: No.

A. J. Babecki, NASA, Goddard Space Flight Center: In an LFW-1 tester you can accurately determine what the Hertzian contact stress is. But in the case of the gear tester, I do not see how you can really determine this stress because of the out-of-roundness of the gears. I imagine that there is a pretty high Hertzian pressure. Is that correct?

D. K. Snediker: I think we are talking about less than 200,000 psi mean Hertzian contact stress.

A. J. Babecki: Would that be somewhat variable as the gear rotated?

D. K. Snediker: For this grade gear, it would be somewhat, but not terribly, variable.

A. J. Babecki: As wear progresses, is the loading on the gears somehow continuously adjusted to take care of this wear so that there is a constant Hertzian stress or does the stress diminish as the wear progresses?

D. K. Snediker: One of the reasons we wanted to stop the test before we began to wear the tooth itself was to avoid this problem. We did not wear the teeth. After the initial run-in period, which lasted only a couple of minutes, there was a relatively thin equilibrium film and I do not think the conformity of the contact changed much. There may have been a 10 to 20 percent change, but we tried to avoid the problem by testing the lubricant film rather than the gear.

A. J. Babecki: From your experience, would you put more credence in the LFW-1 test data than in the actual gear data for evaluating coating performance?

D. K. Snediker: I usually trust real machine element data provided it is carefully developed and the variables are controlled more than test machine data. With solid lubricants, every case is different and one must be very careful about generalizing. The list of lubricants we evaluated resulted from some generalizing on the basis of test machine data and some of them turned out to be perfectly dreadful. The Fel-Pro C-200 that Bobby McConnell used performed pretty well in a journal bearing for something that can be purchased at the hardware store. We tried it on a gear and it did not work.

SESSION IV

CHEMICAL

COATINGS

Chairman: Lt.R.S.Miller
Office Of Naval Research

VAPOR DEPOSITION OF WEAR-RESISTANT COATINGS

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Vapor deposition processes by which a variety of wear and environment resistant coatings are applied are described. Criteria for selecting coating/substrate systems are discussed in the light of economic and technological changes.

Several examples of vapor-deposited, wear-resistant coatings are given in addition to specific examples of commercial applications.

Keywords: Chemical; coating; deposition; vapor; wear

Broadly speaking, the term vapor deposition describes any process by which a solid is formed, the materials having arrived at a surface as a gas. Thus, the "pack cementation" processes by which parts are chromized or silicided are properly termed, vapor deposition, since coating materials move from particles within the pack to the parts by vapor transport. Similarly, certain atmosphere heat-treating processes are included since the atmosphere contributes to the product as in nitriding and carburizing of steel parts.

Physical vapor deposition (PVD) has expanded rapidly in recent years as dramatic improvements in vacuum technology have been made. Thus, PVD has moved beyond the classical vacuum coating by vaporization of metals to include reactive sputtering, ion plating, etc. However, it is with chemical vapor deposition that we wish to deal here.

Chemical vapor deposition (CVD), like vacuum coating and electrodeposition, is a molecular forming process; that is, the deposit is built up atom by atom or molecule by molecule. The starting material in the case of CVD is a gaseous compound which is caused to react chemically at the substrate to form the deposited material. The substrate is usually heated to activate the process, although sometimes it may be cooler than the source temperature, thus establishing a new equilibrium that causes the gas mixture to give up some of the desired product.

CVD is applicable to the formation of a wide variety of materials - metals, alloys, semiconductors, carbides, oxides, nitrides, sulfides, silicides, and borides. These are deposited by the appropriate chemical reaction of gases or the vapors of volatile compounds such as fluorides, chlorides, bromides, iodides, hydrides, hydrocarbons, organometallics, and carbonyls.

PROPERTIES AND CHARACTERISTICS

Table 1 lists some of the useful chemical reactions. The required substrate temperatures cover a wide range, depending upon the chemical reaction used, and the desired structure of the deposited materials, which is a sensitive function of temperature. The greatest flexibility in the choice of reactions lies in the range of 800 C and above. The requirement in many cases for processing at elevated temperature, coupled with the use of gases or vapors which can be corrosive, poisonous, inflammable, or air-sensitive are disadvantages of the process which tend to limit its use. Fortunately, CVD has a number of advantages, in that it:

(1) Provides superior throwing power - unique adaptability to coating in crevices or the inside bores of small tubing

(2) Has unique adaptability to coating particles in a gas-fluidized bed

(3) Provides dense coatings of some materials not readily obtained by other methods

(4) Is adaptable to the vapor forming of difficult-to-fabricate materials

(5) Provides for control of coating structure - ranges from epitaxial growth, through large grained, small grained, and amorphous, to powder

(6) Can yield products of high purity or controlled composition; feed materials readily purified; doping readily accomplished and controlled; alloying feasible in some cases

(7) Can be carried out in simple equipment if operation at atmospheric pressure is feasible.

The limitations of CVD relate primarily to the availability of reactions that will proceed at temperatures compatible with the nature of the substrate. Not only must the substrate be chemically inert toward the coating atmosphere at the required temperature, but for coats thicker than in the micron range, the coefficients of thermal expansion of the coating and substrate must be reasonably closely matched. Otherwise, the stress resulting from differential contraction of the coating and substrate on cooling from the coating temperature may well be sufficient to rupture brittle coatings. If possible, the choice of configuration should leave the coating in compression to minimize the effect of differential thermal expansion.

Generalizations concerning CVD processes are dangerous, in that each reaction has its own characteristics. To successfully apply CVD processes other than those that have been developed to the "cookbook" stage, one must have an uncommonly good understanding of the reaction chemistry, the compatibility of the materials involved, and the mass transport characteristics of the gas stream.

For example, a coating may be satisfactory on the upstream surfaces of the substrate, while eddies at a downstream surface may provide enough dwell time of the reactant gases to result in "snowing out" or powder, either of the coating material or of some intermediate solid product. Thus one generally seeks to:

(1) Maximize chemical compatibility

(2) Minimize thermal expansion differentials

(3) Maximize uniformity of exposure of substrate to the reactant gases.

APPLICATIONS

To present a better understanding of the state-of-the-art of CVD and the potential for future applications, several examples will be given of instances in which modern technology actually depends on CVD.

Titanium carbide coatings on cemented carbide tool inserts, on stamping and punching dies, and on thread guides, etc., are having a significant impact on industry. Wilhelm Ruppert, while at the Metallgesellschaft was the first to recognize and apply the superior wear resistance of CVD TiC coatings on metal working tools (1-5). Although work on the TiC coating of cemented carbides was started in 1958 and proposed in a 1960 patent (6), it was not until 1968 that sintered hard carbide tools with TiC coatings were applied on an industrial scale, as reviewed by Hinterman, Gass, and Lindstrom(7).

Figure 1 compares the wear resistance of TiC coated and uncoated cemented carbide tool inserts after machining 600 in ^{2} to a depth of 0.2 inch at 0.018 in /rev from AISI 4340 steel at a surface speed of 500 ft/min. The wear resistance in this case is attributed to the decrease in friction between the hot chip and the tool surface just behind the cutting edge. Such inserts are coated by reaction of titanium tetrachloride with methane in a hydrogen atmosphere at about 1000 C in a retort similar to that shown in Figure 2.

Figure 3 shows several thread guides coated by the same process.

Figure 4 shows a wide variety of parts coated by CVD. This photo is by courtesy of the Laboratoire Suisse de Recherches Hologeres (Research Laboratory of the Swiss Watchmaking Industry)(8).

Through the years CVD work at Battelle has most often been oriented toward achieving environmental protection of parts. That is, offering improved resistance to heat, corrosion/erosion, radiation damage, etc. However, certain recent work is of interest in relation to wear studies. In this connection, hardness of candidate coating materials is of prime interest. Table 2 is a compilation of hardness data for selected materials. Table 3 gives the chemical reactions by which six of these materials are deposited. The choice of coating materials is limited by stability of a particular substrate in the coating atmosphere at the required temperature. In addition, suitable match of coating to substrate thermal expansion is required to retain an integral coating upon cool down and subsequent thermal cycling. Limited accommodation to thermal expansion mismatch may be made by limiting the thickness of the coating to a few micrometers.

On an experimental basis coatings are applied in two ways. Figure 5 illustrates the application of a coating by heating the substrate by induction in a stream of reactant gases.

Figure 6 shows a graphite tube coated with about 80 mils of silicon carbide in such a system.

Figure 7 illustrates the coating of parts while immersed in a bed of fluidizing particles.

Figure 8 shows steel parts coated by the fluidized bed process.

Figure 9, 10, 11, and 12 are photomicrographs of typical coatings in metallographic cross section.

FUTURE

Turning to a brief consideration of cost, it is apparent that CVD processing is quite expensive for small numbers of pieces because of the necessity for custom design of equipment and processing procedures. Nevertheless, the processes are already in commercial use for highly specialized parts, as well as for large numbers of small parts, such as coated carbide tool inserts. The CVD processing industry has grown slowly but at this stage continued growth seems assured

(1) As specific procedures are devised and rendered more reliable

(2) As the unique advantages of CVD become more widely known

(3) As industrial economics place increasing premium on extended servicibility.

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(8) Brochure of Laboratoire Suisse de Recherches Horlogères, Rue Brequet 2, Neuchâtel 7, Switzerland.

