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SOLID LUBRICANT FILM RESISTANT TO CORROSION

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This invention relates to improved solid film lubricants, that is, lubricants which are applied to a friction surface in the form of a coating or film which is cured to solid form on the surface. The friction surface may be a rotary bearing or bushing surface or any other surface which in use is subjected to mechanical friction.

Lubricant films embodying the invention include organic or inorganic binder materials within which are distributed a large number of finely divided solid lubricant particles, such as graphite and molybdenum disulfide, which are held in fixed positions in the binder after it is cured. The film is desirably applied to a minutely irregularized surface, to assure optimum integration of the film and the coated part. In prior solid film lubricants of this general type, one difficulty has been that of positively preventing corrosion of the surface metal to which the lubricant film is applied.

In order to prevent corrosion of the base surface, we incorporate in the film composition minute particles of one or more materials which have been known in other arts, for example the paint industry, as "corrosion inhibitive pigments" (see for example the text "Protective Coatings for Metal" by R. M. Burns and W. W. Bradley, 1955, Reinhold Publishing Co.), which materials are adapted to exert a passivating influence on the base metal to which a protective coating is applied. These corrosion inhibitive pigments may be of any of various materials such as the metallic chromates, e.g. zinc chromate, barium chromate and cadmium chromate, strontium chromate, barium carbonate, red iron oxide (Fe_2O_3), dicalcium phosphate, red lead oxide (Pb_3O_4), or any other such pigments which are capable of exerting the corrosion inhibiting characteristics of these materials. Preferably, the inhibitor is chosen from the group of materials specifically listed above. The use of the word "pigment" in connection with the corrosion inhibitive materials is of course not intended in any sense to imply that the particles are used for coloring, but rather is used merely as a part of the phrase employed to refer to the corrosion inhibiting materials with which we are concerned.

During the experimentation that resulted in the present invention, it was learned that these corrosion inhibiting pigments, though highly satisfactory for their intended purpose, have one very decided disadvantage for use in a solid film lubricant. Specifically, these materials tend to increase excessively the wear rate of the lubrication film, and in so doing decrease its wear life to a degree requiring corrective prevention. This disadvantage is of such importance as to virtually preclude the commercial use of a solid film lubricant in which the only additive is a corrosion inhibitive pigment.

In the films of the present invention, we utilize corrosion inhibitive pigments for preventing corrosion of the coated surface, and at the same time we avoid the above mentioned disadvantage of such pigments, by employing in combination with the corrosion inhibitive material a finely divided second additive which has the effect of overcoming or compensating for the wear life reducing effect of the inhibitor, to give the film as long a wear life as if the inhibitor were not present. This second additive is a very finely divided metal, which for best results is one of the softer metals, preferably chosen from the group consisting of cadmium, lead, zinc, indium, silver and tin. However,

other metals may if desired be used, even such hard metals as iron, tungsten, molybdenum and chromium, though with somewhat less effectiveness than the softer metals. The metal may take the form of a powder, or may be in finely divided flake form. To date we have been unable to arrive at any satisfactory theoretical explanation as to exactly why a metal pigment should have the effect of overcoming wear life reducing tendencies of the corrosion inhibitive pigment, but the effect has been noted and discovered by us in actual practice and has been utilized in commercial production with very definite success.

The surface to be treated may be irregularized in any of various ways which will produce a multitude of minute substantially microscopic irregularities or cavities distributed uniformly and in closely spaced relation over the entire surface. For example, these irregularities may be produced by sand blasting the surface, or by phosphatizing, acid etching, or if the bearing part is aluminum, by anodizing. When acid etching or "pickling" is selected as the irregularizing method, this process is performed by immersing the metal part for a short period (say about two minutes) within an acid, such as sulfuric acid, hydrochloric acid, or hydrofluoric acid, the acid preferably being in concentrated form. After the irregularizing treatment, the irregularized surface should of course be thoroughly cleaned before coating.

The binder in the coating composition may be of any of various materials which can be easily coated on the surface in composition with the other ingredients, preferably as a liquid composition, and can then be cured to a hardened solid form in which the binder tightly and continuously adheres to the surface, and holds the contained particles in fixed positions in the binder. For most purposes, it is preferable that the binder include, or be entirely composed of, a resinous plastic material, typically the known thermosetting B-stage phenolformaldehyde, butyral modified phenolic, alkyd and polysiloxane resins. Illustrative commercial resins are:

(1) Thermosetting phenolic resin—GE 75121, as sold by General Electric Co., 1 Textolite Avenue, Coshocton, Ohio.

