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BONDED SOLID FILM LUBRICANTS

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INTRODUCTION

Development of bonded solid film lubricant products began in the late 1940s in the aircraft industry. Their use accelerated in the 1950s with the birth of the national space program and its need for lubricants in outer space subject to wide temperature extremes, radiation, and vacuum and other extreme environmental conditions. In the intervening years, bonded solid film lubricant technology has grown considerably and is now applied to a wide variety of industrial, automotive, military, and of course, aerospace applications.

The subject of solid lubricants is covered in Volume II of this series.[1] Bonded solid film lubricants contain materials with inherent lubricating properties (solid lubricants as covered in Volume II of this series) which are firmly bonded to the surface of a substrate. Major methods of bonding are resin bonding, burnishing, mechanical impingement, and sputtering, with resin bonding having the most commercial significance. Often the environment in which the component is to operate and the required tribological properties affect the type of bonded solid film lubricant to be used. There are three major areas which have to be addressed: first, solid lubricant pigment selection; second, resin or binder selection; and third, ratio of pigment to binder. Once these three areas have been defined, the formulations are augmented with flow agents, corrosion inhibitors, surfactants, and various solvents to ease application and to provide a variety of ancillary properties.

This chapter will explore the different types of bonded solid film lubricants, the different mechanisms for bonding solid lubricants to the substrate, and corresponding performance properties which can be expected.

Design Considerations

In order to select the proper solid lubricant or blend, a number of design parameters must be addressed to properly define the necessary performance properties for a specific application. Examples would be coefficient of friction, load carrying capacity, corrosion resistance, electrical conductivity, temperature, vacuum, humidity, and presence of liquid oxygen or radiation. Once these have been defined, solid lubricant materials can be selected. The most commercially significant solid lubricants are molybdenum disulfide, graphite, and polytetrafluoroethylene (PTFE). However, as described in Volume II, there are many other solid lubricant materials which are used, often as blends with molybdenum disulfide or graphite.

In selecting the appropriate binder, similar design parameters which must be addressed include cure temperature limits, wear life (short-term, long-term), solvent resistance, low VOC (volatile organic component), and substrate material.

Ratio of lubricant pigment to binder also has a significant effect on the overall performance properties. For example:

Low Pigment-to-Binder Ratio	High Pigment-to-Binder Ratio
High coefficient of friction	Low coefficient of friction
Gloss appearance	Dull appearance
Hard	Soft and powdery surface
Durable	Poor corrosion resistance
Good corrosion resistance	

Most products involve a compromise between the extremes to establish optimum results for the conditions imposed. Solvent selection is governed primarily by the resin binder system. Other factors may include flash point, evaporation rate, toxicity, EPA regulations, OSHA regulations, volatile organic components, and shipping and storage. A variety of additives are also used to improve manufacturing efficiency, ease of application of bonded solid film lubricants, and overall performance. Typical additives include dispersants, anti-settling aids, wetting agents, flow agents, corrosion inhibitors, and colored pigments or dyes.

Application of bonded solid film lubricants to the substrate material is of critical importance. As much as 80% of field failures are due to poor pretreatment and misapplication of the solid film lubricant, as opposed to improper selection of the product.[2] Most bonded solid film lubricants are applied by techniques similar to those in the painting industry. One critical factor that must be controlled is film thickness: the normal recommended is between 0.0002" and 0.0005".

Several factors which govern selection of the application methods include:

Number of parts
Available equipment
Size of parts
Labor
Type of parts
Cost
Film thickness tolerance
Masking
Blind holes

The coating may be applied by conventional spray equipment, electrostatic spray equipment, dipping, roll coating, brushing, etc. While all of these methods are frequently used, spraying is the most effective in terms of wear performance and lubricity.

COATING CLASSES

As we have seen in Volume II of this Handbook, a wide variety of materials can be used as solid film lubricants. The key to their use, however, involves getting them to adhere to the substrate in a uniform, thin film. The variety of bonded solid film lubricants developed over the years includes the following coating classes.

Impingement

In the beginning, solid lubricant coatings were obtained by simply rubbing or burnishing the solid lubricant onto the substrate surface. These thin films adhere purely due to van der Waals and similar forces of attraction. The burnished films generally exhibited extremely short endurance life and were primarily used for assembly or mild forming operations. In order to enhance performance, impingement techniques were developed which in effect blast the substrate surface with a solid lubricant. Impingement films usually incorporate a low concentration of a proprietary inorganic binder system to enhance adhesion of the substrate. Surface morphology of the substrate is of prime importance and is usually achieved by abrasive blasting under controlled conditions. The resulting thin films find their major applications on fine-thread machine screws, high vacuum applications such as air bearings on satellite telescopes, and precision "clockwork" mechanisms such as timing and fusing devices in ordinance applications. These thin films can also be used as mold release agents.

The impingement processes are generally described by the following specifications:

Aerospace material specification	U.S. Navy specification
AMS 2525A	7310060
AMS 2526A	OS 10626A

Air force specification	U.S. military specification
70A18101P1	MIL-L-835645A

Resin-Bonded Coatings

Resin-bonded solid film lubricants represent the largest and most commercially significant class of solid film lubricant products.[3] As such, these products vary widely in their performance properties. For example, some products containing an air-cured acrylic or vinyl binder in small concentrations relative to the lubricating pigments provide minimal adhesion to the substrate. However, such products give inexpensive short-term lubrication, are suitable for forming applications, and are useful where excessive build-up of coating thickness is of concern. Other products contain minimal lubricating solids and are utilized more for their paint-like properties.