TABLE 1. REPRESENTATIVE CVD REACTIONS

$$Ni(CO)_4(g) \xrightarrow[100\text{-}250\ C]{} Ni(s) + 4CO(g)$$

$$WF_6(g) + 3H_2(g) \xrightarrow[300\text{-}800\ C]{} W(s) + 6HF(g)$$

$$CH_4(g) \xrightarrow[900\text{-}2300\ C]{} C(s) + 2H_2(g)$$

$$4BCl_3(g) + CH_4(g) + 4H_2(g) \xrightarrow[1000\text{-}1500\ C]{} B_4C(s) + 12HCl(g)$$

$$2AlCl_3(g) + 3CO_2(g) + 3H_2(g) \xrightarrow[700\text{-}1500\ C]{} Al_2O_3(s) + 3CO(g) + 6HCl(g)$$

TABLE 2. COMPARISON OF MICRO-HARDNESS VALUES

Material	Hardness, H_s Knoop, 100 g load
Steel, AISI A-6	≈350
Cr_7C_3	1700
WC	1700-2400
TiC	2000-2750
SiC	2200-2950
B	2900-3300
W_2C	3000
Al_2O_3	3000
TiB_2	3000
B_4C	3800-5000

TABLE 3. SELECTED CVD REACTIONS BY WHICH WEAR RESISTANT MATERIALS ARE DEPOSITED

$$TiCl_4 + B_2H_6 \xrightarrow[700\text{-}900\ C]{H_2} TiB_2 + 4HCl + H_2$$

$$2AlCl_3 + 3H_2O \xrightarrow[700\text{-}1500\ C]{H_2} Al_2O_3 + 6HCl$$

$$4BCl_3 + CH_4 + 4H_2 \xrightarrow[1000\text{-}1500\ C]{} B_4C + 12HCl$$

$$TiCl_4 + CH_4 \xrightarrow[1100\ C]{H_2} TiC + 4HCl$$

$$SiCH_3Cl_3 \xrightarrow[1100\text{-}1300\ C]{H_2} SiC + 3HCl$$

$$Cr(C_9H_{12})_2 \xrightarrow[450\text{-}500\ C]{} Cr_7C_3 + \text{cumene fragments}$$

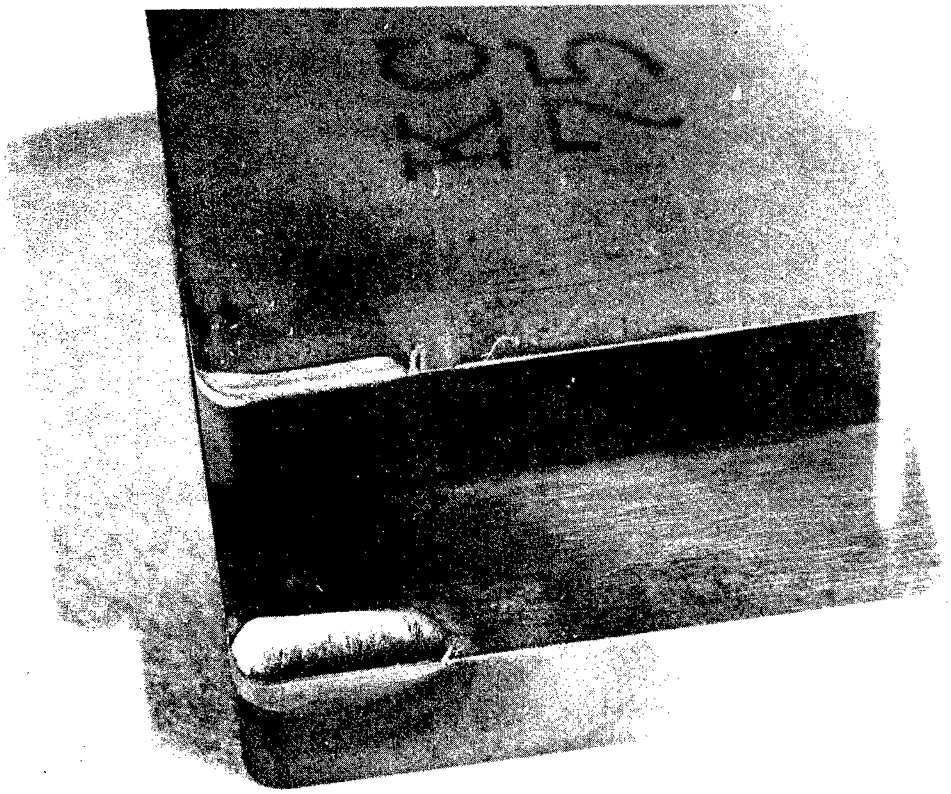


FIGURE 1. COMPARISON OF WEAR OF COATED (ABOVE) AND UNCOATED CEMENTED CARBIDE TOOL INSERTS (Courtesy Kennemetal, Inc.)

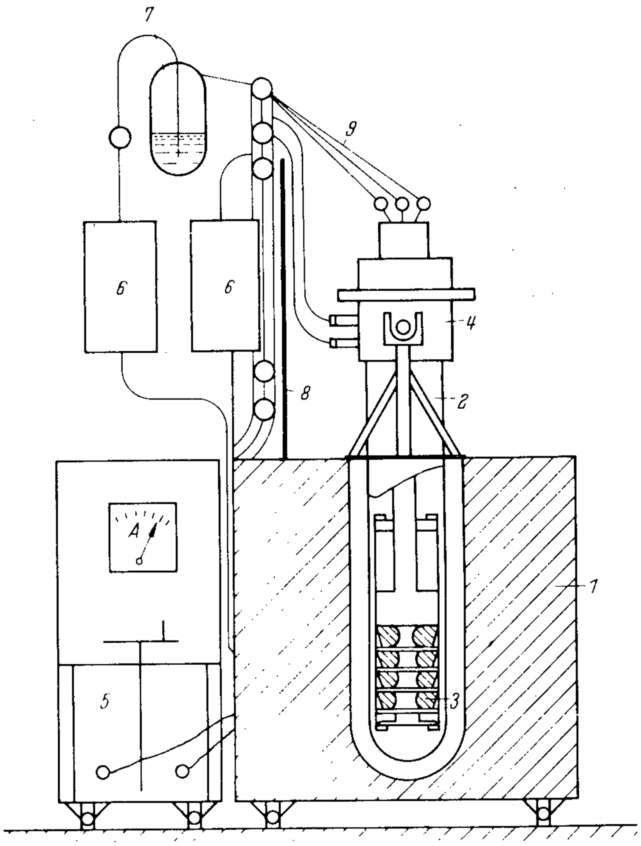


FIGURE 2. CLOSED RETORT FOR TiC COATING: 1-FURNACE, 2-TUBE, 3-PARTS TO BE COATED, 4-COLD FLANGE AND SUPPORT, 5-POWER SUPPLY, 6-GAS FLOW CONTROLS, 7-$TiCl_4$ VAPORIZER, 8-RADIATION SHIELD, 9-GAS PIPING

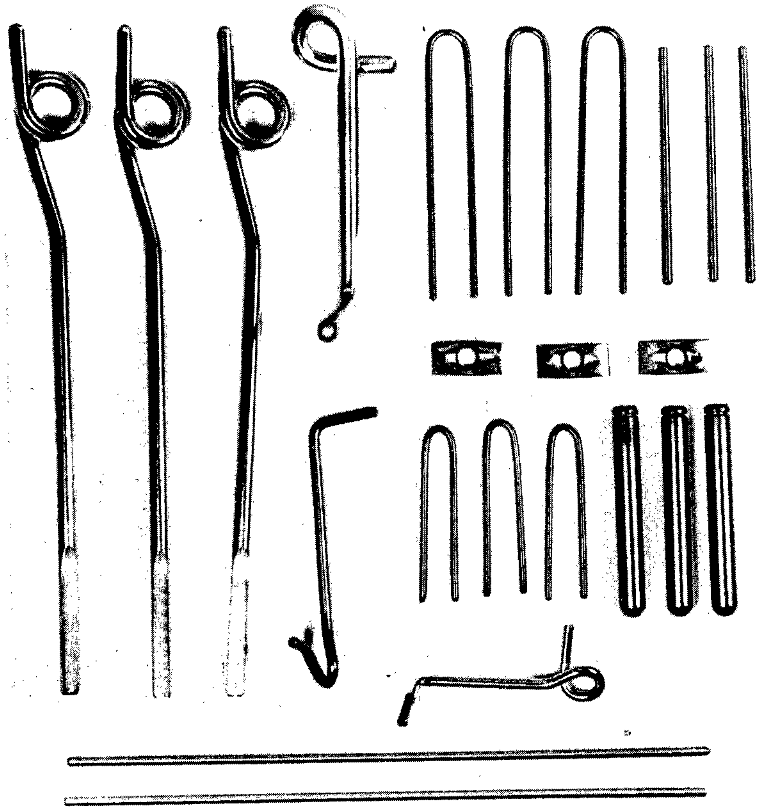


FIGURE 3. TiC-COATED THREAD GUIDES (Courtesy W. Ruppert, Ed. Dörrenburg Söhne)