(2) Butyral modified phenolic thermosetting resin—FM-47, as sold by Bloomingdale Rubber Co., Chester, Pennsylvania.

(3) Triazine-formaldehyde thermosetting resin—Uformite MX61, as sold by Rohm & Haas, Philadelphia, Pennsylvania.

The resin may be thinned by a suitable solvent or diluent, to a condition giving the composition proper fluidity for application by spraying, brushing or whatever application process may be used. The solvent or diluent can of course be any of the known solvents or diluents for the particular resin being employed. Typical solvents and diluents which may be used are dioxane, secondary butyl alcohol and diacetone alcohol.

For high temperature applications, as for instance on bearings which may be subjected to temperatures in excess of 800° F. when in use, the binder may be a ceramic material, such as any of various known porcelain enamel frits capable of being fused to a continuous, smooth, uniform thickness film form on the surface to be treated. Any suitable conventional porcelain enamel binder may be employed, as for instance that sold by Ferro Corporation, 5309 South District, Los Angeles, California, under the trade designation FB80E. As in the case of most other frits for this purpose, the above designated frit is composed essentially of lead oxide, silica, alkali metal oxides (such as potassium oxide and sodium oxide) and titanium dioxide. Two other typical porcelain enamel frits are the product bearing the trade name of "Porcenell," sold by Allied Porcenell, Inc. of Waukegan, Illinois (a porcelain enamel designed primarily for steel);

and the product sold as "Aluminum Porcelain Enamel No. L388," sold by E. I. du Pont de Nemours.

When a porcelain enamel binder is employed, there may also be utilized an appropriate addition agent for improving the adhesion characteristics of the film and preventing "tearing" of the film. This agent may typically be any of various water soluble silicates or oxides, such as sodium silicate, potassium oxide, silicon dioxide, sodium oxide, boron trioxide (B_2O_3), silica dioxide, or calcium oxide, and may be added to the mixture in the form of a water solution. Also, a quantity of water, or another suspending liquid or carrier, is added to the frit composition to give it a proper fluid consistency for spraying, brushing, dipping, or the like.

The solid lubricant particles in the film forming composition may be any of various known materials which are useful for this purpose (or mixtures thereof). Several typical lubricant materials which may be used in a resinous binder are:

*Graphite
*Molybdenum disulfide
Sulfides of titanium (such as titanium disulfide and trisulfide)
Molybdenum selenide
Molybdenum telluride
*Boron nitride
*Lead oxide
Cadmium oxide
*Silver sulfate
Cadmium iodide
Cadmium chloride
*Tungsten disulfide

The materials marked with an asterisk above may also be utilized in a porcelain enamel binder, as may the following additional lubricants:

Vermiculite
Mica
Ferrous chloride
Ferrous sulfide

All of the various ingredients distributed in the binder, that is the solid lubricant particles, corrosion inhibitive pigments and metal particles, as well as the frit particles and other ingredients where used, should be milled to an extremely finely divided condition. Preferably, all of these particles except the frit should be predominantly (preferably substantially entirely) not over about 10 microns in size (maximum particle dimension), and for best results not more than about 3 microns in size.

The composition is applied in liquid form to the irregularized surface, and is then cured to a hardened solid film form. The curing is normally effected by heating the coated part to a proper temperature for polymerizing its resin binder (where a resin is employed), or fusing its porcelain enamel frit binder material (where employed) to a solid vitreous enamel form. The coating when first applied, and also after curing (this term being used to include the fusing of a frit), should preferably be not more than about $\frac{1}{1000}$ of an inch in thickness. With regard to proportions, it is desirable that the corrosion inhibiting particles constitute between about 3% and 35% by weight of all materials contained in the binder (not including the binder). Also, the metal particles added to counteract the abrasiveness of the corrosion inhibitor should by weight be equal to between about one-eighth and twice the weight of the corrosion inhibitive pigments. The total weight of all materials contained in the binder may be between about three-fourths of a pound and three and one-half pounds per gallon of the binder.

When a resin binder is used, it is normally desirable to incorporate in the composition a thickening agent. Best results to date have been obtained through use for this purpose of a cation-modified clay such as is described in

U.S. Patent No. 2,531,427, issued November 28, 1950, to Ernst A. Hauser. These cationic materials are essentially ammonium-base derivatives of the clays, such as the ammonium, phosphonium, oxonium, sulfonium, arsonium, stibonium and telluronium derivatives. Typical thickening agents for use in the compositions are the materials supplied by the National Lead Company under the trade names "Bentone 34," "Bentone 18C" and "Bentone 38." These materials are all chemically described as dimethyldioctadecylammonium bentonite. They have a specific gravity of 1.8, and are desirably of a small particle size when used, being in the form of platelets of about .05 to 1.0 micron (maximum dimension) by .002 to .004 micron in size. The concentration of the thickening agent may vary over wide limits, but for superior results the concentration should vary from about .025% to .2% by weight of the total composition.