Organic Air Dry Coatings

These generally provide improved performance vs. impingement coatings because, in addition to lubricity, they provide additional properties such as corrosion protection. Since they can be packaged in aerosol form, they are suitable for many field applications. Of all solid film lubricant types, these are probably least expensive and most easily applied, but with overall lower performance properties. The organic bonding agents are typically acrylics, alkyds, one and two-part epoxies, vinyls, and acetates.

While most are not covered by military specifications, a few typically describe these products. For example, currently canceled MIL-L-46009 is typically an aerosol molybdenum disulfide/graphite mix with a minimum amount of resin binder to hold the solid lubricant to the surface for a wide variety of short-term applications. MIL-L-23398 and MIL-L-46147 are quite similar, but with much improved properties over 46009. MIL-L-23398D, used widely by all branches of the military, provides products with outstanding lubrication and reasonably good corrosion protection. The products are available in both aerosol and bulk form, which air cure in 6 hours.

They are resistant to a wide variety of fluids such as aircraft turbine oils, solvents, and jet fuels. As a general rule, air-dry resins used in bonded solid film lubricants lack sufficient crosslinking and molecular weight when fully cured to compete with organic thermoset products in solvent resistance, wear life, and durability. A possible exception would be two-part epoxy and catalyst-cured silicone systems which substitute chemical energy for thermal energy to effect the resin change.

Organic Thermoset Coating

Organic thermoset solid film lubricants are the largest single class of resin-bonded solid film lubricants. In addition to providing lubricity, a wide variety of products are used in thermal applications from cryogenic to about 750°F; coating applications involving extreme solvent or chemical resistance; and decorative applications from colored to the typical gun metal gray color characteristic of molybdenum disulfide and graphite. In addition to the most common thermoset phenolic and epoxy-phenolic resins, silicones, epoxies, urethanes, polyimides, polyamides-imides, and phenoxies are used. Representative specifications which describe products in this large class of solid film lubricants include the following:

- Automotive
  - GM-6046 (GM)
  - M21-P8A (Ford)
  - PS-7001 (Chrysler)

A black PTFE-containing solid film lubricant used primarily on fasteners for corrosion protection and torque tension control.

- DDC 95350 (Detroit Diesel)

A PTFE solid film lubricant with a relatively soft resin binder used to seal threads on freeze plugs on diesel engines.

- Air frame
  - FPS-3006 (General Dynamics)
  - BMS 3-8 (Boeing)
  - LAC 34362 (Lockheed)
  - PS18021-3.1A (McDonnell Douglas)
  - RL-5A (Northrop)
  - LSM 146003 (Grumman)

Typically molybdenum disulfide and/or graphite with a phenolic binder system capable of extreme wear resistance, high load-carrying capability with low coefficient of friction, and resistance to all aviation lubricants and fluids.

- Jet engines
  - A50TF147 (General Electric)
  - PWA 474 (Pratt & Whitney)
  - EMS 52402 (Garrett)
  - 11700A (Allison)
  - PWA 550 (Pratt & Whitney)

Typically molybdenum and/or graphite in an epoxy or phenolic binder system.

- Military
  - MIL-L-46010 TY I/II
  - MIL-L-8937D
  - WS 20290

Molybdenum disulfide with an epoxy or phenolic binder system.

Organic Thermoplastic Solid Film Lubricants[4]

Typically these coatings are self-lubricating polymers which are applied in powder or dispersion form at coating thicknesses from 1 to 50 mils or more. The polymer is then fused to the surface of the part to provide a thick barrier coating which provides lubricity, abrasion resistance, chemical resistance, or release properties. Typical of these polymers are:

Polytetrafluoroethylene (PTFE) — A completely fluorinated polymer which melts about 620°F and is useful up to temperatures of 500°F. It has outstanding antistick characteristics, a low coefficient of friction, good resistance to most chemicals, and high dielectric constant. Typical applications include chemical processing equipment, high temperature cable insulation,

and molded electrical components. This material, in lubricating grade powder form, is also used as a solid lubricant in resin-bonded products as described earlier.

Fluorinatedethylenepropylene copolymer (FEP) — FEP is a copolymerization product of tetrafluoroethylene and hexafluoropropylene. It typically has a melting point of 550°F and a useful working temperature up to about 400°F. The material has outstanding weatherability, low friction, and is typically used for chemical process equipment, roll covers, and wire and cable applications. This material is also used in powder form in resin-bonded products, primarily as a release agent.

Perfluoroalkoxy resin (PFA) — PFA is generally similar to PTFE and FEP, although with somewhat better mechanical properties. It is useful to temperatures as high as 500°F.

Ethylenechlorotrifluoroethylene copolymer (ECTFE) — ECTFE is predominantly a 1:1 alternating copolymer of ethylene and chlorotrifluoroethylene forming linear chains. With a melting point of approximately 470°F, it is useful from cryogenic temperatures up to about 330°F. Its strength, wear resistance, and creep resistance is significantly greater than those of PTFE, FEP, and PFA. ECTFE is resistant to most corrosive chemicals and organic solvents over a wide temperature range. While fairly expensive, it is probably the most effective product in its most common use as a corrosion resistant coating. Lubricity is of secondary importance.