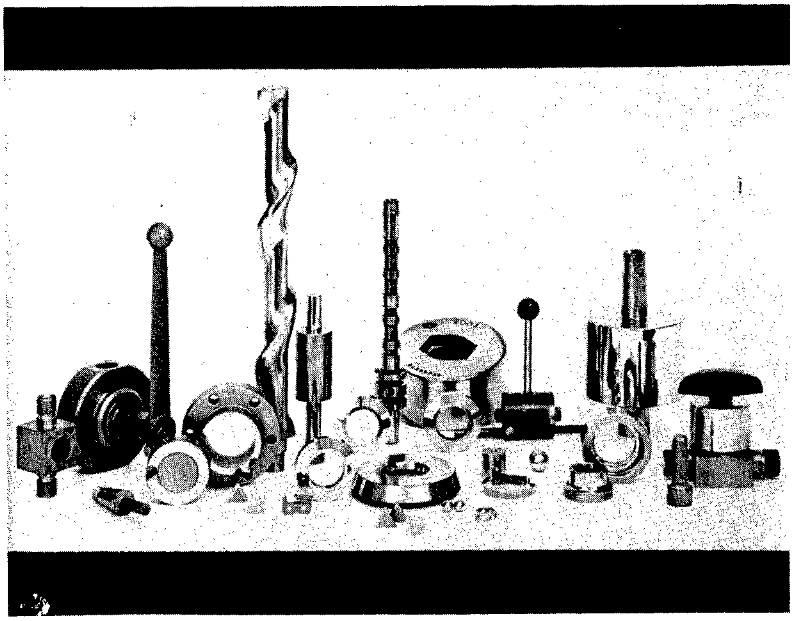
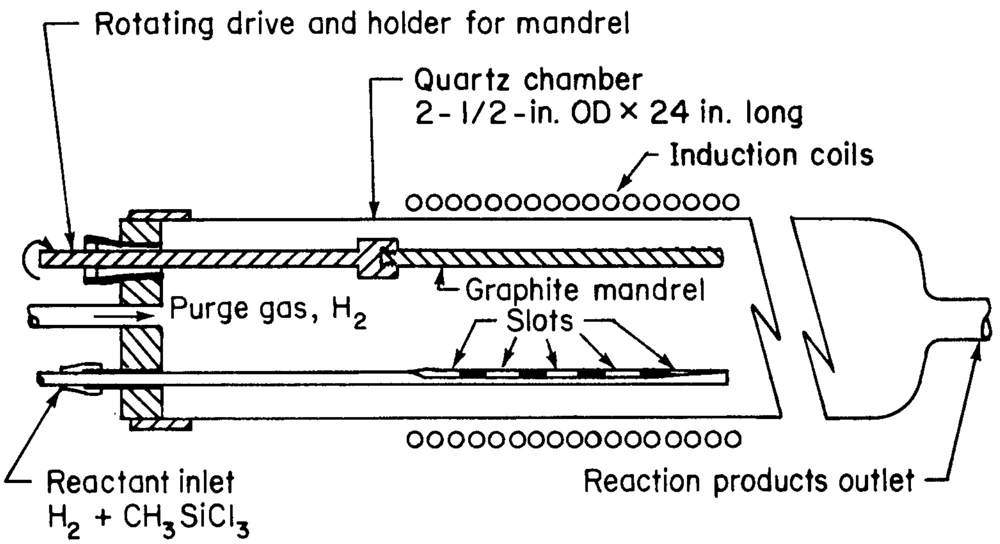
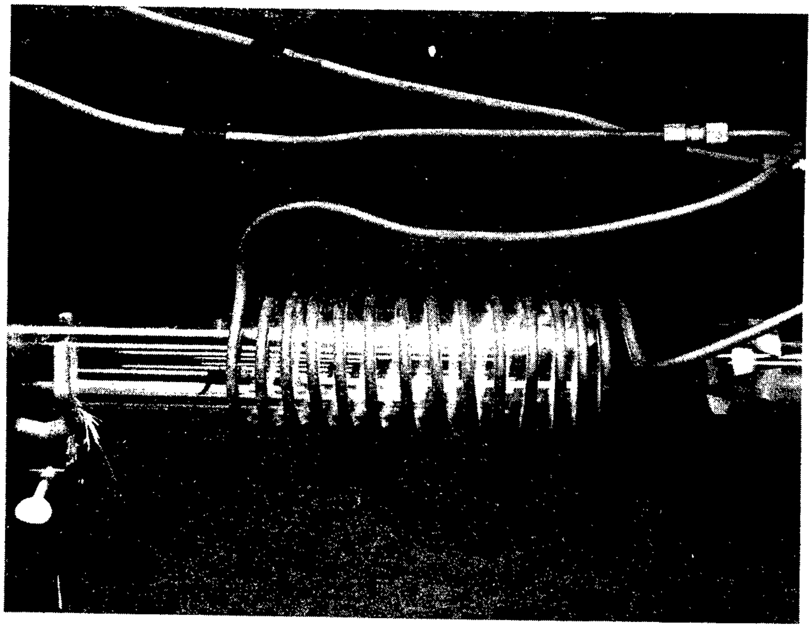


FIGURE 4. VARIOUS CVD APPLICATIONS (Courtesy of Laboratoire Suisse de Recherches Hologères)



