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MANGANESE COATING BATH WITH MOLYBDENUM

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ABSTRACT OF THE DISCLOSURE

Composition and method for producing a fine grained manganese-molybdenum phosphate complex as a coating on a metal surface, primarily for break-in wear applications.

BACKGROUND OF THE INVENTION

The term "phosphating" is used to include applying various metal phosphate solutions to a base metal. The metal phosphate cations are generally iron, zinc or manganese and the anions are the phosphate ions. Mixtures of metal phosphates may be used. Some of the first phosphating done was described in U.S. Pat. 8,663 to Caslett who protected iron and steel against oxidation by treatment with hot dilute phosphoric acid. Caslett also found zinc phosphate was useful to form a protective coating on iron and steel. These innovations of Caslett were followed by the introduction of manganese carbonate into the phosphoric acid solutions by R. G. Richards in 1911. Thus, at this early date, the foundation work for our present day manganese phosphate metal surface treatment was established.

Among other things, phosphating has application (a) for corrosion protection, (b) as a bonding coat for subsequent finishing processes, (c) for electrical insulation, (d) for facilitating forming in drawing, pressing and similar operations and (e) for reducing friction between moving parts. Metal phosphate surface treatment technology has advanced according to the particular application of the phosphate.

For instance, zinc phosphate coating and improvements thereof as described in the prior art (for example, U.S. Pat. 3,090,709) has advanced toward use of zinc phosphate for corrosion inhibiting and paint-bonding purposes. To a lesser extent, zinc phosphate coatings are used as a base for lubricants in metal-forming operations. Iron phosphate coatings are used mostly for paint-bonding coatings. These coatings are generally thinner and less expensive than zinc phosphate coatings. Often, in fact, light weight phosphate coatings comprise a mixture of zinc and iron phosphate. Manganese phosphate coatings which are of concern in the present invention have developed toward break-in wear applications.

The functions and requirements of a coating for break-in wear application are totally unlike those of paint-bonding corrosion or any other of the aforementioned applications. In other words, after a metal part has been carefully machined, the coating treatment necessary for smooth operation of the part becomes of foremost importance. The factors controlling such smooth operation do not relate to the same factors as affect paint bonding and corrosion. For example, in a break-in wear application, such factors as thickness, variance and weight all must be carefully controlled and refined.

It has been found by the method of the present invention that fine grained coatings having a variance of less than about 50 microinches can be produced. In the prior art the variance has been a minimum of about 75 to 150 microinches, and such minimum variance has only been achieved by use of cleaners such as emulsifier solvents or

vapor degreasers. Cheaper and more readily available alkali cleaners have been considered useful for producing only coarse grain size. Now by the method of this invention, it is possible to produce fine grain size by the use of alkali cleaners.

Then too by the method of this invention, after cleaning and surface treatment, it has been discovered that there is only a slight etch pattern on the treated surface, whereas in the prior art the etch pattern ranged from medium to heavy. Thus, the original high quality surface of the base metal part is retained with minimum metal loss due to etching.

The present invention is directed to the use of a manganese phosphate bath containing limited amounts of certain soluble molybdates to provide a manganese phosphate-molybdate coating to any metal surface and is especially adaptable to the characterized disc-type limited slip differential. Other metal surfaces which may be advantageously coated are cutting tools, drawing discs, pistons, piston rings, cylinder walls and other surfaces requiring contact with one another. Where the coating is not removed by metal to metal contact, the coating has properties which assist in lubrication of the moving parts by providing an infinite number of minute oil reservoirs. Even where the coating is removed, the reduction of etch alone is significant to create extremely beneficial results. The coating is formed on metal surfaces, which have been previously finished into final form. That is, the metal surface is ready for final assembly when treated.

The success of the present invention is to a large measure based on the refinement of the etch pattern. It is believed that with a slight etch pattern, the properties of the base metal part are retained as originally designed after the coating has worn off the contacting surfaces. Thus, in an application as found in a limited slip differential where tolerances are extremely close, it is highly desirable that the moving parts retain their designed dimensions.

It is, therefore, an object of this invention to produce a coated metal surface, which metal surface, after such coating has been removed, has only a slight etch pattern.

It is another object to provide a coated metal surface of extremely fine grain size.

It is yet another object of the present invention to coat a metal surface so as to form a protective coating thereon.

It is still another object to provide a coating capable of protecting load bearing surfaces during break-in wear operations.

Another object is to provide a coating for a metal surface which coating assists in conditioning the metal surface for subsequently applied shear producing loads.

It is another object to provide a wear resistant coating for metal surfaces.

These and other objects will become more apparent from the following description.