Polyvinyladine fluoride (PVDF) — PVDF is a high molecular weight polymer of polyvinyl fluoride with a melting point of about 340°F. PVDF has substantially greater strength, wear resistance, and creep resistance than PTFE, FEP, and PFA. It resists most chemicals and solvents including liquid bromine and bromine salt solutions. PVDF is more commonly used for lining chemical piping systems and reaction vessels than as a lubricant.

Low Volatile Organic Component (VOC)

In the early 1980s, the Southcoast Air Quality Management District (SAQMD) in Southern California promulgated rules 1124, 442, 443, and 1145, which served notice to the paint and coatings industry that fundamental changes would have to be made. Compliance with the earliest of these regulations was often accomplished by reformulation of solvent systems, including the use of so-called "compliant solvents". However, in the area of bonded solid film lubricants, the development of technology has been more difficult and regulatory agencies have extended compliance deadlines.

Exemptions have been issued and the specialty coating[5] subdivided into even more narrow groupings with differing regulatory limits. These changes result in a dynamic regulatory program which maintains a realistic balance with available technology.

Technology has been developed to meet the requirements for less volatile organic component emissions while maintaining the performance of many solid film lubricant products. Typical of this new generation of products are solid film lubricants which meet the performance requirements of MIL-L-46010B Type II, but with a VOC of 250 g/l, well below most regulatory goals. Likewise products have been developed under MIL-L-85614, an aluminized fastener coating commonly used in the aircraft industry. New low VOC solid film lubricants will undoubtedly be an area of intense future R & D involvement.

Inorganic Bonded Solid Film Lubricants

These generally provide resistance to vacuum outgassing or resistance to liquid oxygen and are useful at high temperatures and in high radiation environments.[3] The most common binder systems are silicates, phosphates, aluminates, and some organometallic materials such as titanates and some silicon based materials. The organometallics, when used in high temperature applications, become inorganic on curing or exposure to extreme temperature. These materials are commonly used in jet engines as antiseize coatings for threaded fasteners

and in a wide variety of fuel control valves and related moving parts. Typical specifications for inorganic solid film lubricants are

- Jet engines
  - A50TF9 (General Electric)
  - PWA 298 (Pratt & Whitney)
  - PWA 36545

Graphite or molybdenum disulfide in a silicate binder.

- Aerospace
  - P20013 (McDonnell Douglas)
  - MS-FC106 (NASA)
  - LB0140-007 (Rockwell)

Typically graphite or molybdenum disulfide lubricants with a phosphate binder for use in liquid oxygen service.

- Military
  - MIL-L-81329
  - MIL-L-47081

Graphite or molybdenum disulfide lubricants with silicate or phosphate binder systems.

Ceramic-Bonded Solid Film Lubricants

This is an "emerging class of solid film lubricants for high temperature application. These products contain high temperature solid lubricating materials such as graphite, a calcium fluoride/barium fluoride eutectic (as developed by NASA) and a variety of proprietary systems still under development."[5] The binder is typically a glass frit which is fused to form a continuous film. In some cases, these materials are applied from powder plasma guns which fuse the binder as it is applied. Other systems involve a liquid dispersion of glass and lubricant which is spray applied and oven cured. These ceramic solid film lubricants are capable of extreme wear resistance, and some can pass a 1/4" Mandrel test without cracking and flaking. Most formulations are proprietary and expensive and are used primarily in developmental aerospace applications. These coatings represent an area of major involvement by solid film lubricant researchers.

Sputtered Films

With development of sputtering deposition in the early 1970s, it became possible to apply very thin solid lubricant films. Inherent films of easily controlled coating thickness from 1/10th to >10 μm with reasonable life and low friction are well suited for precision bearing elements and for extreme vacuum applications in spacecraft. The fundamental problem with sputtered deposited films is their morphology. Sputtered films generally develop a low density, two dimensional columnar-void structure.[6] In the case of molybdenum disulfide, the platelets of molybdenum disulfide grow nearly normal to the substrate with the edge sites exposed outward. These edge sites, in turn, readily react with oxygen or water vapor, causing increased friction and wear of the film. In addition to molybdenum disulfide, other materials such as gold, silver, lead, lead-tin alloys, and cubic boron nitride have been applied by this technique to lower coefficients of friction. Research is currently directed toward modifying the film behavior by alloying (co-deposition), by forming multilayered films, or by bombarding with high energy ions. More recently, enhanced sputter deposition techniques

have deposited dense molybdenum disulfide films with the platelets parallel to the substrate surface and exhibiting increased resistance to oxygen and water vapor and decreased friction and wear.

Composite Coatings

In an effort to reduce cost and weight, and to improve performance, increasing use is being made of composite coatings using more than one coating technology. Some examples are described below:

Anodization/impregnation and impingement — Wear resistance of aluminum is substantially improved by anodizing. Since an anodized surface is somewhat abrasive and is not lubricious, commercial processes have been developed for impregnation of lubricating material into the pores of the anodize. The most common lubricant has been PTFE under tradenames such as Nedox and Sintef. These processes can also provide a more attractive appearance than conventional anodize with better scratch and mar resistance. Additionally, molybdenum disulfide has been impinged into the surface of anodized parts with satisfactory results.