Schematic of Coating Chamber



Unit in Operation 2090VD

FIGURE 5. COATING UNIT USED IN VAPOR FORMING SILICON CARBIDE CLOSED-END TUBES

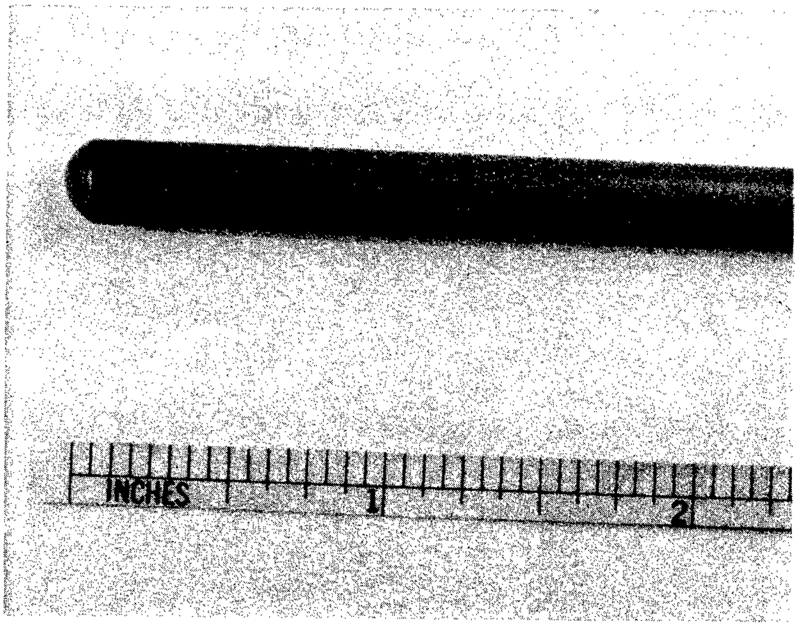


FIGURE 6. PHOTOGRAPH OF GRAPHITE ROD COATED WITH ≈80 MILS OF SILICON CARBIDE

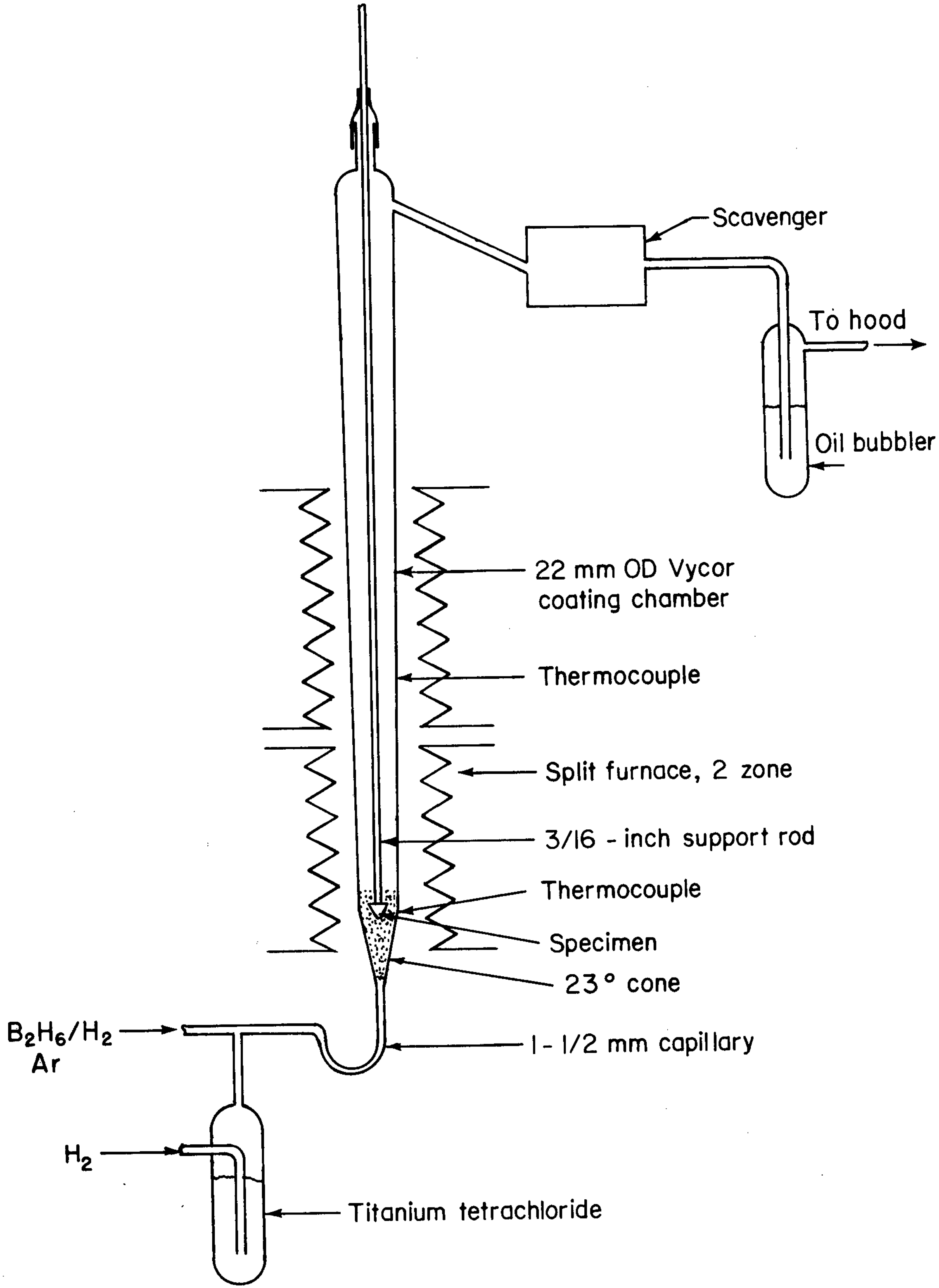
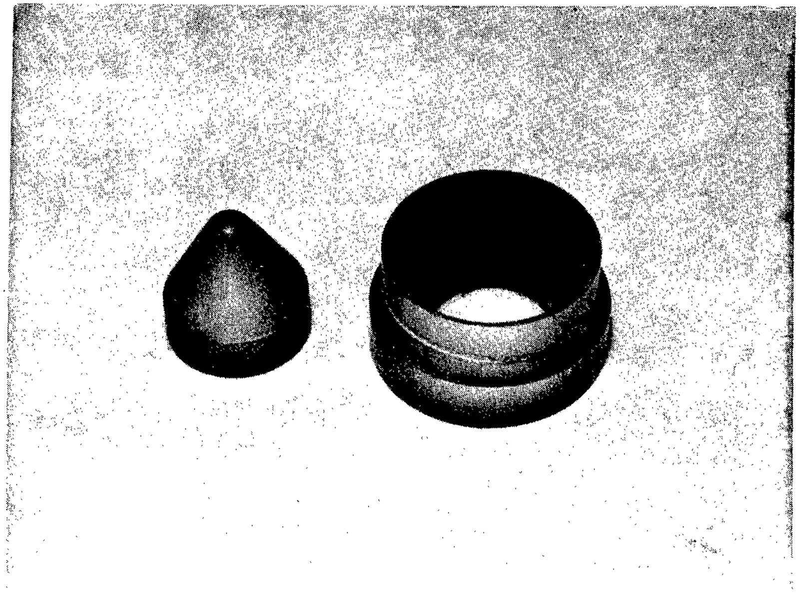
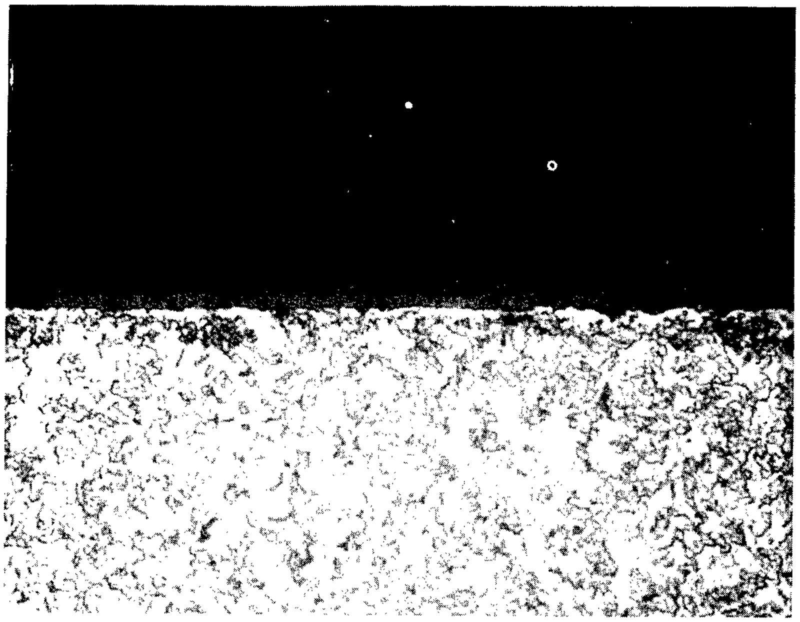


FIGURE 7. SCHEMATIC OF APPARATUS FOR COATING EXTRUSION PARTS WITH TITANIUM BORIDE IN A FLUIDIZED BED



2276VD

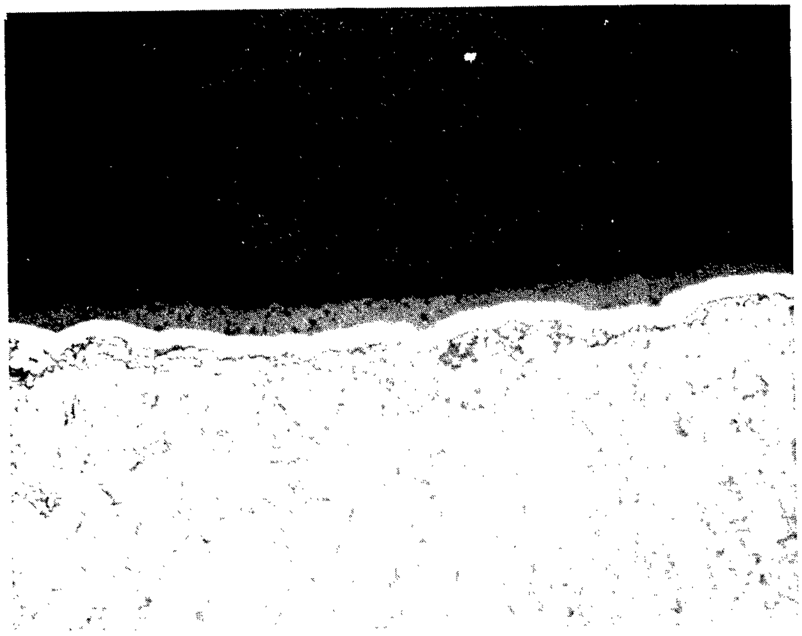
FIGURE 8. STEEL PARTS COATED WITH TITANIUM DIBORIDE BY FLUIDIZED BED PROCESS



1000X

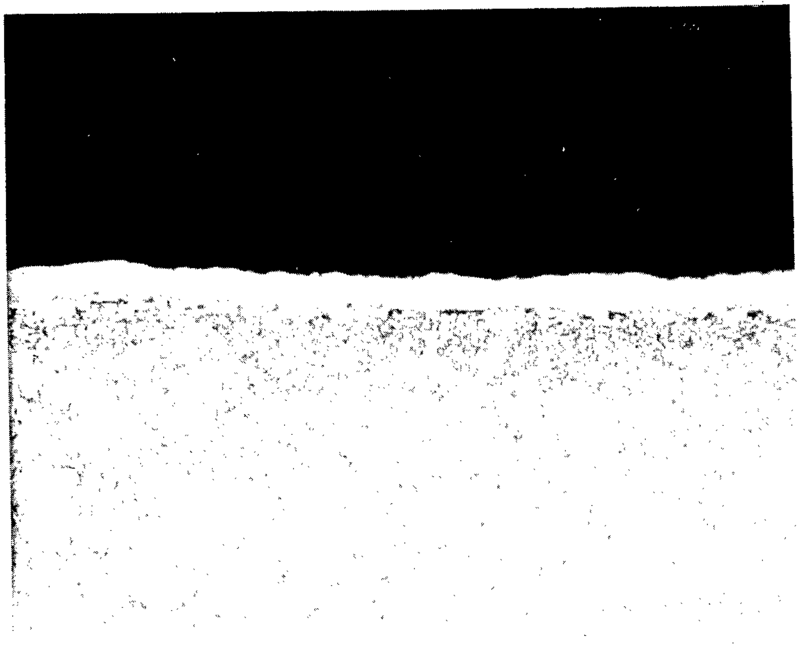
2287VD

FIGURE 9. PHOTOMICROGRAPH OF VAPOR DEPOSITED ALUMINA COATING ON EXTRUSION PARTS



1000X 2285VD

FIGURE 10. PHOTOMICROGRAPH OF VAPOR DEPOSITED CHROMIUM CARBIDE OVERCOATED WITH ALUMINA ON EXTRUSION PARTS



1000X 2286VD

FIGURE 11. PHOTOMICROGRAPH OF VAPOR DEPOSITED TITANIUM DIBORIDE ON EXTRUSION PARTS

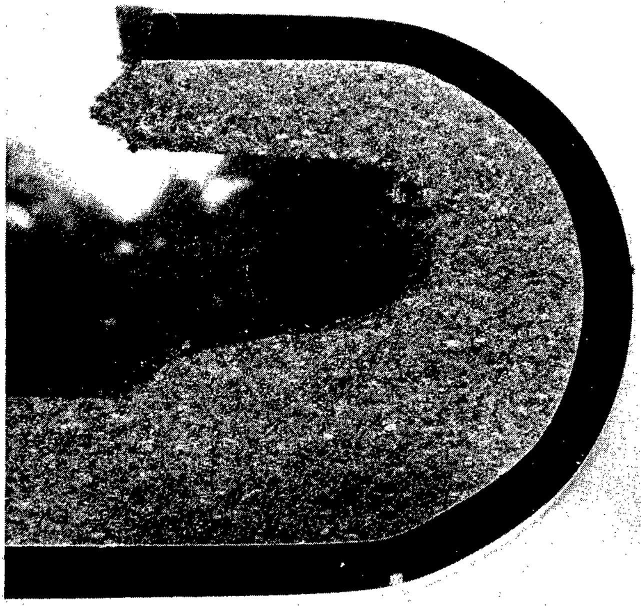


FIGURE 12. PHOTOMICROGRAPH OF VAPOR FORMED CLOSED END SILICON CARBIDE TUBE WITH GRAPHITE MANDREL PARTIALLY REMOVED

DISCUSSION

R. S. Miller, Office of Naval Research: Is the compatibility of crystal structures between the substrate and the overcoat important?

