United States Patent

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[15] **3,637,497**

[45] **Jan. 25, 1972**

[54] **MOISTURE RESISTANT DRY FILM LUBRICANTS**

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[22] Filed: **June 12, 1968**

[21] Appl. No.: **736,287**

[52] **U.S. Cl.**....................................**252/29,** 252/12, 252/25, 252/54.6, 252/396

[51] **Int. Cl.**....................**C10m 7/24,** C10m 7/06, C10m 7/04

[58] **Field of Search**......................252/12.2, 12, 25, 29, 54.6, 252/396

[56] **References Cited**

UNITED STATES PATENTS

2,628,958	2/1953	Bittles	252/54.6
3,281,362	10/1966	Di Sapio	252/25
3,305,325	2/1967	Le Brasse et al.	252/12.2

FOREIGN PATENTS OR APPLICATIONS

712,426	7/1954	Great Britain	252/12.2

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[57] **ABSTRACT**

Chemical and galvanic corrosion of metallic substrates, by dry film lubricants, is prevented by application over the lubricant surface of a hydrophobic organic polymer coating having a melting point between 100° to 325° C. and a critical surface tension of 31 dynes/cm. or lower.

2 Claims, No Drawings

MOISTURE RESISTANT DRY FILM LUBRICANTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to improvements in dry film lamellar lubricant coatings and bearings and more particularly pertains to protecting metals contacting these lubricants from corrosion, caused by the lubricant, without sacrificing lubrication properties. The lubricant is covered with a thin coating having a melting point between 100° and 325° C., and a critical surface tension of 31 dynes/cm. or lower which imparts hydrophobic properties to the hydrophilic lubricant.

2. Description of the Prior Art

In the field of lamellar dry film lubricants, it has been the general practice to employ layer-lattice materials such as graphite, MoS_2, CdI_2, $CdCl_2$, WS_2, $CoCl_2$, Boron nitride, hydroxides and halides of divalent metals, and sulfides, selenides and tellurides of tetravalent metals, or the like, as dry lubricants to prevent metal wear. Of these, molybdenum disulfide and graphite are most commonly used.

For many applications of solid lubrication, it is convenient to deposit or bond the lubricant film to a metal substrate. Dispersions of graphite and molybdenum disulfide, in volatile fluids, are available commercially for forming films by spraying, dipping or brushing. Cohesion between individual lubricant particles and adhesion to the substrate is often improved by incorporating binders in the lubricant solvent dispersion.

In addition to placing dry films directly on the metal part, the lamellar lubricants are often compacted into a solid mass that can be loaded against a wearing surface to transfer lubricant continuously. This method has been used for lubrication of wheel flanges, cylinder pistons, bearings, gears and the like. Binders such as polytetrafluoroethylene, thermoplastic and thermosetting resins, aluminum oxide, inorganic silicates, and ceramic compositions have been employed. These binders many times adversely affect the solid lubricant. For instance, ceramic binders must be fired at 500° C. to obtain adhesion while polytetrafluoroethylene binders require a 380° C. sintering temperature. At these temperatures materials will oxidize. For example, molybdenum disulfide oxidizes to a more abrasive material molybdenum trioxide. Furthermore, some metal substrates undergo serious deterioration of physical properties.

Polytetrafluoroethylene has been used alone as a thin film solid lubricant because of its very low coefficient of friction. The difficulty in using polytetrafluoroethylene is the difficulty of forming an adherent surface film. Also, for many applications, the high temperature required to sinter the polymer, 380° C. or better, cannot be used because of oxidation, metal fatigue, etc. Furthermore, the polytetrafluoroethylene tends to coat only on the surface of porous material and temperature changes tend to separate the film from its substrate.

Surface films of polytetrafluoroethylene have been suggested by LeBrasse et al. U.S. Pat. No. 3,305,325, for coating composite bearing materials containing molybdenum disulfide in plastic binder to improve the bearings antifrictional characteristics during break in. Lubrication is obtained solely due to the polytetrafluoroethylene and not from the dry film lubricant. This application is severely limited by the high-sintering temperature required which decomposes most binders and by the tendency of the polyetrafluoroethylene to coat the surface only, failing to penetrate into the pores of the bearing. The high-sintering temperature required to fuse polytetrafluoroethylene in effect prevents the use of most plastic-type binders used to produce dry film lubricant and bearings.

