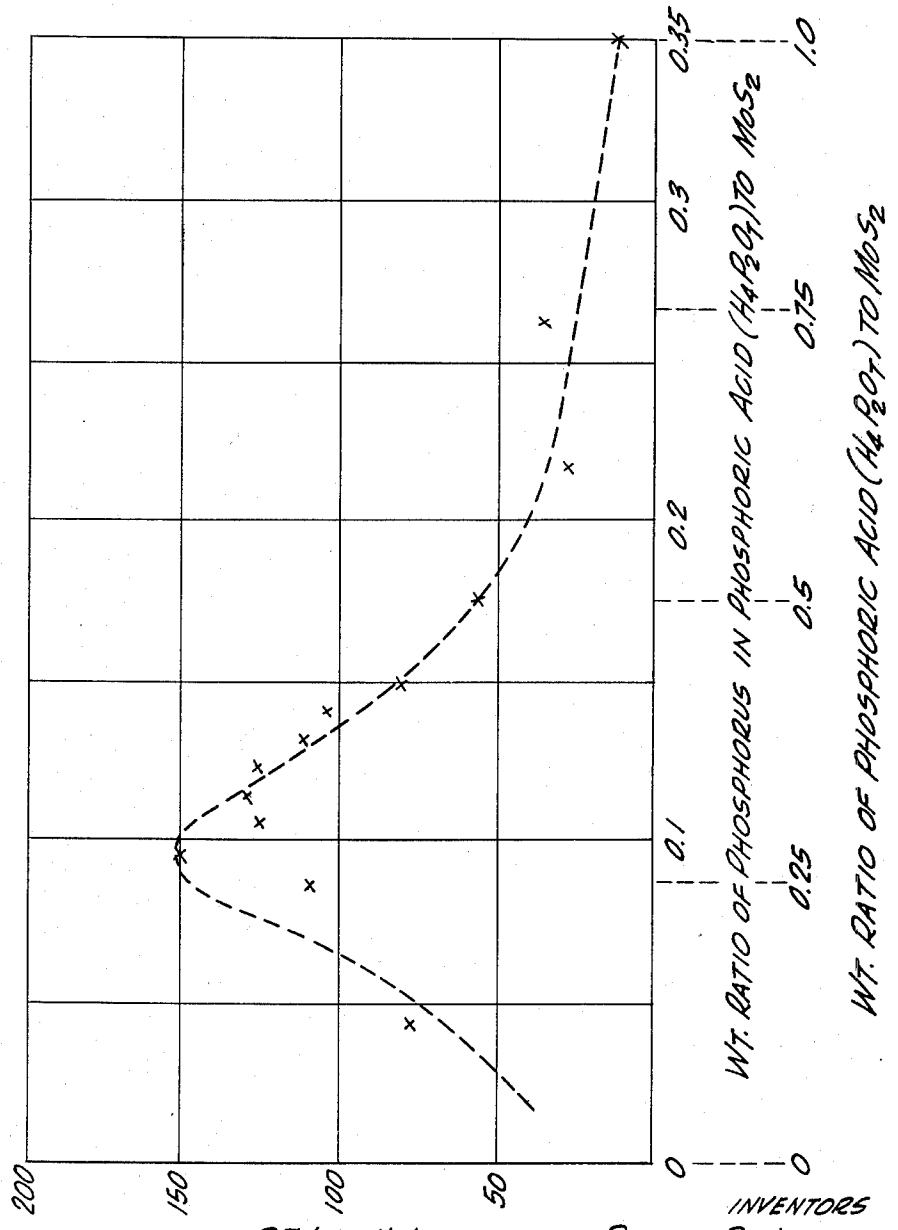
June 7, 1960 D. P. JENSEN ET AL 2,939,809

DRY FILM LUBRICATION

Filed Dec. 7, 1956



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United States Patent Office 2,939,809 Patented June 7, 1960

2,939,809

DRY FILM LUBRICATION

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Filed Dec. 7, 1956, Ser. No. 626,975

23 Claims. (Cl. 148—6.17)

This invention relates to dry film lubrication. More particularly, it relates to a new composition of matter useful for forming a dry solid lubricant film containing molybdenum disulfide lubricant powder on the surface of a metallic element subjected in use to mechanical friction and bonding the molybdenum disulfide dry lubricant within the film and the film to the metal surface, relates to the process of forming such a dry solid lubricant film on the surface of such a metallic element, relates to the method for lubricating the surface of such a metallic element by the application of such a lubricant film thereto with such a composition, and relates to the articles resulting from such process having such a dry solid lubricant film bonded to the surface of the metallic element.