W. J. Wilson: It is a very important consideration. The nature of the substrate in this particular coating operation is probably even more critical than in other types of coating operations. However, if we can use the fluidized bed approach, we ordinarily get frequent renucleation by the impingement of particles on the substrate. Therefore, the crystal nature of the substrate is not so important. If an extended surface is not bathed in a bombardment of particles, then the substrate is very important. This sometimes results in very large crystals which is normally a grave disadvantage.

P. Weinberg, Naval Air Systems Command: Can this technique be used to coat the rollers in bearings with substances such as silicon carbide and maintain satisfactory accuracy and tolerances?

W. J. Wilson: Yes, the fluidized bed technique is ordinarily used to put this material on a symmetrical part such as a bearing. The control of thickness is good from our frame of reference. If better control of thickness is necessary, a bearing of this kind can be ground to a very close tolerance, but the cost could be great. Generalizations are dangerous until one determines the thickness of coating that is required and the nature of the substrate. If a ceramic substrate can be used for the bearing and if the proper sphericity can be obtained, then a bearing of this kind would be feasible. It depends on the individual design.

A. J. Babecki, NASA, Goddard Space Flight Center: It appeared in the micrographs that you showed that there was a good metallurgical bond between the coating and the substrate. I assume from that that there is some kind of diffusion into the substrate as occurs in nitriding. Is that true?

W. J. Wilson: Generally not--in some cases in vapor deposition from a boron atmosphere, borides may produce a diffusion bond. In most cases, reaction of the substrate with the material which is deposited, or reaction with the atmosphere before the deposition, creates a layer which separates the substrate from the deposit. The bonding characteristics of this layer depend upon its nature. Sometimes the bond can be improved with heat treating. More often than not, the layer is a powdery material which ruins the whole operation.

A. J. Babecki: If you want to use one of these hard, wear-resistant coatings, would it be necessary for the substrate to be hard enough to sustain the load applied to it?

W. J. Wilson: Yes, it is of no value to put a brittle, hard coating on the surface of a metal and then expose it to conditions in which the substrate deforms. The coating simply pops off.

R. S. Miller: Can the process be made into a continuous operation?

W. J. Wilson: In some cases, for example the coating of wire, it has been made into a continuous operation. The process is ordinarily a batch operation.

R. S. Miller: What is the general range of exposure times for your process?

W. J. Wilson: The rates of deposition vary greatly. If rapidly moving vapors impinge on the surface, the rates of deposition can approach 20 mils an hour. On the other hand, a relatively stagnant atmosphere surrounding the surface will lead to a very slow deposition rate to get an acceptable product. This condition occurs with diffusion in the gas phase, which is the limiting step.

BARRIER FILMS FOR MINIATURE BEARINGS

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Abstract

Miniature bearings (less than 30 mm O.D.) are employed in large numbers by the Navy in synchro-servo motors, guidance systems and general instrument use. The most frequent cause of malfunction of these mechanisms is bearing lubricant failure; in the majority of instances, failure is induced by migration of the lubricant away from the balls and races, both during storage and service. As a result of long-term basic studies at NRL on wetting and spreading of liquids, a low-energy, non-wetting "barrier film" was developed, which when applied to bearing race surfaces, effectively prevented migration of the lubricant. The increasing use of these films has resulted in major reductions in replacement costs and maintenance, and has significantly increased the reliability of the mechanisms involved.

Keywords: Barrier Films; Bearings, Fluorinated Polymers; Lubricant Migration; Lubricants; Spreading Prevention

Synchro-servo motors and other rotating devices are important components of computers, guidance controls, navigation instruments, fire control systems, etc., and reliable performance of the miniature bearings used in these systems is imperative. There are a variety of failure modes associated with these bearings, including corrosion (rust, fretting), lubricant degradation (oxidation, catalysis, etc.), friction and wear (boundary film failure), and non-wetting of the surfaces. It was shown, however, that the principal cause of unsatisfactory service and storage life of these devices is the migration of lubricant away from the bearings (1). The high costs associated with these failures prompted a Naval Research Laboratory study which has resulted in the development, outlined here, of a novel oil-retaining technique (2,3). Use of this technique has permitted a five to ten-fold life increase of treated bearings.

The tendency of a liquid to spread on a solid surface depends on the relative surface energies of the solid and the liquid; a useful index of wettability of the solid by liquids is the "critical surface tension of wetting", γ_c (4). The value of γ_c is obtained by plotting the cosine of the contact angle (θ) of each member of a homologous series of liquids on a smooth solid surface against the surface tension of those liquids. The intercept of the resulting straight line with $\cos\theta=1$ ($\theta=0^\circ$) is referred to as γ_c (Fig. 1). For example, if γ_c of a

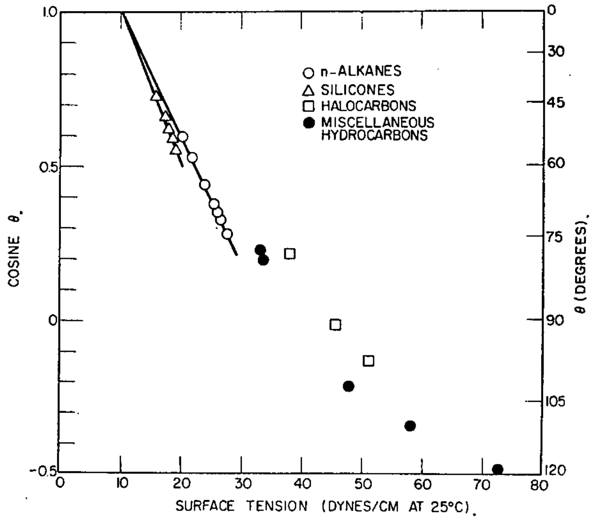
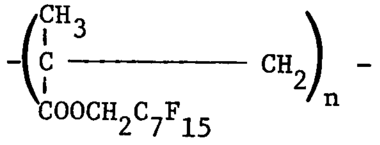


Figure 1: Wettability by various liquids of cast film of polymer



$$-\left(\underset{\substack{| \\ COOCH_2C_7F_{15}}}{\overset{\substack{CH_3 \\ |}}{C}} - CH_2\right)_n -$$

solid surface is 20 dynes/cm, generally any liquid having a surface tension less than 20 dynes/cm will spread on that surface, whereas any liquid with a surface tension above 20 dynes/cm will not spread. Most lubricants have surface tensions between 20 and 60 dynes/cm, and common bearing materials (metals, ceramic, etc.) have γ_c's much higher than 100; lubricants thus tend to readily spread and migrate away from bearing surfaces. However, if a solid surface or film with a γ_c lower than 20 dynes/cm surrounds the lubricated area, it will effectively prevent the oil from spreading past that area.

The lowest γ_c values thus far found are exhibited by solids whose outermost surface layer is composed of closely-packed perfluoromethyl groups (4). A methacrylic polymer containing fully fluorinated side chains which satisfy these requirements was found highly suitable as a non-wetting solid (5) because of its exceptionally low γ_c of 10.5 dynes/cm (Fig. 1). When a thin film of a dilute solution of this fluoropolymer is applied to bearing races, and the solvent permitted to evaporate, a solid adherent barrier coating, approximately 1 micron thick, is formed (2,3). Figure 2 demonstrates the ability of such circular barrier films to retain drops of various lubricating oils (including silicones, diesters, fluorinated diesters, and petroleum fractions) for over 10 years at ambient temperature within the confines of the area circumscribed on a stainless steel plate.

The effectiveness of barrier films formed as described above is dependent on their location, continuity, adherence to the metal substrate, and stability in contact with lubricants over prolonged periods under varied conditions of temperature and humidity. Exposure of barrier films surrounding drops of various oils to 100% R.H. and 50°C does not significantly alter their wetting characteristics, and subsequent drying restores their original properties; immersion in a variety of organic polar and nonpolar liquids for prolonged periods at ambient temperature shows no deleterious effects (6). The coatings are stable to 100°C in contact with various oils; at these higher temperatures, however, the performance of the coatings is somewhat dependent on the type of solvent

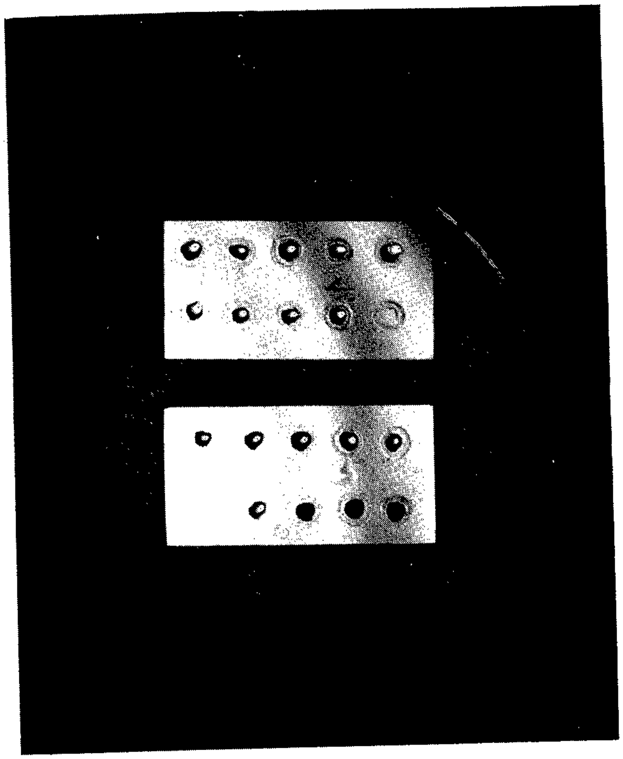


Figure 2: Drops of various lubricating oils on stainless steel contained within barrier films after 10 years exposure at ambient temperatures.

used for the preparation of the barrier films solutions (7). When deposited from a relatively volatile solvent, the film is not homogeneous or sufficiently adherent. Slow solvent evaporation is therefore an important requirement for acceptable barrier coatings, and the most useful solvents have a minimum boiling point of 100°C. Since the polymer is highly fluorinated, only highly fluorinated solvents such as hexafluoroxylene and Freon TF are compatible with it; this is advantageous in that the barrier coatings are not attacked by conventional solvents used in routine cleaning of equipment.

