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COATED FERROUS METAL ARTICLE AND METHOD OF PREPARING SAME

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The present invention relates to coatings for metals which prevent corrosion and provide other advantages, and more particularly to methods of providing such coatings and to the coatings provided thereby.

In general, in accordance with the invention, a metal surface is treated to form a coating of a complex mixture of phosphates of the metal thereon which not only prevents corrosion of the metal but dissipates or removes corrosion previously present. The coating also provides a most effective bond for paints and the like which it may be desired to apply to the surface, and itself forms a decorative as well as protective finish for the surface. In addition, the coating increases the lubricity of the metal surface and facilitates metal forming operations, such as drawing and cold extrusion. The coating adheres very tightly to the metal, being integrally bonded to the base, is continuous, very dense and uniform, of greater weight than it has heretofore been possible to attain and impervious to corrosive agents. To achieve the superior coating of this invention, the metal is treated with a preferably aqueous solution of certain acid pyrophosphates or other substances which yield the pyrophosphate negative radical, the solution preferably being acid and heated to a suitable temperature. The metal surface is subjected to the solution for a period sufficient to obtain the desired coating. Only a relatively low concentration of the coating-productive substance is required in the solution, and no additional materials are necessary, although a material synergistic to phosphatization may be employed if desired. In this manner, a coating having the desirable characteristics mentioned hereinabove is obtained simply, economically, and in a short period of time. By the method of the invention, a ferrous metal surface, for example, may readily be provided with a phosphate coating of a weight well in excess of one hundred milligrams per square foot of surface, and the weight may easily be increased to five or six hundred milligrams, and even more, no precise upper limit having been found. In contrast, prior iron phosphate coatings on ferrous metals have normally been limited to not more than fifty to seventy-five milligrams per square foot for production applications, and in addition to being light have usually been non-uniformly formed and required accelerators and other materials to be employed in addition to the phosphatizing substance. The present invention provides important advantages and greatly improved results in the coating of metals and the method of providing the coatings.

It is an object of the invention to provide for improved phosphate coating of metal surfaces.

Another object is the provision of a novel and improved method of forming phosphate coatings on metal.

Another object is the provision of improved coatings on metal articles comprising mixtures of phosphates of the metal.

Other and further objects, advantages, and features of the invention will be apparent to those skilled in the art from the following description.

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The invention employs an acid pyrophosphate selected from the group of sodium, potassium, lithium, ammonium, and amine pyrophosphates to provide the corrosion-preventing, paint-bonding coating on metal. These pyrophosphates are preferred because of their relative cheapness, availability, solubility in water, safety, and ease of handling. Other materials or substances which contain or include these acid pyrophosphates, or from which such pyrophosphates may be derived, or more accurately substances which yield the pyrophosphate negative radical, such as the polyphosphates of the specified materials, and pyrophosphoric acid or polyphosphoric acid, may be used. Thus, sodium polyphosphate, so called in the literature and commercial use, may be employed because its chemical structure encompasses the pyrophosphate. Certain of such other materials or substances, however, require addition of acid to provide the desired result. Thus, for example, barium, magnesium, or calcium pyrophosphate may be dispersed in water and dissolved therein by hydrochloric, sulphuric, or other suitable acid. Mixtures of the several substances mentioned can be employed if desired. Orthophosphates and orthophosphoric acid do not produce the desired results. The invention therefore contemplates the use of acidified substances included in the group consisting of the sodium, potassium, lithium, ammonium, and amine pyrophosphates and polyphosphates and metal substitution products thereof, pyrophosphoric acid and polyphosphoric acid, and mixtures thereof, and other compounds or agents, which yield the pyrophosphate negative radical.

While the invention is applicable to practically all metals, it is contemplated as being of greatest use in connection with iron, zinc, cadmium, and aluminum and alloys thereof, since corrosion effects or difficulty with paint adhesion on other metals are ordinarily of less practical importance. The ferrous metals are at present believed to provide the greatest and most important field for the invention, because of their widespread use and susceptibility to corrosion.

In general, the method employed to practice the invention comprises, after cleaning the metal surface which is to be coated, subjecting the cleaned surface to the action of a solution of one or more of the acidified substances described hereinabove, and then rinsing the surface. If desired, the coated surface may additionally be rinsed with a solution of a substance serving as a sealer for the coating, as for example chromic acid, where the greatest possible protection against corrosion is to be achieved because of expected subjection of the surface to extreme conditions. In cleaning the surface, it is only necessary to remove dirt, film, oil, and the like, while the products of corrosion which has already occurred, as for example rust on ferrous metals, may be allowed to remain because the coating solution will itself effect the removal thereof. It is to be noted, however, that in the interests of economy and speed in production, it may be more advantageous to remove heavy scale and rust or other corrosion before application of the coating solution. The cleaning of the surface may be accomplished in any desired manner and by any appropriate means, and it will be apparent that such cleaning is a step preliminary to the actual method of the invention rather than a step in the method itself, and in many cases may be dispensed with because the metal surface is already sufficiently clean.