Molybdenum disulfide is known as a dry solid lubricant. Various processes have been devised for applying molybdenum disulfide in a film to the surface of metal subjected in use to mechanical friction. For example, molybdenum disulfide has been applied to the metal surface in the form of a film simply by dusting the molybdenum disulfide powder onto the surface. It has been applied by spraying or brushing a dispersion of the powder in a liquid, such as corn syrup, asphalt-base varnish, silicones, glycerine, ethylene glycol, and polyglycol, and allowing it to dry and cure. It has been applied by first phosphating the metallic surface to produce a crystalline layer having a porous surface and then filling with molybdenum disulfide powder. Another method of application is by incorporation of the molybdenum disulfide in a resinous binder followed by application of the mixture to the surface, which must be pre-treated for satisfactory results, such as by phosphatizing steel, anodizing or alodining aluminum, acid etching copper or bronze, sandblasting stainless steel surfaces, and then baking the mixture. Some of such processes are described in the publication of Climax Molybdenum Company, 500 Fifth Avenue, New York, entitled "Molybdenum Disulfide as a Lubricant" and Technical Note 2628 of the National Advisory Committee for Aeronautics, entitled "Bonding of Molybdenum Disulfide to Various Materials to Form a Solid Lubricating Film, I—the Bonding Mechanism." None of such processes of application, however, except with some resinous binders, produces a film which has a satisfactory wear life in use, especially under heavy loads. This is particularly revealed as tested by the well-known Falex Machine. Moreover, even those films resulting from the use of a resinous material which are satisfactory at high loads require a number of steps for their production, making the process relatively uneconomical, especially as compared with the simple process of this invention, which renders many of these steps unnecessary.

In accordance with our invention, the surprising and unexpected discovery has been made that a satisfactory dry lubricant film of molybdenum disulfide can be formed on and bonded to the frictional surface of a metallic element by the very simple expedient of using only a mixture of a suitable phosphoric acid, fine molybdenum disulfide lubricant powder, and solvent. This mixture contains the phosphoric acid in solution and molybdenum disulfide particles in suspension, and, because of the presence of the solvent, is of such consistence that it can be sprayed or brushed onto the surface of the metal.

In accordance with our invention, it is possible not only to produce a lubricant film of molybdenum disulfide formed on and bonded to metal surfaces substantially as good as or superior to those produced using the well-known resinous binders, but also the method in accordance with the invention requires fewer steps and materials and is simpler and more economical. No special pre-treatment, either chemical or mechanical, of the metal surface is required. The surface, of course, should be clean so that the applied film can contact the metal surface to which applied. Moreover, it is an especially important advantage that the film formed in accordance with the invention is inorganic, will withstand high temperatures, and does not oxidize or otherwise deteriorate or form undesirable reaction products.

Accordingly, it is an object of our invention to provide a new composition of matter useful in forming and bonding a dry solid lubricant film of molybdenum disulfide to the frictional surfaces of metallic elements.

It is another object of our invention to provide a method of bonding a dry solid lubricant film of molybdenum disulfide to the surface of a metallic element subjected to mechanical friction during use in which the bonding is effected by means of phosphoric acid.

It is still another object of the invention to provide a method of lubricating the surface of a metallic element subjected to mechanical friction in use by applying to the frictional surface a dry solid film lubricant of molybdenum disulfide bonded thereto with phosphoric acid.

A further object of our invention is the provision of metallic elements the frictional surfaces of which carry a dry film lubricant of molybdenum disulfide bonded by means of phosphoric acid.

Other more particular objects, advantages and uses of the invention will be apparent from the specification describing the invention taken with the accompanying figure.