Use by the Navy of barrier films in conjunction with an improved synthetic ester-based instrument oil (8) for prelubricated miniature ball bearings, has resulted in reduced maintenance costs and smaller stockpile requirements; it has been estimated that these procedures have generated an estimated $4,000,000 in annual savings to the Navy. This system is now available commercially and used by airlines for flight safety improvement, by NASA for space guidance systems in satellites, and by the computer industry. It is anticipated that even wider use of the barrier film concept will occur as information about its value becomes more available.

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DISCUSSION

A. J. Babecki, NASA, Goddard Space Flight Center: Can you tell me the difference in surface energy between methacrylic polymers and Teflon?

M. K. Bernett, Naval Research Laboratory: The surface energies for the barrier film and Teflon are about 10 dynes and 18 dynes, respectively. Therefore the difference is 8 dynes.

A. J. Babecki: One of the problems we have in the spacecraft business is the contamination of mirrored surfaces by condensed outgassing of polymeric or organic molecules. I was wondering if a very thin barrier film on a mirrored surface would preclude that sort of condensation?

H. Ravner: I don't think it would preclude condensation on the surface. If condensation occurred on the barrier film, it would ball-up and roll off.

A. J. Babecki: We really don't get enough condensation to form liquid droplets. It is a haze that forms on the surface of the mirror.

H. Ravner: The barrier film would reject the droplets in the sense that they would not spread. They would remain as droplets balled up. What would happen to them afterwards depends on the configuration of the device.

A. J. Babecki: Have you done any work with reflectance measurements?

H. Ravner: No.

G. H. Kitchen, Bell Telephone Laboratories: First, I want to tell you how grateful we at the Bell System are for the years of satisfactory performance we have had with this material. One of the things it has enabled us to do is design around things that creep rapidly such as silicone fluid. I guess I am one of the people responsible for changing from hexafluoroxylene to Freon TF. The reason for the change is that Freon TF is much faster drying than the xylene-hex. We must mass produce these parts; we make about one million contacts a week using this process. Although the xylene-hex is less volatile, its use was questionable with OSHA.

H. Ravner: I appreciate your comment. A too volatile a solvent cannot be used for barrier coatings because the film itself is not physically a good film. It does not adhere well, it is not coherent, it wrinkles up, etc. It can be cut back with a less volatile solvent.

J. E. Stern, NASA, Goddard Space Flight Center: You have used a barrier film with many fluids and lubricants. What has been the reaction of the barrier film to fluorinated lubricants like Krytoxes?

H. Ravner: Barrier films are marginal with the Krytox materials and other fluorinated materials. These are the only materials in which there was some question as to usability.

J. E. Stern: How do you determine whether a treated bearing does not have a film on the raceways or on the balls?

H. Ravner: The bearings must turn with very little applied torque. So they are examined on a more or less routine basis to make sure that, after they are lubricated, they are, in fact, wetted by the lubricant and there is no debris which would foul up their use once they are installed.

G. Hurt, Detroit Diesel, Allison Division: What is the largest size bearing that can be coated?

H. Ravner: A combination of bearing size and speed are the limiting factors in the use of the barrier film. Miniature bearings are lubricated with a very small amount of lubricant, just a couple of milligrams. It wets the surface completely. Because the diameter is small, the centrifugal force that would tend to drive the lubricant away is not as large as it would be for a larger bearing rotating at the same speed. In a larger bearing, there would be liquid lubricant rather than just the thin film applied to small bearings. You can't have too large a bearing with too much lubricant rotating too rapidly. That is why, for the most part, the Navy experience has been limited to precision bearings which are 3/8 in in diameter.

R. G. Brown, David Taylor Naval Ship Research and Development Center: We have run tests that indicate that barrier films are temperature dependent--at least in the 200-250 F range.

H. Ravner: You're absolutely right. I should have indicated that these are not high temperature films. Two hundred degrees C would be too much for them. At about 150 C, they could probably last almost indefinitely. The temperatures to which they are exposed in the applications I was talking about are, for the most part, temperature controlled.

R. G. Brown: In the larger bearing sizes, the bearing itself generated enough heat to cause a rather short life.

P. Weinberg, Naval Air Systems Command: Maybe I can elaborate on one of the operational procedures. After they are coated with lubricant, all the bearings are checked for wetting.

G. H. Kitchen: Nancy Kitchen and Bud Russell of Bell Laboratories reported at last year's ACS meeting on the effect of temperature on the lifetimes of barrier films. At 160 C, the lifetime is measured in days, at 120 C, months, and at 100 to 80 C, something on the order of 15 years. This barrier material is not a barrier against gravity flow of fluids. It was never intended to be that. When a bearing is pumped up and the fluid is heated so that the lubricant is thinned, and there are a number of G's of centrifugal force developed, the lubricant will move over the barrier every time. So all you have to do is use common sense, because it is an excellent material.

POTENTIAL OF SPUTTERED COATINGS FOR IMPROVED GAS BEARING INSTRUMENT PERFORMANCE

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ABSTRACT

Sputtered coatings were applied to I-400 beryllium substrates to determine and eventually optimize their friction and wear performance relative to their potential for gas bearing inertial instrument applications. Solid lubricant-carbide basecoat combinations were sputter deposited under varying conditions of substrate bias and thicknesses. The surface morphology and chemistry of the coatings were characterized prior and after friction and wear evaluations using scanning electron microscopy and scanning Auger microscopy techniques. The friction and wear tests consisted of sliding a 1/8 inch TiC ball under load on the coated disc specimens rotating at 60 RPM. MoS_2-Sb_2O_3 solid lubricants were deposited on TiC, WC and B_4C sputtered undercoats at varying thicknesses and sputtering conditions. The solid lubricant combinations exhibited consistent wear life behavior showing moderate and strong dependency on the substrate bias and solid lubricant thickness, respectively, regardless of the underlying substrate. Correlations between coating chemistry, morphology, sputtering conditions and friction and wear performance are given.

Key words: Antimony trioxide; friction; molybdenum disulfide; spin axis gas bearings; sputtered coatings; surface characterization; wear life.

Introduction

The sputter deposition of solid lubricant materials to a wide variety of sliding, oscillating and rolling machine elements is growing rapidly as a result of the intrinsic advantages of this method of application. (Reference 1, 2 & 3). In comparison to conventional bonded or burnished lubricant materials, this technique offers improved adherence, uniform thickness, higher density, better particle-to-particle bonding, lower debris generation during wear and, of great practical significance, the ability to readily coat curved and complex shaped surfaces. Traditionally, inertial instrument gas bearings have depended on the use of hard, wear resistant materials (oxides, carbides, metals) or boundary film lubricants such as beryllium stearates and chromium behenates to maintain the structural integrity of gyroscope spin bearings surfaces. Laborious machining, lapping, and application procedures, porous coatings. adherence, debris generation and lubricant degradation are problems common to these two approaches.

Scope

Sputtered coatings were applied to I-400 beryllium substrates (circular disc specimens) to determine and eventually optimize their friction and wear performance relative to their potential for gas bearing inertial instrument applications. Solid lubricant - carbide basecoat combinations were sputter deposited under varying conditions of substrate bias and at varying thicknesses. The surface morphology and chemistry of the coatings were characterized prior to friction and wear evaluations via scanning electron microscopy and scanning Auger microscopy. The friction-wear test conditions consisted of sliding a 1/8 inch (3.2mm) TiC ball under a 15 gram load on the coated disc specimen that was rotating at 60 RPM. The sliding velocity was 1.25 in/sec (31.8mm/sec) at an initial contact stress of 108,000 psi (744.0 MN/m^2). All frictional wear measurements were made in air under ambient conditions.

The common methods of determining wear, such as measuring wear scar width and/or depth, were considered insensitive due to the narrow width and thinness of the initial coatings. Coating life was based on the time to reach a friction coefficient of 1.25 x the normal operating coefficient, at which time the experiment was terminated. The onset of failure based on this 1.25 value was characterized by a significant increase in the variation of friction coefficient. The various coating combinations, sputtering parameters, and thicknesses are shown in Table 1. The wear tracks of the coated discs were subjected to post test chemistry and morphology evaluations. As reflected in Tables 1 and 2, phase 1 results involved the evaluation of MoS_2-Sb_2O_3 solid lubricant top coating over I-400 beryllium, tungsten carbide, titanium carbide and reactive TiC undercoats for low and high substrate bias conditions at two thicknesses (for each bias condition).

Phase 2 involved testing of MoS_2 sputtered over TiC with low substrate bias at three thicknesses. (All thicknesses are ± 20% the reported values in Tables 1 and 2)

Results

The MoS_2-Sb_2O_3 top coat combinations exhibited consistent wear life behavior irrespective of the underlying substrate. In all cases, for an identical bias condition, the thick solid lubricant coatings exhibited better than 2 times the wear of the thin coatings. Similarly, for a constant solid lubricant thickness, the low substrate bias yielded wear lifes 1.5 to 2 times greater than the high bias coatings. However, as shown in Table 1, the thickness of the MoS_2-Sb_2O_3 coating was more influential to the life of the coating than the degree of bias of the substrate.