Another ingredient which is preferably incorporated in the composition when a resin binder is employed, is a wetting agent, which may be any of various surfactants, ionic or nonionic, usable for this purpose, such as alkyl aryl sulfonates (e.g. sodium dodecyl benzene sulfonate), fatty acid sulfates (e.g. lauryl sulfate), fatty acid amides, alkylolamides, and the like.

As illustrations of specific examples of the invention, actual coated parts embodying the invention have been made as follows:

Example I

The bearing surface of a rotary bearing made of aluminum was pretreated by anodizing, to form minute irregularities distributed continuously in very closely spaced relation over the entire bearing surface. This surface was then cleaned, and a coating composition was sprayed onto the entire irregularized surface, the composition consisting of the following ingredients, in the proportions designated (these proportions and all others in this application being by weight unless otherwise designated):

	Parts
Graphite particles	14.6
Molybdenum disulfide particles	128
Zinc chromate powder	40.8
Cadmium powder	20.4
Butyral modified phenolic resin (FM 47, Bloomingdale Rubber Co.)	391.5
Dioxane	1210.0
Wetting agent (sodium dodecyl benzene sulfonate)	.5
Thickening agent (dimethyl-dioctadecylammonium bentonite)	5.1

In this composition, the graphite and molybdenum disulfide were the solid lubricant particles, the zinc chromate was the corrosion inhibitive pigment, and the cadmium powder was the metal utilized to overcome the wear accelerating tendencies of the zinc chromate. The butryal modified phenolic resin was of course the binder, with the dioxane being employed as a solvent to thin the composition to proper liquid consistency for spraying. All of the pigment particles in the composition, including the graphite, molybdenum disulfide, zinc chromate, cadmium and bentone 34 were milled to a condition in which the individual particles were substantially all not more than 10 microns in size (maximum dimension).

The above mixture was sprayed onto the irregularized surface to a uniform thickness of .00035 of an inch, and the coated bearing was then baked at 325° F. for one hour to drive off the solvent and polymerize the thermosetting resin to a hard solid film form. The polymerization tightly and continuously bonded the film to the irregularized bearing surface, with the binder and its contents being embedded in the irregularities, and with the various pigments or particles all held firmly in place by the binder. The bearing coated in this manner was tested

under frictional load for 40 hours without suubstantial wear, and successfully withstood a salt spray, without corrosion, for 250 hours.

Example II

A high crabon steel bearing surface was irregularized by phosphatizing, by treatment with the product sold as Lubrite No. 2 (manganese phosphate) by Parker Rustproofing Co. The surface was then cleaned and coated as in Example I, except that the coating mixture had the following different composition:

	Parts
Graphite	16
Molybdenum disulfide	64
Zinc chromate	23
Cadmium powder	11.5
Wetting agent (lauryl sulfate)	.3
Thickening agent (dimethyl-dioctadecylammonium bentonite)	.3
Phenolic resin (GE–75121)	79.4
Polyvinyl butyral resin (B76 Shawinigan Resins Corp.)	21.8
Secondary butyl alcohol (solvent)	818

The film was cured at 400° F. for 30 minutes, and proved under test to have a very long wear life and to be highly corrosion resistant.

Example III

A steel bearing surface was irregularized by sandblasting, and was then coated with a mixture of the following composition:

	Parts
Graphite	14.6
Molybdenum disulfide	128
Barium carbonate (corrosion inhibitive pigment)	40.8
Lead powder to overcome abrasiveness	20.4
Wetting agent (fatty acid amide)	.5
Thickening agent (dimethyl-dioctadecylammonium bentonite)	5.1
Xylene (solvent)	1210
Triazine-formaldehyde thermosetting resin	250

The composition was cured at 400° F. for 30 minutes. The particle size and other features and characteristics of this example and Example II were the same as in Example I except for the particular differences mentioned specifically above.