The figure is a plot showing the relationship of wear life of films as tested on the Falex Machine with variations in the composition of the relative proportions of the pyrophosphoric acid to molybdenum disulfide and of the phosphorus content in the phosphoric acid to molybdenum disulfide. This figure is more particularly described in connection with Example 2 below.

In general, the compositions of the invention are made by mixing molybdenum disulfide lubricant powder with phosphoric acid dissolved in solvent. The molybdenum disulfide (MoS_2) powder is preferably a dry lubricant powder of fine particles, in general known and used for lubrication. The phosphoric acids discovered to be especially suitable for the invention are the polymerizable phosphoric acids in which the phosphorus is pentavalent and bonded to four oxygen atoms, particularly including orthophosphoric acid (H_3PO_4) pyrophosphoric acid (diphosphoric acid, $H_4P_2O_7$), and triphosphoric acid ($H_5P_3O_{10}$). The solvents for the phosphoric acid include

water, ethyl alcohol, butyl alcohol, normal propanol, ether, dioxane, and benzene.

In carrying out the process of the invention for forming and bonding the dry film lubricant on the metal surface, a liquid film of this composition is applied to the surface of the metal, the solvent is removed by evaporation or drying, and the liquid film is then cured by air drying or heating, preferably the latter, to set the phosphoric acid, producing a relatively hard tenacious film bonded to the metal surface.

Evidence indicates that the setting of the film and bonding to the metal surface results from (1) a reaction between the metal surface and the phosphoric acid forming metal phosphates at the metal-film interface to effect the bonding and (2) a condensation polymerization of the phosphoric acid to effect the setting. This condensation polymerization of the phosphoric acid, which may be augmented by heating, produces a set which holds the MoS_2 particles in the film probably by forming an interlocking structure about the MoS_2 particles. Moreover, the metal phosphates formed at the interface of metal and film are also probably interlocked with the condensation polymers of phosphoric acid.

The cendensation polymerization of phosphoric acid by itself is negligible at room temperature (70° F.), even on a phosphated surface, proceeding more rapidly as the temperature is raised. However, in accordance with the invention, the condensation polymerization takes place in a few hours at room temperature after the composition is applied on the metal surface to be lubricated. At the same time, the composition has a relatively long shelf life when packaged in bottles. These facts suggest that there is a complex interaction between the metal phosphates, formed by the action of phosphoric acid on the metal, and the molybdenum disulfide, which produces a catalytic action on the condensation polymerization of the phosphoric acid.

The reaction of phosphoric acid with the metal should not take place to such an extent or at such a rapid rate, after the liquid coating is applied, as to cause a bubbling and consequent blistering of the film from evolution of too much hydrogen gas. This will, of course, depend on the particular metal and can be controlled for any particular metal, in accordance with the invention, by maintaining the temperature of curing sufficiently low to avoid too much bubbling or by choosing a solvent in which the reactivity of phosphoric acid with the metal is sufficiently low to avoid such bubbling, or by a combination of both. For any particular metal and particular solvent, a simple test of applying a small portion of the coating to specimens of the metal and heating to various temperatures will quickly indicate the temperature above which undesirable blistering will result and the temperature below which curing should be carried out.

If it is necessary to so lower the temperature that satisfactory curing or polymerization does not take place to produce a film sufficiently hard to act as a satisfactory binder for the molybdenum disulfide, a solvent in which the phosphoric acid is less reactive with the metal may be used. The condition of the film may readily be determined by rubbing or scraping with a knife. If the film can be easily removed, the cure or polymerization is not satisfactory. In accordance with the invention, it has been discovered that the reactivity of phosphoric acid is greatest when water is used as the solvent and that ethyl alcohol and butyl alcohol, in that order, follow water with respect to the reactivity of phosphoric acid. Combinations of such solvents and of the other solvents previously mentioned may also be used to obtain a solvent mixture with the desired reactivity of the phosphoric acid for the particular metal upon which the film is to be applied and for the desired temperature of curing. The temperature of curing will usually be within the range of room temperatures of about 70° F. to as high as about 400° F., but, as pointed out above, should not be so high as to cause the film to blister.