Aluminum alloy/solid lubricant — Properties of aluminum metal have been enhanced by powder metallurgy technology. In one case, aluminum alloy (6061) was sintered into a metal matrix composite with as much as 14 vol% of graphite. These composite materials showed improved wear rates vs. aluminum metal, and improvement increased with increased graphite volume fraction.[8] Aluminum matrix composites with up to 5 wt% molybdenum disulfide show similar reductions in wear rates.[9]

Physical vapor deposition/impingement — Physical vapor deposition (PVD) is a new technology used primarily to provide very thin, very hard, wear-resistant coatings to metal substrates. The most common example is titanium nitride. These coatings are advantageous in some applications as substitutes for hard chrome plating and similar hard surfacings used in the past. PVD coatings are nonpolluting to the environment, eliminate the possibility for hydrogen embrittlement, and, because of thinness, eliminate the need for subsequent machining and polishing. These coatings generally exhibit a high coefficient of friction on the order of 0.4 to 0.5 However, taking advantage of the fact that these films typically have a low density, two-dimensional columnar void structure, it is possible to combine physical vapor deposition with the impingement processes. These thin films have a relatively limited lubricating life owing to the thinness of the lubricating layer. Since the lubricant actually enhances interfacial shear rather than intrafilm shear between mating layers,[6] the surface roughness of the parts to be coated is of critical importance. Coatings are most commonly used on precision parts such as guidance bearings, high temperature fuel control valves, and related precision hardware.

Composite sputtered films — As alluded to earlier, lubricating solids deposited by various sputtering or PVD processes have certain limitations caused by the crystal morphology of the film (crystal orientation and density). Co-sputtered films of molybdenum disulfide with chromium, cobalt, nickel, tantalum, and gold have all improved the performance of these films.[10]

Electrolytic platings and lubricants — In many cases, solid film lubricants are formulated to provide very precise lubrication, for example with threaded fasteners where a specific application torque is desired to achieve a precise clamp load. Since it may be difficult or impossible to formulate the solid film lubricant with other performance characteristics such as corrosion resistance, in these cases solid film lubricants are commonly applied over platings. The plating is often coated with a chromate to further enhance corrosion protection before application of a solid film lubricant. This must be done with care in order to achieve adequate adhesion of the solid lubricant to the plated chromated substrate. In

some cases, for example, a preferred process would employ a zinc phosphate designed specifically for zinc plating, followed by clear chrome seal rinse and subsequent topcoating with a solid film lubricant.

Electroless plating/lubricants — Corrosion and wear properties of steel substrates have been improved for a number of years through composite technology, where materials such as PTFE are codeposited along with an electroless nickel coating. In these processes, the electroless nickel coating contains as much as 25% by volume PTFE. This provides a wear-resistant coating with a lower coefficient of friction, but at the expense of corrosion protection. Electroless nickel also can provide a good substrate for conventional resin-bonded solid film lubricants to enhance corrosion protection. Electroless nickel has also been combined with impingement processes to further reduce the coefficient of friction.

SURFACE PREPARATION FOR SOLID FILM LUBRICANTS

General

Pretreatment of the metal substrate surface prior to application of bonded solid film lubricants is the single most critical item affecting performance. Pretreatments are performed on a metal substrate to modify surface roughness, hardness, and/or chemical reactivity to promote adhesion and enhance lubrication performance. It is extremely important to properly perform the optimum pretreatment for the specific metal in order to achieve maximum performance. Since solid film lubricants by themselves do not exhibit uniquely outstanding wear life, improper or inadequate pretreatment results in approximately 80% of most solid film lubricant failures.

Resin-Bonded Lubricants

Ideal pretreatment processes for resin-bonded solid film lubricants fall into three basic operations: degreasing, grit blasting, chemical treatment. Each of these will be covered in some detail, with recommendations of the preferred approaches. Since each of these operations add cost, however, it is often necessary to compromise performance. The design engineer must be careful that these compromises do not ultimately result in a poorly designed, non-cost-effective component.

Degrease

Degreasing is necessary to remove machining oils, corrosion inhibitors, and related solvent soluble contamination. Failure to remove these contaminants usually results in poor adhesion of the solid film lubricant. There are three methods commonly used to degrease metal parts. The preferred vapor degreasing is typically done in accordance with MIL-T-7003 in specially designed equipment using common solvents such as 1,1,1-trichloroethane, trichloroethylene, or perchloroethylene. If vapor degreasing is not practicable, an alternative is cold degreasing immersed in a solvent such as 1,1,1-trichloroethane. Care must be taken that the solvent does not become excessively contaminated because it will leave a residual thin film of oil on parts. Finally, a wide variety of commercial caustic cleaners are used with outstanding results. With care that the caustic cleaner bath does not become contaminated or neutralized, this method is particularly useful for large volume production in applications such as automotive fasteners.