The advantages of the invention are especially brought out in connection with a limited slip differential of a clutch design as described in U.S. Pat. No. 3,073,424. One of the major problems of such differentials, which utilize a disc pack to retard differentiation, centers around the co-efficient of friction between the discs of the disc pack or, in other words, the shearing surfaces of the disc pack. The dynamic and static co-efficients of friction should be approximately the same value, otherwise there is chattering and squealing. One method of controlling the co-efficient of friction is by modifying the shear surface as done in such patent.

As described in the patent, the modified or characterized discs have planar-projecting portions or lands which constitute about 25 percent (usually about 200 lands per square inch) of the total projected area, the remainder being groove area. The patent discloses that the area of land should not exceed 0.002 square inch. The depth of

the grooves between the lands is at least about 0.003 inch with a groove width of about 0.005 inch. The grooved area serves to promote lubrication and insures an oil film always being present between the surfaces.

With such close tolerances, it is easily seen how medium and heavy etching of the surface with the consequent removal of metal from the surface distorts the original, carefully considered design features so as to diminish the value of the design and defeat its purpose of reducing chattering. It is to be remembered that in such a differential there are usually 18 discs, or 36 faces, so that if each face suffers a distortion of only thousandths of an inch, the distortion is magnified 36 times.

THE INVENTION

According to the present invention, it has been discovered that an aqueous solution of manganese phosphate and a molybdate soluble in the aqueous solution deposited on a metal surface produces, when dried, a uniform and highly satisfactory wear resistant coating with optimum grain size, and after application of a shearing force and removal of the coating, there remains only a slight etch pattern.

In the practice of this invention, a metal surface is treated with the aqueous solution of manganese phosphate and molybdate at a temperature of about 175° F.–225° F. at a pH below about 4 for a period of about 20 minutes. The molybdate in the aqueous solution is any molybdate, soluble or capable of being solubilized, in the desired phosphate solution. Examples of such molybdates are alkali metal, alkaline earth metal and ammonium molybdates. The molybdenum is present in solution in amounts of from about 0.001 to about 0.05 weight percent based on total solution used to treat the metal surface.

The metal surface to be coated can be conditioned by dry or wet methods. For example, surface roughness of the type such as produced by emery treatment, brushing, sanding and sand blasting, generally yields fine crystaline coatings. Traditionally, the best dry method of surface preparation for the production of fine grained coatings is by sanding. The sanding results in a considerable increase in surface area which allows a high rate of nucleation on the metal surface.

Another method of pretreatment of the surface is by a wet chemical method. This is generally done by alkali cleaning and solvent cleaning. As aforementioned in the prior art, it has been taught that alkali cleaning generally produces a coarse grained surface while solvent cleaning produces a fine grained surface. Cleaning can be used to assist in the formation of large numbers of uniformly distributed crystaline nuclei. It must not interfere with subsequent crystaline growth of the coating. The cleaning treatment must reach the metal surface rapidly and uniformly so that crystal growth will begin immediately all over the surface. The cleaning should leave a surface which is uniformly clean and slightly roughened. After chemical pretreatment, it is often necessary to rinse thoroughly in cold water.

Hard to remove substances such as rust, scale and corrosion can be removed from the metal surface by a pickling process. Pickling is usually conducted in 10 percent sulfuric acid or hydrochloric acid.

After conditioning by cleaning and pickling, the metal is ready for treatment with the protective coating bath solution of this invention. The basic manganese phosphate solution is prepared preferably by combining phosphoric acid, manganese carbonate and water. The manganese can be in any form, such as manganese oxide or manganese carbonate, which will combine with phosphoric acid to form manganese phosphate. Other substances may be added as needed. For instance, it is often desirable to add nickel in the form of nickel carbonate in order to accelerate or catalyze the coating operation. Large amounts of water are used. Oxidizers such as nitrates, chlorates and bromates may be used. Accelerators such as salts of copper and iron may also be used. Wetting agents may be used.

The subject solution is usually prepared first as a concentrate. The phosphoric acid, manganese carbonate and water are mixed in a weight ratio of about 2:1:4 although the total amount of water can be greater. The resulting solution will desirably have a total acid point (explained subsequently) of about 7.0.

The manganese phosphate concentrate solution is then used to form a somewhat diluted bath wherein the manganese phosphate is present in the bath solution in an amount of from about 2 to 20 weight percent, preferably 3 to 10 weight percent based on total solution. To this solution is added the soluble molybdate, desirably in amounts of from about 0.001 to 0.05 weight percent molybdenum, based on total bath solution to form the solution of this invention. This solution or bath, heated to from 175° F. to 225° F. is ready for application to a metal surface for coating. The coating can be applied to the surface by immersion or spraying. The reaction between the metal surface and the coating solution usually begins immediately upon immersion. Coating growth is complete after about 20 minutes. Since the growth of the coating protects the base metal against the solution, coating formation ceases after a period of time. Care is taken in the control of the bath solution temperature in order to maintain uniform coatings.