The composition of the invention can be used to provide a lubricated surface on such metals as low carbon steels, alloy steels, corrosion resistant steels, cadmium-plated steels, aluminum alloys, anodized aluminum, magnesium alloys, bronze, copper and titanium. The composition of the invention is particularly useful on cadmium plated steel, producing films with greater load carrying capacity than previously obtained with the commercial products using a resinous binder. The use of the composition of the invention on cadmium-plated steel is more particularly described in Example IV below.

As previously mentioned, the reactivity of phosphoric acid varies with the different metal surfaces involved. With the magnesium alloys, for example, the reaction is rapid and vigorous, and care should be exercised in the manner previously mentioned to prevent excessive blistering of the metal. With the corrosion resistant steels, the reaction proceeds more slowly, and heat is required to complete the curing of the film.

The most satisfactory combinations of temperature and solvent can be ascertained for any particular metal surface by those skilled in the art from the foregoing description and particularly with the simple tests described, taken with the examples below, which illustrate the invention.

The relative proportions of the three essential ingredients, phosphoric acid, solvent, and molybdenum disulfide will in general be determined in accordance with the following considerations. The minimum requirement for the phosphoric acid is that there be enough phosphoric acid to provide a binder for the molybdenum disulfide. There should be a sufficient amount of the molybdenum disulfide particles to cover the metal surfaces within the polymerized phosphoric acid binder and form a lubricating coating. On the other hand, the relative amount of the molybdenum disulfide should not be so great as to impair the binding action of the phosphoric acid upon polymerization, resulting in a film that will brush or scrape off too readily. The minimum requirement for the solvent is that there be enough to form a mixture of the phosphoric acid and molybdenum disulfide which can be applied as desired, as by brushing, spraying, or by dipping of the part to be coated in the mixture. The solvent should not be present in such large amounts as to make the mixture too thin to produce a satisfactory film.

More particularly, in accordance with the invention, it has been found that the longest wear life of the lubricant film, as measured by the Falex tester, is obtained when the weight ratio of the phosphoric acid to the molybdenum disulfide or, expressed in other terms, when the weight ratio of the phosphorus content in the phosphoric acid to the molybdenum disulfide is within a controlled range. When pyrophosphoric acid is used with the molybdenum disulfide, the longest wear life is obtained when the weight ratio of pyrophosphoric acid to molybdenum disulfide is within the range of about 0.06 to 0.6. The optimum results are obtained when the weight ratio of pyrophosphoric acid to molybdenum disulfide is in the range of about 0.15 to 0.5. When these results are expressed as weight ratios of phosphorus content in the phosphoric acid to MoS_2, the preferred range is from about 0.02 to 0.20 with the optimum results in the range from about 0.05 to 0.16. These results are more particularly described in Example II below with its accompanying table.

As previously mentioned, orthophosphoric acid (H_3PO_4) may also be used in the composition of the invention. However, allowance should be made for the greater reactivity of orthophosphoric acid upon the metal surfaces involved. The use of orthophosphoric acid is more particularly described in Example III below. In

addition to pyrophosphoric and orthophosphoric acids, triphosphoric acid ($H_5P_3O_{10}$) may be used. Also, mixtures of these phosphoric acids may be used.

The thickness of the cured film is dependent to a large extent upon the method of application of the coating. Films which have been applied by brushing generally have greater thickness than those which have been applied by spraying. In general, the cured film should not be so thick as to interfere with the function of the lubricated part or so thin as to present an ineffective lubricating surface. In accordance with the invention, it has been found that the preferred thickness of the cured film is in the range of from 0.0003" to 0.0005". Although longer wear life can be obtained with thicker coatings they are more subject to scuffing wear in handling and fitting of the parts prior to use.

The article in accordance with the invention is a metallic element with a surface subject to friction in use, which surface is coated with a dry lubricant film made from the compositions described above and bonded to said surface by the process described above. The film contains fine molybdenum disulfide dispersed over the surface and held in position by the polymerized phosphoric acid and by the reaction products of the phosphoric acid with the metal surface.