A major problem in using inorganic metallic lubricant compounds and graphite, as dry film lubricants, is the tendency of the lubricant to cause corrosion in the presence of moisture. DiSapio, U.S. Pat. No. 3,281,362 suggests forming a wax film over MoS_2 particles to prevent corrosion. Waxes having melting points below 65° C. and having fair lubricant properties are employed. However, the use of oils, greases, and waxes in conjunction with lamellar solids cause significant loss in the durability or life of such dry film lubricants. Over a large portion of the normal operating temperature of dry film bearings, above 60° C., waxes and the like are in a liquid state and act as vehicles for wear debris and contaminants while promoting wear much like lapping compounds. These liquid lubricants, under frictional pressure, also generate hydrostatic pressure within the lamellar crystalline structure of lubricants such as molybdenum disulfide, graphite, etc., and cause fracturing and disintegration. These liquid wax lubricants also reduce self healing of the dry film lubricant.

SUMMARY OF THE INVENTION

The general purpose of this invention is to provide a dry film lubricant or bearing with a coating which is resistant to the penetration of moisture and which does not appreciably influence lubricating properties or wearing properties of the lubricant. The coated bearings of this invention are particularly useful at the higher operating temperature range of dry film, say 100° C. and up. Use of the coating of this invention results in at least an order of magnitude reduction in the corrosivity of the dry film lubricant material on metallic substrates and wearing parts. The improved coated dry film lubricants of this invention have the advantages of providing lubrication at temperatures from 100° to 325° C. without contaminant wear, hydrostatic destruction, or thermal destruction of the coating. The coatings penetrate the lubricant material itself or the bearing to give improved lubricant adhesiveness and provide a moisture barrier at least twice as good as that heretofore obtained. An object of the present invention is to provide improved moisture resistant and temperature resistant coated dry film lubricants which reduce appreciably the corrosivity of dry film materials in the presence of moisture.

A further object of the invention is to provide a coated and partially impregnated dry film or bearing having improved wear resistance and operating life.

A still further object is to provide coated dry film lubricants and bearings which may be cured at temperatures which do not cause hydrolytic or thermal changes of the lubricant.

A further object of this invention is to provide a dry film lubricant coating which prevents ice adhesion to the film when exposed to low temperature.

Still another object is to provide a coating which prevents abrasive contamination of hydrophilic dry lubricant films.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention pertains to the alteration of the high-surface energy of lamellar dry film particles through the use of hydrophobic, relatively stable coating applied to the finished lubricant, whether film or bearing. A thin film of the coating is applied to the dry film lubricant or bearing and is caused to at least partially permeate its structure. For coatings dispersed in a diluent the film or bearing is rapidly heated to a temperature sufficient to diffuse the coating into the lamellar lubricant. A temperature between 100° and 325° C. is sufficient with the temperature preferably maintained near the coatings melting point. Coatings dissolved in volatile diluent solvent are merely applied to the lubricant at ambient temperature with the solvent subsequently allowed to evaporate. The impregnation of the dry film or bearing produces low-surface energy and resistance to moisture and contamination without changing appreciably the frictional behavior of the dry film lamellar solid particles.

The coating is applied to any conventional precoated substrate or bearing containing lamellar particles such as graphite, molybdenum disulfide, or the like. The coating is applied by spray brush, dip coating, or the like. Sufficient coating is applied to at least partially impregnate the lubricant and to coat the surface of the lubricant.

Useful coatings are those materials which are hydrophobic, not easily hydrolyzed or thermally degraded, and which have a melting point between 100° and 325° C. and a critical surface tension of 31 dynes/cm. or lower (20° C.). Examples are: polymerized olefins such as polyethylene, polypropylene or the like; polymerized fluoro-olefins such as poly(vinyl fluoride), poly(vinylidene fluoride) or the like; polyfluorosiloxanes such as

$$\left(-\underset{\substack{|\\ R}}{\overset{\substack{X\\ |\\ (CH_2)_n\\ |}}{Si}}-O-\right)_z$$

where; R is lower alkyl for example methyl, hexyl, etc., or aryl such as phenyl, X is perfluoroalkyl or omega hydro perfluoroalkyl having one to 12 carbons, n is at least two, and z is 1–2,000; polytetrafluoroethylene telomers, dispersed in solvent, and polyfluoroacrylate-type polymers dissolved in solvent. Particularly preferred are the polytetrafluoroethylene telomers and the polyfluoroacrylate-type polymers.