Grit Blast

After vapor degreasing, abrasive blasting or grit blasting is recommended. For most metals, aluminum oxide is the preferred medium. A wide variety of mesh sizes is available; for most work 220 mesh is preferred (see Figure 1). In addition to aluminum oxide, sand, starulite, walnut shells, peanut shells, and glass beads are commonly used, particularly on
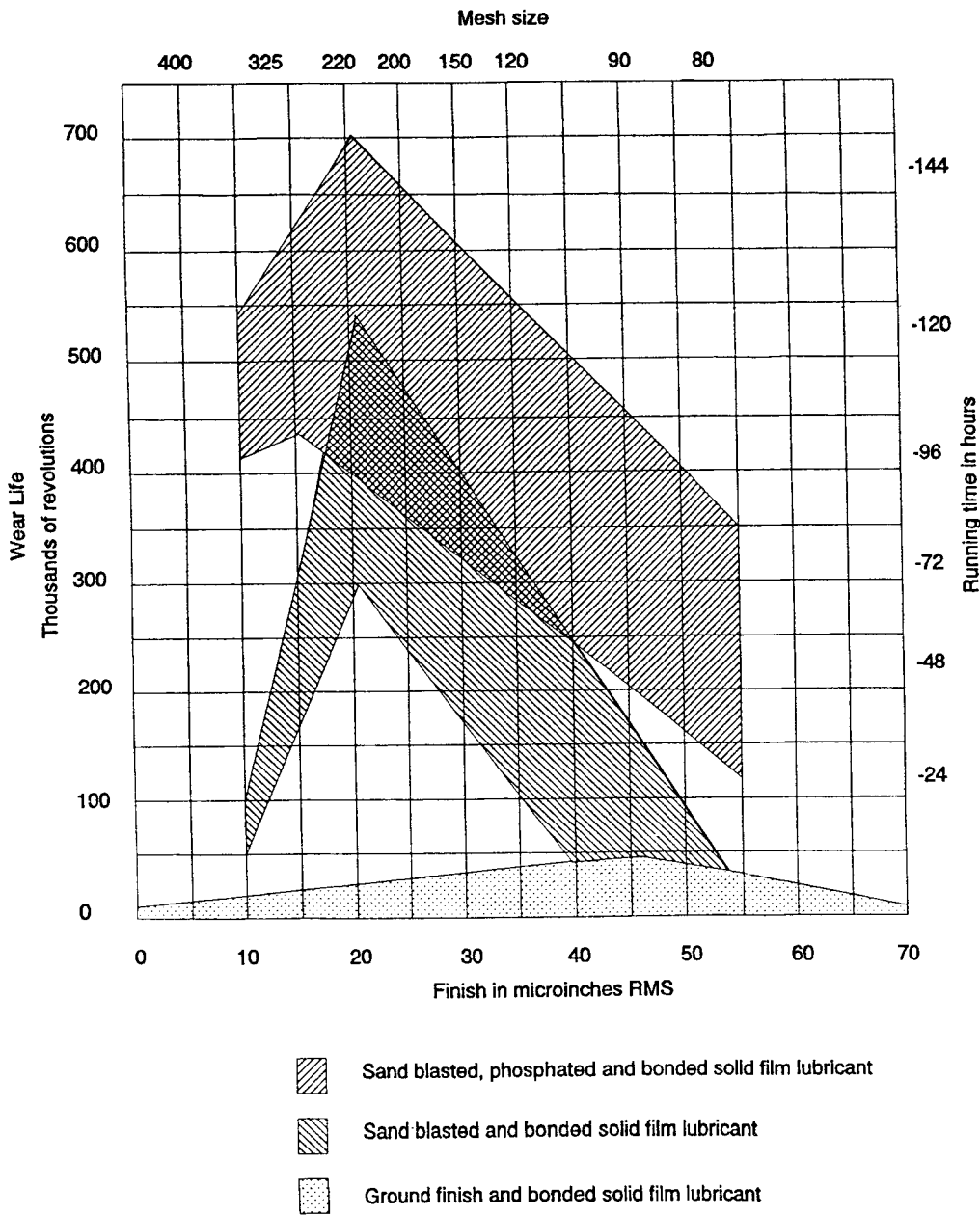
FIGURE 1.   Wear life vs. surface finish.

some of the softer metals. The goal of grit blasting is to provide a uniform surface profile with a surface roughness about 16 to 32 rms for most applications. Table 1 shows the effect of various grit sizes of aluminum oxide on aluminum, titanium, and stainless steel.

Chemical Treatment

The final operation necessary for optimum performance of bonded solid film lubricants is a chemical treatment. Usually this represents some kind of conversion coating such as a phosphate for ferrous metals and zinc; anodization for aluminum, magnesium, or zinc; passivation for corrosion resistant steels; black oxide for copper and iron; chromate for

Table 1
TYPICAL GRIT BLAST FINISHES (rms)
(ALUMINUM OXIDE, 30–60 psi, 30–60°)

Grit size (mesh)	Aluminum	Titanium	Stainless steel
400	40–65	15–30	20–30
220	70–85	35–45	30–40
120	90–110	40–55	30–45
80	150–180	60–80	50–100

Table 2
PHOSPHATE PRETREATMENT

Type	Market	Use	Advantage	Coating weight (mg/ft²)
Zinc (DOD-P-16232)	Military/commercial	SFL/paint	Corrosion/adhesion	600–2,000
Manganese (DOD-P-16232)	Military	SFL	Wear/adhesion	2,000–3,000
Calcium/zinc	Commercial	Paint	Corrosion/adhesion	100–400
Iron	Commercial	Paint	Adhesion/corrosion	25–100

copper, aluminum, cadmium, anodized metals, phosphated ferrous metals, and zinc; and various etchants for corrosion resistant steels, ferrous metals, copper, zinc, and titanium.

Phosphate

The preferred phosphate process is described in DOD-P-16232 (see Table 2). Under this military specification there are two primary phosphate types, zinc phosphate and manganese phosphate. Manganese phosphate provides a better wear-resistant base for solid film lubricants. Zinc phosphate provides additional corrosion protection, a desirable for many applications. In addition to these phosphates, calcium/zinc phosphate, iron phosphate, and nickel/manganese phosphate are used, although these are more applicable to paint systems.