Example IV

An aqueous suspension was formed of Porcelain Enamel Frit FB80E sold by Ferro Corporation, 5309 South District, Los Angeles, California, the suspension being 80 percent frit and 20 percent water. This suspension was ball milled until substantially all of the frit solids (at least 99%) would pass through a 200 mesh screen, and were therefore not greater than about 74 microns in size. This suspension was then mixed with other ingredients to give the following composition (aqueous suspension):

	Parts
Frit FB80E	50
Lead oxide (PbO) (solid lubricant particles)	50
Graphite (solid lubricant particles)	50
Zinc chromate	46.5
Cadmium powder	23.5
Water	400

The composition was sprayed onto a No. 410 stainless steel bearing surface which had been irregularized by sandblasting, and the coated part was then heated to 250° F. for one-half hour, and finally to 1000° F. for 15 minutes. This fused the frit into a porcelain enamel binded tightly fuse bonded to the roughened bearing surface and having the various particles firmly held and uniformly distributed therein. The bearing was able to operate for extended periods at high temperatures, and to resist corrosion effectively. The lead oxide, graphite, zinc chromate and cadmium particles used in the film were in the case of each material substantially entirely under about 10 microns in maximum particle dimension. The ultimate film in this example was about .0004 inch.

Example V

This example is identical with Example I, except for the substitution of strontium chromate for the zinc chromate, the same number of parts being used.

We claim:

1. The combination comprising a part having a surface which is subjected in use to mechanical friction, said surface having irregularities forming minute depressions distributed substantially uniformly thereacross, and a lubricant coating bonded to said surface, said coating including a binder cured to solid form on said surface and continuously bonded thereto, finely divided solid lubricant particles distributed within the binder across substantially said entire surface, finely divided particles distributed within the binder separately from said surface and formed of a corrosion inhibitive inorganic compound operable to resist corrosion of said surface but which compound would normally tend to accelerate frictional wearing of the coating, said inorganic compound being selected from the group consisting of zinc chromate, barium carbonate, barium chromate, cadmium chromate, strontium chromate, red iron oxide (Fe_2O_3), dicalcium phosphate and red lead oxide (Pb_3O_4) and a large number of finely divided metal particles distributed within said binder in addition to the above mentioned materials in sufficient amount to counteract the wear accelerating tendency of said corrosion inhibitive pigment.

2. The combination as recited in claim 1, in which said coating has a thickness under $\frac{1}{1000}$ of an inch.

3. The combination as recited in claim 1, in which all of said particles are predominantly under about 10 microns in maximum dimension.

4. The combination as recited in claim 1, in which said binder includes a thermosetting resin polymerized to hardened condition on said surface.

5. The combination as recited in claim 1, in which said metal particles are chosen from the group of metals consisting of cadmium, lead, zinc, indium, silver, tin, iron, tungsten, molybdenum and chromium.

6. The combination as recited in claim 1, in which said solid lubricant particles are chosen from the group of materials consisting of graphite and molybdenum disulphide.

7. The combination as recited in claim 1, in which said binder is a ceramic material.

8. The combination as recited in claim 1, in which said binder is a porcelain enamel material.

9. The combination as recited in claim 1, in which said corrosion inhibitive particles constitute by weight between about 3% and 35% of all materials contained in the binder, but not including the binder.

10. The combination as recited in claim 9, in which the weight of said metal particles is equal to between about one-eighth and twice the weight of said corrosion inhibiting materials.

11. The combination as recited in claim 10, in which the total weight of all materials contained in the binder is equal to between about three-fourths of a pound and three and a half pounds per gallon of the binder.

12. A lubricant composition to be coated onto an irregularized surface which is subjected in use to mechanical friction and to be cured in place on said surface, comprising a uniform mixture of a binder adapted to be cured to a solid film on said surface and bonded continuously thereto, finely divided solid lubricant particles distributed within the binder, finely divided particles distributed within the binder and formed of a corrosion inhibitive inorganic compound operable to resist corrosion of said surface but which compound would normally tend to accelerate fric-

tional wear of the coating, said inorganic compound being selected from the group consisting of zinc chromate, barium carbonate, barium chromate, cadmium chromate, strontium chromate, red iron oxide (Fe_2O_3), dicalcium phosphate and red lead oxide (Pb_3O_4) and finely divided metal particles distributed within said binder in addition to the above mentioned materials in sufficient amount to counteract the wear accelerating tendency of said corrosion inhibitive particles in the coating.

13. A lubricant composition as recited in claim 12, in which all three types of said particles are predominantly under about 10 microns in maximum dimension.

14. A lubricant composition as recited in claim 12, in which said binder includes a thermosetting resin polymerizable to hardened condition on said surface.

15. The lubricant composition as recited in claim 12, in which said metal particles are chosen from the group of

soft metals consisting of cadmium, lead, zinc, indium, silver and tin.

16. The lubricant composition as recited in claim 12, in which said solid lubricant particles are chosen from the group of materials consisting of graphite and molybdenum disulphide.

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