The dynamic friction coefficients correlated directly with substrate bias and wear life performance, yielding lower values with the long wear lives of the low bias condition. However, the change in friction coefficient with thickness of the MoS_2-Sb_2O_3 coatings at a constant bias was insignificant for the various carbide base coated samples and markedly lower for the thicker non-carbide coated (uncoated Table 2) specimens.

TABLE I

WEAR PERFORMANCE OF SPUTTERED COATED GAS BEARING SPECIMENS

Phase 1
MoS_2-Sb_2O_3 Lubricant

Base Coat	Substrate Bias	Lubricant Coating (Microinches) Thin (5.0) Wear time, min.	Lubricant Coating (Microinches) Thick (10.0) Wear time, min.
Uncoated	High	8.9	22
	Low	12.6	49
WC	High	8.5	22.6
	Low	16.3	59.4
TiC	High	*Short Life (2 gm, 5 min)	52.2
	Low	20.8	* Long Life (2 gm, 28 min) No failure
TiC Reactive	High	12.8	26
	Low	28.7	51.4

Phase 2
MoS_2 Lubricant

TiC (Microinches)		Thickness (Microinches) 1.0	5.0	15.0
4.5	Low	.8	7.5	18.3
9.0	Low	1.1	4.7	11.4

*Tested with cylinder instead of TiC ball

TABLE 2

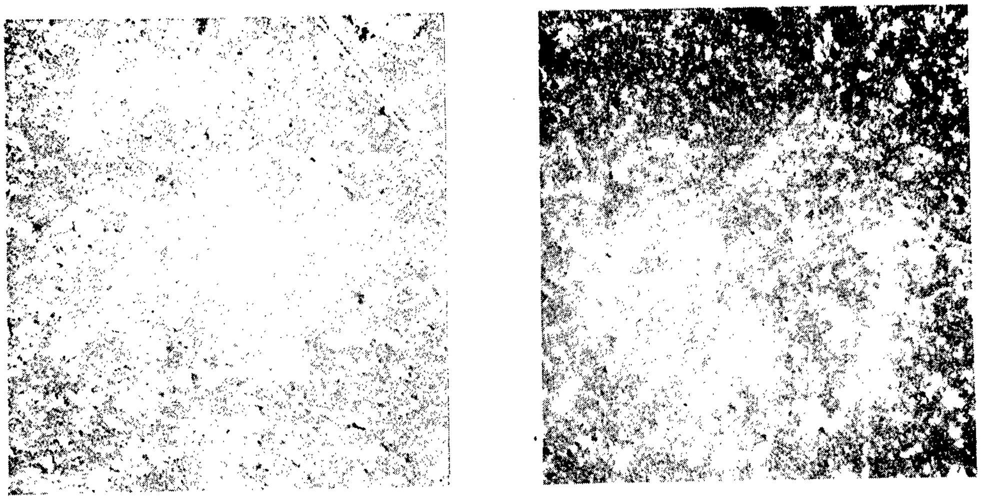
DYNAMIC FRICTION OF SPUTTERED COATED GAS BEARING SPECIMENS

Phase 1
MoS_2-Sb_2O_3 Lubricant

Base Coat	Substrate Bias	Thin MoS_2			Thick MoS_2		
		Friction Coefficients					
		Start	Low	Finish	Start	Low	Finish
Uncoated	High Bias	.187	.093	.200	.040	.029	.072
	Low Bias	.061	.027	.069	.016	.016	.048
WC	High Bias	.125	.112	.144	.128	.120	.163
	Low Bias	.093	.040	.104	.107	.085	.133
TiC	High Bias	(0.14)	(0.05)	(.20)	.213	.173	.218
	Low Bias	.147	.096	.149	(0.1)	(.07)	(0.1) failure
TiC Reactive	High Bias	.181	.149	.203	.128	.100	.143
	Low Bias	.131	.096	.136	.133	.108	.147

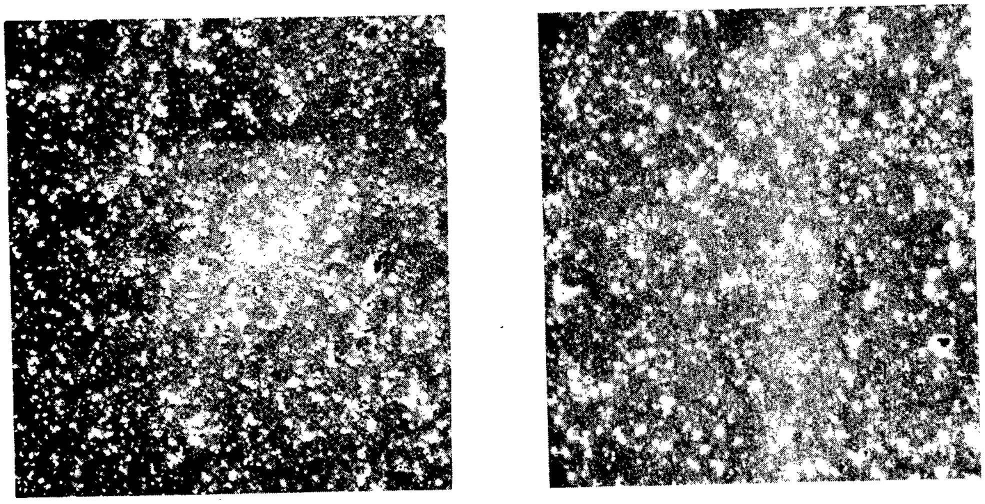
Phase 2
MoS_2 Lubricant

		Thickness (Microinches)					
		1		5		15	
		Friction Coefficients					
TiC (Microinches)		Start	Finish	Start	Finish	Start	Finish
4.5	Low	.245	.693	.277	.501	.256	.395
9	Low	.331	.693	.256	.400	.176	.363



Uncoated - 200 X

WC - 200 X



TiC - 200 X

reactive TiC - 200 X

Figure 1. Thick (10 μ ins) MoS_2-Sb_2O_3 d.c. sputtered on various base coats under low substrate bias

The MoS_2 sputtered coatings exhibited higher friction coefficients and considerably shorter wear lives in air than the MoS_2-Sb_2O_3 coated samples. In contrast to the MoS_2-$Sb_2$03 coatings, however, was the decrease in dynamic friction coefficents with increasing thickness of MoS_2 (Phase 2, Table 2).

Chemistry-Morphology Characterization

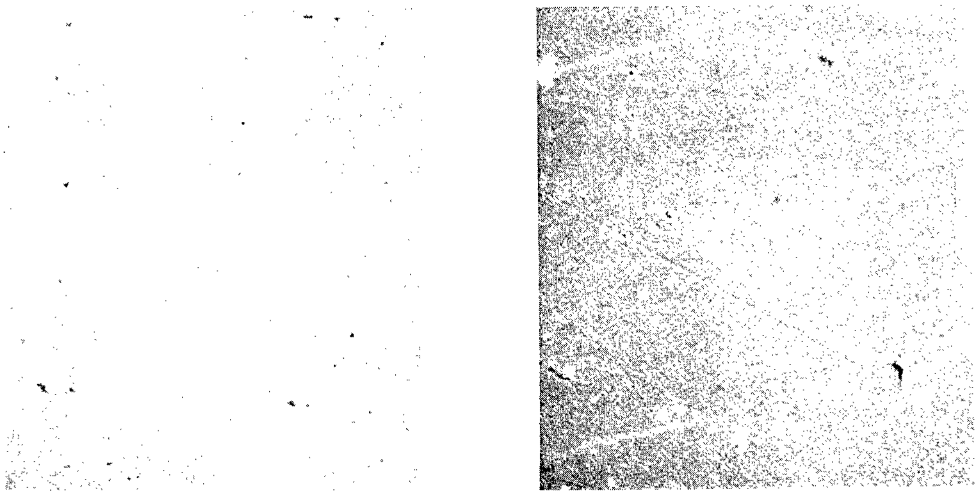
Although the chemistry surface morphology characterization of pre and post wear tested specimens is incomplete, some observations relating the friction-wear performance and the coating chemistry-surface morphology are offered. The consistent friction and wear behavior of MoS_2-Sb_2O_3 discs for identical sputtering conditions irrespective of the underlying substrate is not surprising in light of the similarity in surface appearance as shown by the scanning electron micrographs (SEMS) of Figures 1 and 2. The integrity and smoothness of sputtered coatings in the wear groove area is typified by the SEM in Figure 3. Of special interest is the highly phase separated appearance associated with the low substrate bias condition. Although the precise chemical composition of the lighter reflecting phase in Figure 1 is unknown, energy dispersive x-ray and scanning Auger analyses have shown that the particles contain primarily antimony.

The experimental scanning Auger data is too preliminary to offer an explanation for the lower friction-longer life behavior of highly phase separated low bias condition. The answer, undoubtedly, resides in the slight variations in coating chemistry and adherence that result from sputtering with high and low biased substrates. The marked decrease in friction coefficient with increasing MoS_2-Sb_2O_3 coating thickness (See Table 2, Phase 2) for the uncoated specimens is probably the result of the greater influence of surface asperities between the TiC ball and the beryllium substrate for the very thin solid lubricant coatings.

The higher friction-shorter life and thickness dependence of friction coefficient for the MoS_2 sputtered discs relative to the behavior of the MoS_2-Sb_2O_3 specimens is probably indicative of the greater degenerative influence of moisture in the air on MoS_2 (Reference 4).