The following examples will illustrate the invention:

EXAMPLE I

A composition of the invention was made by thoroughly mixing 20 grams of finely powdered molybdenum disulfide with 5.5 grams of liquid pyrophosphoric acid ($H_4P_2O_7$, 100%) dissolved in a solvent mixture of 18 milliliters of 190 proof ethyl alcohol and 18 milliliters of normal butanol, forming a suspension of the molybdenum disulfide particles in the pyrophosphoric acid and alcohol mixture. The molybdenum disulfide powder used was a commercial grade of molybdenum disulfide solid lubricant ground in a ball mill for 24 hours to a fineness such that 75% of the particles were less than 11 microns, 95% of the particles were less than 25 microns, and none of the particles was larger than 44 microns (325 mesh). The solvent was used to provide a spraying consistency to the suspension. The mixture of ethanol and butanol gave the desired degree of reactivity of the phosphoric acid on the metal surface on which the composition was applied and served to produce the desired hard, resin-like film upon condensation polymerization of the phosphoric acid.

The composition was sprayed upon heat-treated (180,000–200,000 p.s.i.) 4130 steel Falex parts (blocks and pins) to form a wet film coating thereon. Except for a solvent wipe, the Falex parts were not given any kind of a chemical or mechanical pretreatment. The applied film was dried at room temperature (70° F.) for about 10 minutes and then cured in a circulating air oven at 400° F. ±10° F. for about 30 minutes. The resulting cured film was about 0.0005" thick. It was hard and tough, resisting ordinary wear, and formed an exceedingly slippery lubricating surface.

These Falex parts carrying the dry lubricant film of the invention were then tested in the Falex Machine under the severe conditions of 299 revolutions per minute at a gauge load of 1,000 pounds, which corresponds to a unit load of about 50,000 pounds per square inch. The full load was first applied and then the machine was started. It ran for the long time of 150 minutes without incipient failure. A five inch-pound increase in observed frictional torque was taken in this test as the point of incipient failure.

EXAMPLE II

The data in Table I illustrate the critical ranges for the weight ratio of the phosphoric acid to molybdenum disulfide for obtaining the longest wear life of the cured film.

Table I

Pyrophosphoric Acid Content, Grams	$H_4P_2O_7/MoS_2$ Weight Ratio	P in $H_4P_2O_7/MoS_2$ Weight Ratio	Falex Wear Life, Mins.
2.5	0.125	0.0438	78
3.75	0.188	0.0658	38
5.0	0.250	0.0875	108
5.5	0.275	0.0963	150
6.0	0.300	0.105	123
6.5	0.325	0.114	128
7.0	0.350	0.123	125
7.5	0.375	0.131	110
8.0	0.400	0.140	104
8.5	0.425	0.149	80
10.0	0.500	0.175	55
12.5	0.625	0.219	28
15.0	0.750	0.263	35
20.0	1.000	0.350	12
30.0	1.500	0.525	16

All compositions shown in Table I were made with 20 grams of molybedenum disulfide using a solvent mixture, as in Example I above, of 18 milliliters of 190 proof ethyl alcohol and 18 milliliters of normal butanol and using the weight in grams of pyrophosphoric acid ($H_4P_2O_7$) shown in the table. Each of the compositions was made up, applied to Falex parts, dried, cured and tested as described in Example I above. Where necessary, a minor proportion of additional solvent mixture was added to render the liquid suspension readily sprayable. The coating thickness varied from 0.0003" to 0.0005" on all parts.

The results shown in Table I are plotted in Figure 1 of the drawings. In Figure 1, the wear life, as measured by the Falex machine, is plotted against the weight ratio of pyrophosphoric acid to molybdenum disulfide and also against the weight ratio of phosphorus in the pyrophosphoric acid to molybdenum disulfide. It will be noted that the longest wear life is obtained when the weight ratio of $H_4P_2O_7$ to MoS_2 is within the range of 0.06 to 0.60 and that the optimum results are obtained when the weight ratio of $H_4P_2O_7$ to MoS_2 is in the range of 0.15 to 0.50. When the results are expressed as weight ratios of phosphorus in the phosphoric acid to molybdenum disulfide, the preferred range is from 0.02 to 0.20 with the optimum results in the range from 0.05 to 0.16.