Generally phosphates are solutions of secondary and tertiary metal phosphates along with other anions, which function as accelerators, and phosphoric acid. Reaction of the solution results in a chemical conversion. For example, when an iron surface is phosphated, an iron/zinc phosphate crystal is created. This crystal becomes an integral part of the chemistry of the metal surface. When operating conditions are correct, the deposited phosphate is adherent with very little residual porosity.

After applying a phosphate, parts are dried under controlled conditions to eliminate trapping of water in the crystalline structure which could cause flash corrosion and poor adhesion. Additionally, it is important to avoid hydrogen embrittlement. In the case of high strength steels, including spring steels, trapped hydrogen in the metal can potentially cause stress corrosion cracking and related failures. Therefore, it is important that the phosphated part be baked at a temperature that will eliminate any entrapped hydrogen.

Anodization

Anodizing is the preferred conversion coating for such materials as aluminum and magnesium. In this process a metal oxide coating is formed electrolytically, as described in MIL-C-8625C. This military specification recognizes three fundamental types: chromic, sulfuric, or hard anodize. Hard anodize is a type of sulfuric acid anodize which leaves a much harder, more wear-resistant coating and is preferable for solid film lubricants. In

addition to these three, phosphoric and oxalic anodize are less commonly used. For magnesium metals, the anodize process is covered under MIL-M-45202. Finally, zinc anodize is performed in accordance with MIL-A-81801 and provides an outstanding substrate for zinc as well. A proprietary process, Ticote, is also effective for anodizing titanium.

Passivation

Passivation generally involves treatment of the substrate metal with nitric acid. The purpose is to dissolve iron from the surface of corrosion resistant steels making the surfaces nickel rich relative to the normal composition of the material. This eliminates any micro corrosion/oxidation which might occur prior to the application of the solid film lubricant. Passivation is typically done in accordance with MIL-STD QQ-P-35.

Miscellaneous Chemical Treatments

Black oxide is used on copper and to a lesser extent on iron, as covered by military specification MIL-F-495 for copper and MIL-C-13924 for iron. This involves sulfide treatment for copper and caustic nitrate treatment for iron. This chemical conversion, while very inexpensive, does not provide the performance of a good phosphate on iron. Chromate conversion is also commonly used on copper, zinc, and phosphated ferrous metals. The purpose of this process is to treat the substrate with hexavalent chromium along with various activators such as acetates, sulfates, and fluorides under a controlled pH. This process provides extra corrosion protection.

Finally, various etchants also represent a cost-effective method for pretreating metal parts. However, use of etchants alone can represent a compromise in performance properties. For corrosion-resistant steels, ferric chloride solution at approximately 40% provides a good base for adhesion. On ferrous metals, a hydrochloric acid etch works well in place of grit blasting. However, care must be taken if hydrogen embrittlement is a consideration. Etching other metals can be accomplished as follows: aluminum with nitric acid and hydrofluoric acid, copper with sulfuric acid and nitric acid, zinc with sulfuric acid and chromic acid, and titanium with nitric acid and hydrofluoric acid. Each of these provides surface "tooth" to promote adhesion.

The critical importance of pretreatment for resin-bonded solid film lubricants is demonstrated in the following test. Three identical Timken T54148 test races were coated with a commercially available, phenolic bonded, MoS_2-graphite product. Coating thickness was 0.00035 inch. All specimens were identically baked, and the only difference was the surface pretreatment each received prior to the application of the lubricant. Each specimen was then tested on the LFW-1 at 72 rpm and 630-lb load (ASTM D-2714). The results are summarized below.

Pretreatment	Cycles to failure
None	Fail on loading
Vapor degrease/sandblast	20,174
Vapor degrease/sandblast/phosphate	672,460

Clearly it can be seen that the effect of pretreatment is dramatic. Table 3 reviews the recommended pretreatment process for the appropriate metals.

Inorganic Bonded

Pretreatment for inorganic bonded solid film lubricants is equally as important as with the resin-bonded products and generally follows the same guidelines of cleaning, degreasing, grit blasting, etc. Since inorganic solid film lubricants are generally used for high temperature applications, phosphating and chromating are usually avoided, since they decompose at temperatures in excess of 450°F and 150°F, respectively. Generally the preferred pretreatment

Table 3
RECOMMENDED PRETREATMENTS FOR VARIOUS SUBSTRATES

Copper and its alloys	Titanium	Aluminum	Stainless steel	Iron and steel
Vapor degrease	Alkaline	Vapor degrease	Vapor degrease	Vapor degrease
Abrasive blast (light)	Abrasive blast	Anodize	Sandblast	Abrasive blast
Chromate conversion	Fluoride phosphate	or	Passivate	Phosphate
	or	Light abrasive blast		
	Alkaline Anodize	+		
		Chromate conversion		

is degreasing and grit blasting with aluminum oxide, and, where applicable, passivation. Inorganic solid film lubricants are generally not used on low melting materials such as aluminum unless the application is for high vacuum where the vacuum outgassing properties of an inorganic solid film lubricant are a primary consideration, or where specific chemical resistance, such as liquid oxygen service, is of importance. Even then, the lubricant cure temperature may be excessive for the grade of aluminum.

Ceramic-Bonded Solid Film Lubricants

Substrates for ceramic-bonded solid film lubricants are pretreated in much the same fashion as for inorganic bonding. Chemical treatment such as phosphates are not used since ceramic solid film lubricants are generally cured at temperatures around 1000°F or higher. Therefore, the preferred pretreatment is vapor degreasing, followed by grit blasting. Since ceramic solid film lubricants are usually applied to corrosion-resistant materials such as Hastalloy and Waspalloy, passivation is usually not required. The main purpose of the pretreatment is to remove any oils, dirt, and loose debris, and to obtain the necessary surface roughness for optimal adhesion.