Describing the method in greater detail, it may be said that it involves four main factors in addition to the particular material employed to obtain the desired coating. These are the quantity of the material used in the solution, or the concentration, the acidity of the solution, the temperature of the solution, and the period of time

during which the metal is subjected to the solution. Only relatively small quantities of the material are required, so that a low concentration of the material in the solution is sufficient, but a high concentration may be employed if desired or advantageous under particular conditions. Thus, a saturated solution may be provided. If the surface to be coated is corroded and the corrosion is to be dissipated or removed in the course of providing the coating, a somewhat higher concentration is advisable than if no corrosion is present. The acidity of the solution may vary through a wide range, but if it is too high dissolution of the metal will occur and the resultant pitting will affect the desired coating adversely, while if it is too low, the time required to form the coating will be considerably increased. The desired acidity is also determined to some extent by the resistance to acidic attack of the particular metal being coated, since if that be not readily affected by acids, a solution of relatively high pH or low acidity will require a longer time to effect coating of the metal than one of higher acidity. The concentration and pH of course vary together, but are not dependent on each other, since the pH may be adjusted by the addition of alkaline or acid materials to the solution. The reaction between the solution and the metal is accelerated by heat, and accordingly it is ordinarily desirable to raise the solution to a fairly high temperature, which may be as high as the boiling point of the solution. If time is not an appreciable factor, however, the method may be carried out with the solution at room temperature or even approaching its eutectic point if desired. The quantity of the coating-productive substance which will go into solution in the water or other solvent increases, of course, with increased temperature. The period of subjection of the metal to the solution varies with the strength, acidity, and temperature of the solution, as already indicated, and also with the weight of coating to be obtained. Ordinarily, a period of a few minutes is employed. Water or water with a slight admixture of alcohol, has been found eminently satisfactory as a solvent, although the invention contemplates the use of any solvent employable with any of the materials described.

Since the various factors affecting the formation of the coating may vary widely while providing eminently satisfactory results, the method of this invention is specifically applicable to a diversity of particular conditions and is readily adaptable within the general limits set forth herein to a great variety of conditions and requirements. The concentration is best expressed in terms of a pyrophosphate radical yielded or provided in the substance or material employed, since the different substances set forth hereinabove vary in the yield of the radical for a given quantity of the substance. The selected substance, or mixture of substances, is dissolved in water or other suitable solvent in a quantity to provide the desired concentration of pyrophosphate ions, which may range from as low as 0.05% to the saturation point, as may be most advantageous under given conditions. Ordinarily a concentration of the order of 1% to 5% is practical for most applications of the invention, and it has further been found in practice that a pyrophosphate ion concentration in the range between 2% and 4%, say about 3% produces a very satisfactory coating while allowing other factors affecting the coating to vary considerably, and this range is therefore preferable for most operations. The pH of the solution may vary between about 1 and about 7, and ordinarily is best held between about 2 and about 5. In most cases, the pH of the solution requires adjustment by the addition of a suitable acid, for example pyrophosphoric acid, since the relatively low concentrations usually employed do not provide a solution of the desired acidity. Orthophosphoric acid is not employed to adjust the acidity of the solution because it introduces undesirable ions. The temperature at which the solution is applied to the metal surface may vary between the freez-

ing and boiling points of the solution, as brought out hereinabove, but warm to hot temperatures, say between 100° F. and 200° F., have been found most useful in practice, particularly those in the range between about 120° F. or 130° F., and 180° F. or 190° F., and this range is therefore preferred under most conditions. The period of application of the solution to the metal is in practice usually desired to be only a few minutes, say from about two to about ten minutes, although it may vary from a matter of seconds to one of hours, days, or even weeks, depending upon the particular characteristics of the solution employed, especially the temperature. In general, a longer time of subjection of the metal surface to the solution at a moderate temperature results in a finer, denser coating than a shorter time at a higher temperature. Any suitable substance synergistic to the phosphatization of the metal may be added to the particular substance employed for producing the coating.

After the metal surface has been coated by the method described, it may be removed from the solution and any adhering solution removed, as by rinsing with hot water, and then dried. The coating produced protects the surface most effectively against corrosion, being integral with the metal, continuous, dense, heavy, and impervious to corrosive agents. It promotes bonding of paint, varnish, and like films to the metal, improves the lubricity of the surface for use under frictional conditions, facilitates drawing, cold extrusion, or like metal forming operations, and imparts a decorative finish to the metal. Although the coating is continuous, fine, dense, uniform, relatively heavy, and substantially impervious to corrosive agents, it may be sealed so as to afford additional corrosion protection or the like under extreme conditions by applying a slightly acid solution of a suitable sealer, preferred substances for this purpose being chromic acid, potassium chromate, and sodium chromate and mixtures thereof.