EXAMPLE III

This example illustrates the use of orthophosphoric acid in the composition of the invention. The composition was made by thoroughly mixing 20 grams of finely powdered molybdenum disulfide with 8.5 grams of 85% orthophosphoric acid (85 percent of H_3PO_4 and 15 percent of water) dissolved in 35 milliliters of normal butanol, forming a suspension of the molybdenum disulfide particles in the phosphoric acid alcohol solution. The molybdenum disulfide power was the same as for Example I above.

This suspension was sprayed upon heat-treated (180,000–200,000 p.s.i.) 4130 steel Falex parts (blocks and pins) to form a wet film coating thereon. This film was dried at room temperature (70° F.) for about 10 minutes and then cured in a circulating air oven at 400° F.±10° F. for about 30 minutes. The resulting film was about 0.0005" thick. It was hard and tough, resisting ordinary wear and formed an exceedingly slippery surface.

These Falex parts carrying this dry solid lubricant film of the invention were then tested in the Falex machine at 299 revolutions per minute at a gauge load of 1000 pounds. Full load was first applied and then the machine was started. It ran for the long time of 95 minutes before incipient failure.

EXAMPLE IV

In order to demonstrate the superior wear life of the composition of the present invention on cadmium-plated steel, the composition described below was prepared and

tested with the Falex machine together with a typical commercial product. The composition of the invention was made by thoroughly mixing 20 grams of finely powdered molybdenum disulfide lubricant with 5 grams of liquid pyrophosphoric acid ($H_4P_2O_7$, 100%) dissolved in a solvent mixture of 18 milliliters of 190 proof ethyl alcohol and 18 milliliters of normal butanol, forming a suspension of the molybdenum disulfide particles in the pyrophosphoric acid alcohol solution. The commercial product used for comparative purposes contained about 20% by weight of molybdenum disulfide and about 80% by weight of a phenolic resin binder.

The tests were run on the Falex machine as described in Example I, except that the Falex parts used were made of cadmium-plated 4130 steel heat-treated to 180,000 to 200,000 pounds per square inch tensile strength. To improve the wear life of the commercial product, one set of specimens was prepared wherein the Falex parts received a chromate pretreatment before application of the lubricant mixture. The results of the tests are shown in Table II.

Table II

Lubricant Coating	Pre-Treatment of Metal	Wear Life (Time to incipient failure) at 100# gauge load
Commercial Product	None	17 minutes.
Do	Chromated	27 minutes.
Example IV Composition	None	90 minutes (plus 25 min. at 500#).

At the end of 90 minutes, before the point of incipient failure was reached, the load on the composition of the invention was increased to 500 pounds gauge and the test continued for 25 minutes more before incipient failure took place.

These comparative tests show that the composition of the invention has outstanding wear life on cadmium-plated steel not only at the load at which the commercial product failed, but also at substantially increased load.

The foregoing describes our invention in its preferred aspects and illustrates our invention by way of specific examples, but alteration and modification may be made thereof within the scope of the appended claims without departing from the invention herein disclosed.

We claim:

1. The composition of matter, in the form of a liquid suspension useful for forming a dry lubricant film of finely powdered molybdenum disulfide lubricant on the surface of a metallic element subjected in use to mechanical friction, consisting essentially of finely powdered, solid molybdenum disulfide lubricant, polymerizable phosphoric acid the phosphorus of which is pentavalent and bonded to four oxygen atoms, and a solvent for said phosphoric acid, said powdered lubricant being in suspension, and the weight ratio of phosphorus content in the phosphoric acid to the molybdenum disulfide being from 0.02 to 0.20, said solvent being present in sufficient proportion to provide a liquid suspension which can readily be applied to the surfaces of a metallic element in a thin wet film by spraying or brushing but not in great enough proportion so that the composition is too thin to produce a satisfactory film which upon curing forms a dry lubricant film.