Sputtered and PVD-Applied Films

Pretreatment for sputtered and physical vapor deposition-applied films generally involves a degreasing/cleaning operation often incorporating ultrasound. In some special cases, vapor honing is also done. However, since vacuum-applied films are usually applied to very smooth surfaces, the abrasive honing is usually accomplished with a slurry of very fine aluminum oxide, followed by subsequent cleaning in an ultrasonic bath. Once cleaned in this manner, the substrate is etched in the sputtering chamber via ion bombardment with an inert gas such as argon. The argon plasma cleans the surface on an atomic level to provide the required adhesion.

Composite Films

Pretreatments for composite films vary considerably with the substrate. For example, the pretreatment for anodization/impingement involves the typical steps called out in MIL-C-8625 for anodization as described earlier. After the anodization process, parts are withdrawn from the bath, dried, and immediately coated by impingement, impregnation, or topcoating. Other composite films have appropriate pretreatments for their specific processes and follow the same pattern as anodized impregnation.

COMPARATIVE PERFORMANCE CHARACTERISTICS

Many resin-bonded solid film lubricant formulations are commercially available to meet the wide variety of engineering applications. Tables 4 and 5[11] attempt to codify performance of a number of common systems. Always, however, testing and prototyping is necessary to fully qualify the solid film lubricant system for each application.

Table 4
PERFORMANCE PROPERTIES OF COMMON SOLID FILM LUBRICANT PRODUCTS

	A	B	C	D	E	F	G	H	I	J	K	L	M 1	M 2	N
													Hughes 760829		
Conformance spec	GM-6064 GM-6174	GM-6183	MIL-L-8937	MIL-L-46010A	N/A	N/A	PWA 550	DPM-5499	MIL-L-81329	MIL-L-23398	AMS2525A MIL-L-85645	AMS2526A MIL-L-85645			MIL-L-85614
Color	Colors	Clear	Gray/black	Gray/black	Gray/black	Gray/black	Gray/black	Gray/black	Gray/black	Gray/black	Gray	Gray	Black	Gray/Black	Silver
Binder resin	Phenolic	Epoxy	Phenolic	Epoxy	Phenolic	Phenolic	Silicone	Silicone	Silicate	Epoxy	Proprietary inorganic	Proprietary inorganic	Epoxy	Phenolic	Phenolic
Solid lubricant	PTFE	PTFE	MoS$_2$	MoS$_2$	Proprietary blend	Proprietary blend	MoS$_2$	MoS$_2$ graphite	MoS$_2$ graphite	MoS$_2$	Graphite	MoS$_2$	N/A	MoS$_2$	Aluminum
Cure condition	300°F	300°F	300°F	375°F	300°F	250°F	Air dry	500°F	400°F	Air dry	300°F	300°F	350°F	300°F	300°F
Coating thickness	0.7 mil	0.7 mil	0.5 mil	0.5 mil	0.5 mil	0.5 mil	0.5 mil	0.5 mil	0.5 mil	0.5 mil	0.0001	0.0001	0.7 mil	0.5 mil	0.5 mil
Design environment	-100°F- +400°F	-100°F- +400°F	-365°F- +500°F	-365°F- +500°F	-365°F- +500°F	-100°F- +400°F	-365°F- +1,300°F	-365°F- +1,000°F	-365°F- +1,200°F	-365°F- +500°F	-365°F- +2,000°F	-365°F- +750°F	-365°F- +500°F		-365°F- +500°F
End use features	Automotive Corrosion Decorative Lubricity	Automotive Corrosion Decorative Lubricity	Aircraft Lubricity Corrosion	Aircraft Lubricity Corrosion	Nuclear Lubricity Corrosion	Prevailing torque nuts	High-temp. Aircraft antiseize	High-temp. Aircraft antiseize	High-temp. Aircraft antiseize	Field application Lubricity Corrosion	Fine threads Lubricity	Fine threads Lubricity	Extreme corrosion resistance and lubricity		Interference fit Corrosion
Pencil hardness ASTM D-3363	5H	3H	4H	2H	4H	5H	5B	5B	5B	2H	N/A	N/A	6H		4H
Abrasion (Taber) mg/1000 cycles ASTM D-1044	6.3	6.4	8.7	11.8	5.8	7.3	.15	4.7	4.5	13.2	N/A	N/A	1.87		13.9
Corrosion resistance[a] salt spray (hrs) ASTM B-117	500	300	500	500	500	100	100	100	N/A	N/D	N/A	N/A	2,500		350
Installation[b] (ft-lb)	20.5	19.7	26.7	24.2	20	16.5	20	13.8	18.6	23.6	55.5	31.7	25		d
Torque (std dev)	3.4	3.1	2.6	2.0	0.1	1.7	0.1	1.3	1.7	2.3	2.3	1.69	1.58		
Falex wear life X1000 cycles[c] ASTM D-2714	120	67	N/A	N/A	130	51	N/A	N/A	N/A	N/A	N/A	N/A	N/A		N/A
Coefficient of friction	.08	.07	.06	.06	.08	.07	.07	.06	.06	.06	.06	.06	.06		N/A

[a] Corrosion resistance was measured on standard 3 × 6 steel Q-panels with zinc phosphate and 0.5 to 0.8 mil coating thickness applied. These results allow for rating of coating type. Actual performance on threaded fasteners will vary based on application method and part shape.