Treatment of a metal surface using the bath solution of this invention produces a fine grain crystaline structure exhibiting uniformity in color, variance and thickness. The microinch variance is less than about 50, usually less than about 30. As is known in the art and described in Tool Engineer's Handbook published by McGraw Hill Book Company, Inc., New York (1949) at pages 1334–1335, microinch variance referred to herein, is determined by the root-mean-square method (RMS). The coating weights generally vary from about 50, desirably 1200, to about 2500 mg./ft.^{2} with a thickness of about 0.0001 to 0.0008 inch. Suitable bath solution temperature is preferably from about 175° F. to 225° F. Treatment times vary from about 1 minute to about 30 minutes.

As aforementioned, temperature is an important factor influencing growth of the coating on the metal surface. By increasing temperature, the rate of reaction is increased, which decreases the metal exposure time in the phosphating bath solution to achieve a desired coverage. For instance, at temperatures below about 125° F., exposure time may exceed an hour or more while at temperatures of 175° F. or better, the exposure time may be less than 5 minutes at about 80 percent coverage.

The carbon content and heat treatment of the metal being coated also influences the coating process. By increasing carbon content and stress in the metal, the ease of application of the coating decreases. In other words, ferrite iron, which has a low carbon content and low stress, is relatively easy to coat, while it is relatively difficult to coat a hypereutectoid martensite steel. A high carbon, highly stressed steel is used in a limited slip differential. By the method of this invention, coatings of high quality on such metals are possible.

Properties and the qualities of phosphate coatings are strongly influenced by the solution composition and particularly by the acidity as measured by titration against sodium hydroxide. The result of the titration is the "point" value. That is, an aliquot of a manganese phosphate solution is transferred to a beaker. Phenolphthalein is added as the indicator and the solution titrated against 0.1 N NaOH to a permanent red end point. The number of ml. of NaOH required is the "point" or "total acid point" value. This value reflects the total phosphoric acid concentration including that present as acid phosphate. The free phosphoric acid concentration can be determined by using bromo phenol blue as indicator. Thus, both the total and free phosphoric acid concentration of the bath can be determined.

The total acid points ratio of free to total phosphoric acid is of importance concerning the growth of the coating, which growth is influenced by the concentration of metal ions and of phosphate ions in the solution. If too much free phosphoric acid is present, the ferrous surface will be attacked vigorously, resulting in thin coatings of less protective value. If the metal ion concentration is too low, the coating process is unsatisfactory. The Total Acid Points ratio of total acid to free acid should be about 4.5:1 to 10:1, preferably 5.2:1 to 6.5:1.

Although advantages are apparent from the present invention, it can only be theorized as to how the improved results are achieved. It is believed that at the point of nucleation on the metal surface, the molybdenum forms a crystal, such as for example, ferro molybdate, and that encircling the molybdate crystal and possibly contacting the nucleau crystal itself there is formed a phosphate crystal, e.g., manganese or iron phosphate. The molybdate thus serves to protect the metal surface from the phosphate and any other material present. This is evidenced by the fact that the pickling effect of the phosphoric acid is inhibited by the presence of the molybdenum. Without the molybdenum, the phosphoric acid pickling proceeds at a much faster rate. By this retardation of activity the effect is refinement of grain size and reduction of etching of the base metal. The crystals so produced are generally rectangular solid in shape, standing erect on the metal surface and much closer together than crystals heretofore produced.

EXAMPLE I

A typical phosphate coating concentrate was prepared using the following formulation:

Component:	Weight percent
Phosphoric acid [1]	29.0
Manganese carbonate	15.0
Nickel carbonate	0.50
Total water	55.5

[1] Added as 70 weight percent solution in water.

A 500 gallon tank was filled with 450 gallons of water and the balance of the tank filled with 50 gallons of concentrate. The reactant bath solution thus produced a Total Acid Point (T.A.P.) of 7.0.

To this solution, heated to 195° F., was added 40 fluid ounces of aqueous ammonium molybdate solution containing 2½ ounces of ammonium molybdate (0.0018 weight percent molybdenum based on total solution weight). Metal discs as described in U.S. Pat. No. 3,073,424 cleaned in a strong alkali solution were immersed in this bath for 20 minutes. After drying, the discs were found to be coated with a fine grained manganese phosphate-molybdate coating. The coating weight was about 1500 mg./ft.^{2}. The average thickness of the coating varied from 0.00025 to 0.0030 inch with a microinch variance of 30. There was only slight etching.