Suitable polytetrafluoroethylene telomers are described in U.S. Pat. No. 3,067,262 to Brady. These polymers have an average molecular weight from 1,300 to 15,000, a crystalline melting point in the range 225° to 320° C. and a particle size from 0.01 to about 100 microns. The polymers are commercially available in dispersion form in a suitable organic solvent such as trichlorotrifluoroethane or the like. These dispersions are available in concentration of 20 percent, 5 percent or 2.5 percent and may further be diluted where desired. Concentrations ranging from 0.1 to 40 percent of fluorotelomer by weight dispersed in the organic solvent may be employed for coating purposes. It has been found that a 2 percent dispersion by weight of the polymer particles is very satisfactory. The preferred telomer has an average molecular weight of 3,700, a crystalline melting point of 300° C., a softening point of 265° C. and an approximate average particle size of 5 microns. Such polymers are available from the DuPont Company under the trade name "Vydax."

Particularly preferred coatings are the acrylate-type polymers used in the textile industry for producing water repellent and dirt repellent fabrics. These materials are preferred because a low-critical surface tension, about 10 dynes/cm. ease of application at ambient temperature, and thermal and hydrolytic stability. These polymers are prepared from acrylate-type esters and have the general formula:

$$CH_2=\overset{\substack{R\\ |}}{C}-\overset{\substack{O\\ \|}}{C}-O-(CH_2)_n-(CF_2)_mX$$

where R is a hydrogen or methyl
n is an integer from 1 to 12
m is an integer from 1 to 12
x is hydrogen or fluorine

specific examples of these esters are: 1H, 1H, 2H-difluoroethyl acrylate, 1H, 1 H-trifluoroethyl methacrylate, 1H, 1H-pentafluoropropyl acrylate, 1H, 1H, 3H-tetrafluoropropyl methacrylate, 1H, 1H, 2H, 2H-pentafluorobutyl acrylate, 1H, 1H, 5H-octafluoropentyl methacrylate, 1H, 1H-tridecafluoroheptyl acrylate, 1H, 1H, 7H-dodecafluoroheptyl methacrylate, 5-(perfluoropropyl) pentyl methacrylate, 3-(perfluorobutyl) propyl acrylate, 1H, 1H, 2H, 2H, 3H, 3H-Nonafluoroheptyl acrylate, 1H, 1H-pentadecafluorooctyl methacrylate, 1H, 1H, 8H-tetradecafluorooctyl acrylate, 1H, 1H, 11H-eicosafluorohemdecyl methacrylate, 1H, 1H-tricosafluorododecyl acrylate, 4-(perfluoroctyl) butyl methacrylate, 8-(perfluorobutyl) octyl acrylate, 8-(ω-hydroperfluorobutyl) octyl methacrylate, 12(perfluoro-4-ethyl cyclohexyl)undecyl acrylate, 12-(perfluorobutyl) dodecyl methacrylate, 12-(perfluorododecyl) dodecyl acrylate, 12-(perfluorodecyl) dodecyl acrylate, 2-(perfluorododecyl) ethyl methacrylate, 12-(ωhydroperfluorododecyl) dodecyl methacrylate, and mixtures of two or more thereof.

The acrylate-type esters are readily polymerized by methods known to the art, for example, bulk polymerization, solution polymerization and emulsion polymerization, using catalysts such as benzoyl peroxide or other free radical initiators of polymerization. For coating purposes a solution of from 0.1 to 40 percent polymer in volatile organic solvent may be used. About 2 percent by weight polymer is preferred for coatings. The coating compositions of this invention may readily be applied to dry film lubricant surfaces by spray gun, brushing, or equivalent art recognized methods.