[b] Installation torque is determined on standard $\frac{1}{4}$-20 bolts and nuts using PLI washers to determine when constant clamp load has been achieved.

[c] Falex wear life is determined at light load corresponding to 12,000 to 24,000 psi. Products containing MoS$_2$ will typically provide 300,000 to 500,000 cycles at >80,000 psi.

[d] Meets requirements of Boeing Material Specification BMS-10-85E.

From Gresham, R. M., Bonded Solid Film Lubricants for Fastener Coatings, Fastener Technology International, April/May 1987.

Table 5
CHEMICAL RESISTANCE PROPERTIES

TEST FLUID	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Lubricating oil MIL-L-6082	o	o	o	o	o	o	o	o	...	o	o	o	o	o
Lubricating oil MIL-L-7808	o	o	o	o	o	o	o	o	N/A	o	o	o	o	o
Hydraulic fluid MIL-H-8446	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Hydraulic fluid MIL-H-5606	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Gasoline aviation MIL-G-5572	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Trichloroethylene O-T-634	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Lubricating oil MIL-L-2104	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Turbine fuel (JP-4) MIL-J-5624	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Lubricating oil MIL-L-23699	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Trichloroethane	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Methyl ethyl ketone	o	o	o	o	o	o	o	o	—	o	o	o	o	o
DC-550 fluid	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Skydrol 500	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Methylene chloride	o	o	o	o	o	o	o	o	—	o	o	o	o	o
Hydrochloric acid (15%)	*	o	*	o	*	*	*	*	—	*	N/A	N/A	o	*
Sulfuric acid (50%)	o	o	o	o	*	o	*	o	—	o	N/A	N/A	o	o
Nitric acid (10%)	o	o	o	o	*	*	*	o	—	*	N/A	N/A	o	o
Sodium hydroxide (25%)	*	o	*	o	o	o	*	*	—	o	N/A	N/A	o	o

Notes: o = PASS, * = FAIR. ASTM D-2510 fluid resistance test required 24 h immersion of a coated specimen in the test fluid followed by tape adhesion testing. The product designations are the same as Table 4.

From Gresham, R. M., Bonded Solid Film Lubricants for Fastener Coatings. Fastener Technology International, April/May 1987.

Use of bonded solid film lubricants on threaded fastener products can prevent galling, provide low prevailing torque, or, most important, provide a narrow consistent torque/tension relationship. This is particularly important in critical applications where the clamp force delivered by the threaded fastener is critical. The action of torquing a threaded fastener assembly stretches the bolt to introduce the critical working clamp load in the system. The torque/tension relationship in the following formula takes into account a number of different factors: type of bolt, material, strength level, type of finish, torquing mode, surface condition of the joint, etc.

$$T = KDL$$

where T is installation torque (lb-in), K is torque coefficient, D is nominal bolt diameter (in), and L is clamp load objective (lb). The prime variable in this formula is torque coefficient (K) which can be controlled by use of bonded solid film lubricant coatings. The torque coefficient itself may vary widely, due to surface conditions of the threads (usually due to manufacturing inconsistencies). A bonded solid film lubricant can reduce torque/tension variability and clamp load variability.[12] As an example, a typical six-sigma variation with zinc-plated fasteners would be ± 30% of clamp force. For M10 plated bolts this variation range might be as much as 7,000 lb. Use of a solid film lubricant could reduce this variability by as much as 50% or 3,750 lb.

REFERENCES

1. **Booser, E. R., Ed.,** *Handbook of Lubrication,* Vol. II., CRC Press, Boca Raton, FL, 1984, 269.
2. **Gresham, R. M.,** Solid film lubricants: unique products for unique lubrication, *Lubr. Eng.,* 143, 1988.
3. **McMurtrey, E. L.,** *High Performance Solid and Liquid Lubricants,* Noyes Data Corp., Park Ridge, NJ, 1987, 5.
4. *Modern Plastics Encyclopedia,* Vol. 57, No. 10A, Oct. 1980, 31.
5. **Sliney, H. L.,** Status and new directions for solid lubricant coatings and composite materials, *Tribology in the 80's,* Proc. Int. Conf. NASA, Cleveland, 1983, 665.
6. **Singer, I. L.,** Solid lubricating films for extreme environments, in *Proc. Symp. Mat. Res. Soc.,* 148, 217, 1989.
7. **Hilton, M. and Fleischauer, P. D.,** in *New Materials Approaches to Tribology: Theory and Applications,* Pope, L., Fehrenbacher, L., Winer, W., Ed., (MRS Proc. 140, 1989).
8. **Jha, A. K., Prasad, S. V., and Upadhyay, G. S.,** Sintered 6061-aluminum alloy-solid lubricant particle composites: sliding wear and mechanisms of lubrication, *Conf. Proc. Wear of Materials,* Vol. 1, Denver, 1989, 9.
9. **Zanzam, M. A.,** Wear resistance of agglomerated and dispersed solid lubricants in aluminum, *Mater. Trans.,* JIM, 7, 516, 1989.
10. **Stupp, B. C.,** *Thin Solid Films,* 84, 257, 1981.
11. **Gresham, R. M.,** *Bonded Solid Film Lubricants for Fastener Coatings,* Fastener Technology International, April/May 1987.
12. **Frederick, W. R.,** Solid Film Lubricants — The fastener finish to minimize clampload variability, Fastener Technology International, December, 1990.