The discs were tested in a break-in application and found to function satisfactorily 2,000 miles of test exposure which is equivalent to 50,000 miles driving.

Thus, it is seen that by the method of this invention, fine grained coatings, with only slight etch patterns on the metal surface, can be expected.

As a control, discs as described in U.S. Pat. No. 3,073,-424 were cleaned in a strong alkali solution, and after drying, treated for about 20 minutes (with the manganese phosphate bath solution), without the addition of the molybdate heated to 195° F. After drying, the coating was coarse grained, had a weight of about 2500 mg./ft.^{2}, an average thickness of 0.0012 inch and a microinch variance of about 120–150. A thickness of about 0.0003 inch and a microinch variance of 30–40 is considered desirable. The discs had a heavy etch pattern.

Thus it is seen that a conventional bath does not produce the beneficial results of this invention.

EXAMPLE II

When 30 fluid ounces of aqueous ammonium molybdate solution containing 2 ounces of ammonium molybdate (0.0014 weight percent molybdenum based on total solution weight) is added in place of the 40 fluid ounces of ammonium molybdate to the solution of Example I and discs coated, improved results were obtained.

EXAMPLE III

When 6 ounces (96 ounces of solution) of ammonium molybdate (0.005 weight percent molybdenum based on total solution weight) is added to the solution of Example I in place of the 40 ounces of ammonium molybdate solution, and discs coated with the solution, the results are similar to those obtained in Example I. This appears to be the optimum concentration.

EXAMPLE IV

When the coating procedure is repeated utilizing a sodium molybdate in place of the ammonium molybdate, mole for mole, the results were similar.

This example shows the interchangeability of molybdates soluble in the aqueous solution.

EXAMPLE V

When 69 ounces (1035 ounces of solution) of ammonium molybdate (0.05 weight percent molybdenum based on total solution weight) is added to the solution of Example I in place of the 40 ounces of ammonium molybdate solution, and discs coated with the solution, the resultant coating was extremely fine (immeasurable in thickness with no etch). The coating weight was 50 milligrams per square foot.

What is claimed is:

1. A solution consisting essentially of manganese phosphate and water and containing from about 0.001 to 0.05 weight percent molybdenum, based on total solution, wherein the total acid point to free acid point ratio is from about 4.5:1 to 10:1, the solution temperature is about 175° F. to 225° F. and the pH of the solution is less than about 4.0.

2. The solution of claim **1** wherein the total acid point to free acid point ratio is about 5.2:1 to 6.5:1 and the manganese phosphate is present in an amount from about 2 to 20 weight percent based on total solution.

3. The solution of claim **2** wherein the molybdenum is introduced into the solution as a soluble molybdate.

4. The solution of claim **3** wherein the molybdate is an alkali molybdate.

5. The process of preventing scoring and etching of a metal surface having a ferrous metal frictional surface and subjected to lubrication under operating conditions, comprising chemically treating the metal surface with an aqueous solution heated to from about 175° F. to 225° F., said solution consisting essentially of manganese phosphate, water and from about 0.001 to 0.05 weight percent molybdenum based on total solution, said solution having a pH less than about 4.0 and a total acid point to free acid point ratio from about 4.5:1 to 10:1; wherein there is applied a coating of from about 50–2500 mg./ft.^{2} with a variance of not more than about 50 microinches (RMS) and after break-in there is only a slight etch pattern on the metal surface.

6. The process of claim **5** wherein the metal surface is alkali cleaned using an alkali-cleaner prior to application of the phosphate coating.

7. The process of claim **6** wherein the metal is a hypereutectoid steel.

8. A metal surface having a coating thereon derived from a solution consisting essentially of manganese phosphate, water and a soluble molybdate, the molybdenum being present in an amount of from 0.001 to 0.05 weight percent based on total solution, said solution having a pH less than about 4.0 and a total acid point to free acid point ratio from about 4.5:1 to 10:1, said coating having a

weight of from 50–2500 mg./ft.^{2} and a variance of less than about 50 microinches (RMS) and the metal surface having only a slight etch pattern after removal of the coating.

9. The metal surface of claim **8** wherein the surface has lands distributed over the surface thereof with grooves between the lands to provide a flow path for viscous fluid, said lands being of a density of at least 200 lands per square inch.

10. The metal surface of claim **9** wherein the metal is a hypereutectoid steel.

11. A solution consisting essentially of manganese phosphate, water and a soluble molybdate, the molybdenum being present in an amount of from about 0.001 to 0.05 weight percent molybdenum based on total solution, said solution having a pH less than about 4.0 and a total acid point to free acid point ratio from about 4.5:1 to 10:1.

12. The process of claim **5** wherein said aqueous solution contains from about 2 to 20 weight percent manganese phosphate based on total solution.

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