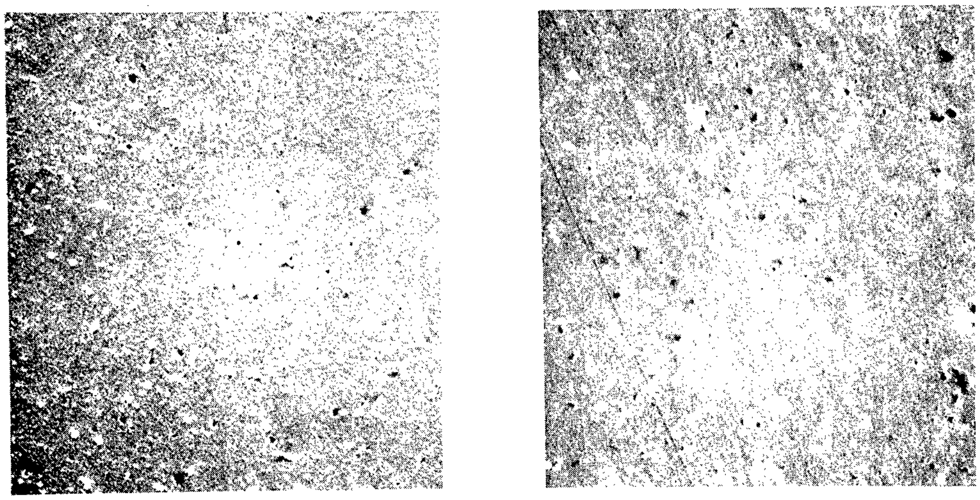
Future Work

Extensive scanning Auger analyses are currently underway to determine the relation between sputtering parameters, coating chemistry-morphology and friction-wear performance. Included is concentration profiling of the individual chemical elements in and outside the wear grooves to determine the mechanical and chemical nature of wear. Future friction-wear testing will include an evaluation of 1) the effect of atmosphere (vacuum testing) on the relative behavior of MoS_2-Sb_2O_3 and MoS_2 specimens; 2) the effect of thickness of TiC and WC hard coating only (TiC and WC); 3) The influence of substrate bias and thickness for the best solid lubricant-carbide coating combination based on the results of 1) and 2) above.



Uncoated 200 X

WC 200 X



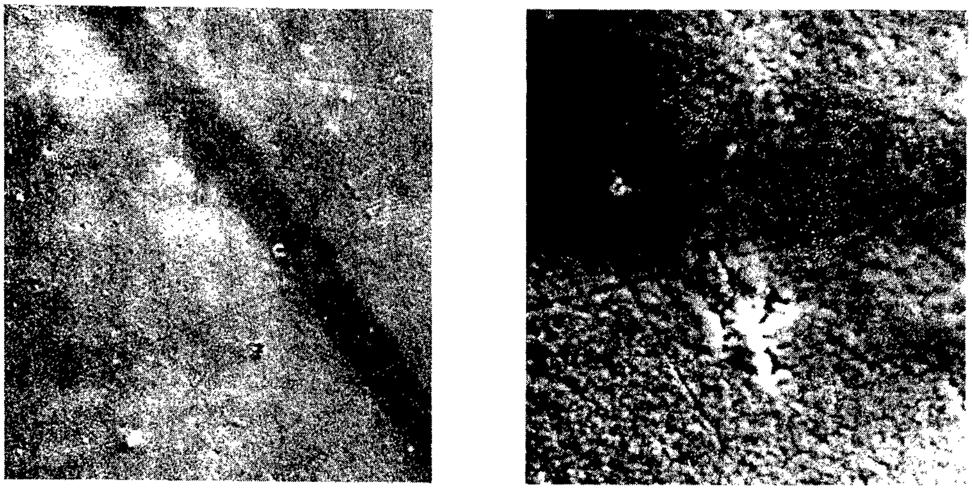
TiC 200 X

reactive TiC 200 X

Figure 2. Thick (10 μ ins) MoS_2-Sb_2O_3 d.c. sputtered on various base coats with high substrate bias.

Conclusions

The capability to reproducibly sputter deposit solid lubricant metal carbide adherent films of high density, controlled thickness and surface properties has been demonstrated. Further, the excellent friction and wear performance of these sputtered coatings under severe sliding conditions in air indicates outstanding potential for spin axis gas bearing applications, especially with the optimization of sputtering deposition parameters.



TiC low bias 200 X

TiC low bias 1000 X

Figure 3. Wear groove on thin (5 μ ins) MoS_2-Sb_2O_3 sputtered coating after 20.8 minutes under sliding friction loading

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DISCUSSION

K. A. Taylor, C. S. Draper Laboratories, Inc.: Do you have any feel for the substrate surface finish as related to the wear test results?

L. F. Fehrenbacher: We didn't vary the surface finish. Other investigators have found that for sputter deposited coatings, wear lives improve with the fineness of the surface finish on the substrate. I'm referring particularly to Mike Gardos' data. The surface finish on these substrates was in the 3 to 4 μin range. I think surface finish would have an effect.

K. A. Taylor: I think it would in the case of the I-400 where the beryllium oxide content is high.

L. F. Fehrenbacher: We put a solid lubricant coating on the beryllium itself and the friction coefficient did decrease as a function of the thickness of the solid lubricant coating. When a carbide undercoat is added to the beryllium substrate, a better surface finish diminishes the influence of the lubricant thickness.

FERROGRAPHY OF POLYMER FORMATION UNDER LUBRICATED RUBBING CONTACT -- AN EXPLORATORY INVESTIGATION

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Ferrographic analysis of lubricant samples from a variety of operational machines and test rigs has revealed the presence of nonmetallic particles. Some of these particles have characteristic shapes and are composed of polymers. For example, under relatively high load nonmetallic particles shaped like rolling pins were formed when a lubricant per specification Mil-L-23699 was used.(2) The same particles were produced when polyphenyl ether was used as a lubricant.(1)

It was speculated that under the conditions of the test the lubricant forms a polymeric film at the rubbing surfaces and it is rolled in the shape of rolling pins when it is pealed off. Furey(3) has shown that polymer films are formed directly on rubbing surfaces and that these films are a factor in reducing wear. Furthermore, it is well known that different additive packages in lubricants meeting the same specifications lead to different wear rates under identical load conditions. It was considered useful to determine if Ferrography could provide further information on the phenomena and to assess if Ferrographic analysis could be used to study the performance of lubricants.

Experimental Procedure

Experiments were carried out utilizing a ball-on-cylinder wear machine described elsewhere.(4) It consists, essentially, of a lathe adapted to hold a 100 mm diameter AISI 52100 steel sleeve between the head and tail stock and a deadweight loading arm holding a 25.4 mm diameter AISI 52100 steel ball.

Tests were carried out on two different ester lubricants at five different loads of 25, 80, 150, 250 and 400 lbs. and at a constant speed of 92 rpm for three hours.

The lubricants designated A and E manufactured to specification Mil-L-23699 contained different additive packages, designed for normal and high loads respectively.

Ferrograms were prepared from lubricants at the end of each test. The wear scars on the balls were carefully examined by optical microscopy immediately after each test and again after cleaning to remove the lubricant. Wear was assessed by the diameter of the wear scar.(Table 1)

Table 1

SUMMARIZED WEAR RESULTS

Load (lb.)	Diam. (mm) of Wear Scar Lubricant A	Lubricant E
25	0.45	0.7
80	---	1.2
150	2.2	1.3
250	---	1.5
400	3.4	1.7

From the results, less wear was experienced at low load (25 lbs.) with lubricant A than with lubricant E, .45 and .70 mm diameter wear scars were seen, respectively. At higher loads there was more wear with lubricant A than with lubricant E, for example the wear scars seen at 400 lbs. load were 3.4 mm and 1.7 mm respectively.

Ferrographic Examination

At a load of 25 lbs. Ferrograms prepared from lubricant A and E showed very few polymer particles. The particles contain small metallic particles embedded in them (Fig. 1). As the load increased to 150 lbs. an increased number of the polymer particles were observed along with a few rolling pins on Ferrograms prepared from oil E, while in the case of oil A the polymer particles were not present but a new type of polymer was present. The polymer was present as a mud like deposit having the appearance of a dry clay bed. This material is referred to as polymud. As the load increased to 400 lbs. oil A produced increased amounts of polymud while oil E produced more of the flat polymer particles along with some deposit of polymud.

Surface Examination

Examination of the wear scars produced under the various test conditions revealed, in the case of lubricant A, surfaces having a relatively rough appearance. However, lubricant E produced comparatively smooth surfaces, even at high load 150 lbs., and revealed patches of polymeric material (Fig. 2). The polymeric material could be easily scored and removed with a cotton swab soaked in organic solvent.

Conclusion

As the difference between the lubricants tested was the additive package, this probably accounts for the different wear performances observed. Apparently the mechanical properties of the friction polymer are influenced by the additive package. In the case of oil E, under heavy load the polymeric film remained intact and was strong enough to be rolled up. Under the same loads, using oil A the polymeric products of friction were of indefinite shape and precipitated as a mud.

Fig.1
Optical photomicrograph of polymeric particles (X1000) on Ferrogram made from oil A at 25 lbs.

Fig.2
Optical photomicrograph of a wear scar (X1120) on the 52100 ball, with patches of polymeric film.

Acknowledgements

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DISCUSSION

W. J. Kelly, Hughes Helicopters: There is a large difference between lubricants A and E. How can both lubricants meet specifications?

A. A. Reda: There is no test to differentiate between them.

W. J. Kelly: We have found that the MIL-L-23699 oil changes color considerably in the atmosphere. It starts out as a light pink color and it will turn dark.

A. A. Reda: The oil that I used turned completely black in about six months.

MECHANICAL FAILURES PREVENTION GROUP

23rd MEETING

The Role of Coatings in the Prevention of Mechanical Failures

List of Registrants

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