2. The composition as defined in claim 1 in which the phosphoric acid is pyrophosphoric acid.

3. The composition as defined in claim 1 in which the phosphoric acid is orthophosphoric acid.

4. The composition as defined in claim 1 in which the phosphoric acid is triphosphoric acid.

5. The composition as defined in claim 1 in which the weight ratio of the phosphorus content in the phosphoric acid to the molybdenum disulfide is from 0.05 to 0.16.

6. The composition as defined in claim 5 in which the phosphoric acid is pyrophosphoric acid.

7. The composition of matter as defined in claim 1 in which said solvent for said phosphoric acid is a member of the group consisting of water, ethyl alcohol, butyl alcohol, propyl alcohol, ether, dioxane and benzene.

8. The composition as defined in claim 1 in which said solvent for said phosphoric acid consists of a mixture of solvents.

9. The composition as defined in claim 8 in which said mixture of solvents consists of a mixture of ethyl alcohol and butyl alcohol.

10. A metallic element subject to mechanical friction in use having a dry lubricant film bonded to the surface thereof, said dry lubricant film consisting essentially of a hard film of polymerized phosphoric acid cured to form a hard film bonded to said surface and having embedded therein a large number of molybdenum disulfide solid lubricant particles covering said surface, the weight ratio of phosphorus contained in the phosphoric acid in said film to molybdenum disulfide being from about 0.02 to 0.20.

11. An element as defined in claim 10 in which said polymerized phosphoric acid is polymerized pyrophosphoric acid.

12. An element as defined in claim 10 in which said polymerized phosphoric acid is polymerized orthophosphoric acid.

13. An element as defined in claim 10 in which said polymerized phosphoric acid is polymerized triphosphoric acid.

14. A process for forming a molybdenum disulfide dry lubricating film on the surface of a metallic element that is subjected in use to mechanical friction comprising the steps of applying to said metallic surface a film of a liquid coating mixture consisting essentially of polymerizable phosphoric acid in a solvent vehicle with finely divided, solid, molybdenum disulfide lubricant particles uniformly suspended therein, the weight ratio of phosphorus content in the phosphoric acid to the molybdenum disulfide being from 0.02 to 0.20, drying and curing said film to polymerize said phosphoric acid and form a substantially hard film of cured phosphoric acid with said finely divided, solid, molybdenum disulfide lubricant particles substantially uniformly distributed within said cured film, said cured film bonded to said metallic surface and said particles bound within the film to thus maintain a lubricating film of molybdenum disulfide dry solid lubricant on said surface during use when said surface is subjected to mechanical friction.

15. A process as defined in claim 14 in which the phosphoric acid is pyrophosphoric acid.

16. A process as defined in claim 14 in which the phosphoric acid is orthophosphoric acid.

17. A process as defined in claim 14 in which the phosphoric acid is triphosphoric acid.

18. An article as defined in claim 10 in which said film has a thickness of about 0.0003 to 0.0005 inches.

19. The article as defined in claim 10 in which the weight ratio of phosphorus contained in the phosphoric acid in said film to molybdenum disulfide is from about 0.05 to 0.16.

20. A method for lubricating the surface of a metallic element that is subjected in use to mechanical friction, comprising applying to said surface a film of liquid coating mixture consisting essentially of polymerizable phosphoric acid in a solvent therefor and having uniformly suspended therein finely divided molybdenum disulfide solid lubricant particles, the weight ratio of phosphorus content in the phosphoric acid to the molybdenum disulfide being from 0.02 to 0.20, drying and curing said liquid film to form a hard dry film of cured polymerized phosphoric acid with said finely divided molybdenum disulfide solid lubricant particles uniformly distributed throughout said dry film, said dry film being bonded to said metallic surface and said particles bound within the film to thus maintain a lubricating film of molybdenum

disulfide dry solid lubricant on said surface during use when said surface is subjected to mechanical friction.

21. A method as defined in claim 20 in which the phosphoric acid is pyrophosphoric acid.

22. A method as defined in claim 20 in which the phosphoric acid is orthophosphoric acid.

23. A method as defined in claim 20 in which the phosphoric acid is triphosphoric acid.

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