The coatings are generally dispersed or dissolved in a suitable solvent and then sprayed coated or brushed onto the lubricant surface. After application of a coating dispersed in a diluent solvent, the coated lubricant is rapidly heated to between 100° to 325° C.; preferably within 25° C. of the coating's melting point to diffuse the coating part way into the lamellar lubricant film or bearing. For example, in dealing with dispersed polytetrafluoroethylene telomers, heating softens the telomer and allows it to flow into the pore structure of the lamellar solids and also causes the evaporation of a solvent. Where a solution of coating in volatile solvent is employed, for example, an acrylate-type polymer dispersed in xylene hexafluoride, the solvent is merely evaporated at room temperature to leave an adherent coating. Ambient temperature application of the coatings is particularly useful where the temperature required to soften or melt a dispersed coating would cause thermal destruction of certain plastic binders used in dry film bearings. The resulting coating applied to the dry film lubricant coated metal substrate or bearing is relatively cohesive and adherent film which is resistant to moisture and other contaminates of the atmosphere. The films provide excellent corrosion inhibiting properties and further aid the lubricating ability of the graphite, molybdenum disulfide or other dry film lubricant.

The invention is illustrated, but not limited, by the following specific examples of the preparation of the coated dry film lubricant. Wherever possible alternate modes of preparation are discussed, but it will be recognized that various additional modifications can be made within the scope of the invention.

EXAMPLE 1

A polytetrafluoroethylene telomer, having an average molecular weight of 3,700, crystalline melting weight of 300° C. and concentration of 2.5 percent fluorotelomer in inert trichlorotrifluoroethane is sprayed from an aerosol container onto a dry film of molybdenum disulfide dispersed in boehmite alumina binder and bonded to a steel substrate. The entire surface area of the film is coated. The coated lubricant is then heated to at least 265° C. to soften and diffuse the fluorotelomer into the lamellar lubricant film. The coated film is maintained at elevated temperature until the solvent vehicle is evaporated. Alternatively the temperature may be lowered and vacuum technique or other equivalent used to remove residual solvent. The coating is sufficient to prevent corrosion of the molybdenum disulfide coated steel for more than 24 hours whereas a control, without coating, corrodes within 1 hour.

EXAMPLE 2

A 2 percent solution of 1H, 1 H-pentadecafluorooctyl methacylate polymer dissolved in xylene hexafluoride is brushed on a cured lamellar coating of molybdenum disulfide supported on a steel plate. Sufficient material is used to coat the entire surface. The coated article is air dried to remove solvent. The coating is sufficient to prevent water corrosion of the molybdenum disulfide coated steel for more than 24 hours whereas a control, uncoated molybdenum disulfide plate, is corroded in less than 1 hour.

EXAMPLE 3

The timing clock is lubricated with a mixture of graphite and molybdenum disulfide in equal parts. Another similarly lubricated clock's lubricant is spray coated as in example 2.

The control, or uncoated device, is inoperable below 40° F. at 65 percent relative humidity even when oil is used to reduce moisture sensitivity. The coated timing device is operable below 0° F. at the same humidity conditions.

The improved coated lamellar dry films of this invention provide equivalent or better lubrication than prior dry films without exhibiting the corrosive nature of conventional dry films. The coating provides added resistance to moisture corrosion, contamination by dirt and other substances contained in the environment, and prevents adhesion of ice to the lubricant at low temperature. The coatings do not require excessive sintering temperatures, experienced for polytetrafluoroethylene, and therefore allow a greater number of binder materials to be used to form solid bearings of dry film lubricant and binder. The coatings also avoid the problems encountered using oils, greases and waxes in connection with lamellar solids since they do not significantly affect the durability or life of the coated dry film lubricant or bearing. Obviously many modifications and variations of the present invention are possible in the light of the above teaching. It is therefore to be understood that, within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A coated dry film lubricant which comprises:

a lamellar lubricant film over a structural surface selected from the group consisting of graphite and molybdenum disulfide; and,

a coating over said film and partially absorbed therein consisting essentially of a polymerized compound of the following formula

$$CH_2=\overset{\overset{\large R}{|}}{C}-\overset{\overset{\large O}{\|}}{C}-O-(CH_2)_n-(CF_2)_mX$$

wherein R is selected from the group consisting of hydrogen and methyl, *n* is an integer from one to 12, *m* is an integer from one to 12, and X is selected from the group consisting of hydrogen and fluorine.

2. The dry lubricant of claim 1 wherein said coating is 1H, 1H-pentadecafluorooctyl methacrylate.

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