One specific manner of practicing the method is exemplified by the following procedure, in connection with a ferrous metal surface. After cleaning of the surface, it is immersed in or sprayed with an aqueous solution of sodium acid pyrophosphate in a concentration of about two ounces per gallon of water equivalent to a pyrophosphate ion concentration of approximately 1.18%, having a pH between 2 and 5, for example about 3, and heated to a temperature of about 140° F. Pyrophosphoric acid may be added to increase the acidity to the desired pH. The surface is exposed or subjected to the solution for a period of about twenty or thirty minutes, then rinsed with hot water and dried. This produces a fine, dense, uniform, integrally bonded, continuous, coating on the surface which comprises a mixture of phosphates of iron, resulting from the reaction or deposition of the pyrophosphate ion with or on the metal, having a weight per square foot of surface of some two hundred milligrams or more. Prior methods of obtaining iron phosphate coatings on ferrous metal surfaces have been found incapable of consistently producing coatings in excess of a weight of only about fifty to seventy-five milligrams per square foot, and the density and uniformity of such coatings have been greatly inferior to those of the coatings provided by this invention.

Another specific example of the application of the method to ferrous metal, in this instance in connection with ferrous metal articles having surfaces subject to rusting in a very short time, is illustrated by the following procedure. The articles, sufficiently clean to require only a preliminary rinsing with hot water, are first subjected, for a period of about three minutes, to a solution of about four ounces of sodium acid pyrophosphate per gallon of water, at a temperature of about 160° F. to 170° F., the pH of the solution being about 3 or 4. The pyrophosphate ion concentration is about 2.36%. This provides a "flash" or light coating on the metal base. The reason for the application of this "flash" coating is primarily to

remove rust formed on the ferrous metal surface in the interval after prior operations thereon, such as machining, and/or the cleaning or rinsing, since the solution dissolves or dissipates rust before deposition of the coating over rusted areas begins, by reaction with the rust to convert it into iron phosphates. The relatively light "flash" coating then protects the surface against rusting before the full desired coating is produced. After the provision of the flash coating, the surfaces are subjected to another aqueous solution of sodium pyrophosphate at substantially the same temperature as the first, 160° to 170° F., in a concentration of about five ounces per gallon, that is, a concentration of the pyrophosphate ions of about 2.94%, with a pH of about 2 to about 3 controlled by the addition of pyrophosphoric acid, for a period of about five minutes. A coating integral and merged with the flash coating is produced, giving a complete coating of approximately two hundred milligrams per square foot of surface, which is fine, dense, continuous, tightly-adhering, and uniform. The articles are then rinsed with hot water, preferably at least at 180° F., which may be followed by rinsing with a slightly acid hot aqueous solution of chromic acid, potassium chromate, or sodium chromate or mixtures thereof.

The coatings of the present invention have been sufficiently described hereinabove as to their characteristics, purposes, effects, and advantages, as well as the manner in which they are produced, and it is not believed that further explanation of them is necessary. It is to be noted, however, that it has long been desired to obtain protective and bonding iron phosphate coatings on ferrous metals appreciably heavier than the fifty to seventy-five milligrams per square foot heretofore achieved by the prior art, but efforts to provide such heavier coatings have been unsuccessful. By the present invention, such coatings well in excess of a hundred milligrams per square foot are readily provided on ferrous metals, and in fact coating weights only slightly more than a hundred milligrams per square foot are relatively light compared to the coating weights obtainable by the invention.

What is claimed is:

1. The method of providing a permanent iron phosphate coating of a weight in excess of one hundred milligrams per square foot on a ferrous metal surface, which comprises subjecting the metal defining the surface for a period of from about one minute to about forty minutes to the action of a solution consisting essentially of a quantity of an acid pyrophosphate selected from the group consisting of the sodium, potassium, lithi-

um, ammonium, and amine pyrophosphates and mixtures thereof to provide a concentration of pyrophosphate ions from about 0.5% to about 5%, said solution having a pH between about 1 and about 7 and a temperature between about 130° F. and about 200° F.

2. A coated article comprising a ferrous metal base having a coating covering a surface thereof and integrally bonded thereto, said coating being of iron phosphates of a weight in excess of one hundred milligrams per square foot of metal surface and obtained by reaction of the metal with a solution consisting essentially of an acid pyrophosphate selected from the group consisting of sodium, potassium, lithium, ammonium, and amine pyrophosphates and mixtures thereof obtained by the method of claim 1.

3. The method of providing a permanent phosphate coating on a metal of the group consisting of iron, zinc, cadmium, and aluminum and alloys thereof, which comprises subjecting the metal for a period of from about one minute to about one hour to a solution consisting essentially of a quantity of an acid pyrophosphate selected from the group consisting of sodium, potassium, lithium, ammonium, and amine pyrophosphates and mixtures thereof to provide a concentration of pyrophosphate ions of at least 0.05%, said solution having a pH between about 1 and about 7 and being at a temperature in the range between about 100° F. and the boiling point of the solution.

4. A coated article comprising a base of metal of the group consisting of iron, zinc, cadmium, and aluminum and alloys thereof which has a coating covering a surface thereof and integrally bonded thereto, said coating being of a complex mixture of phosphates of the metal obtained by reaction of the metal with a solution consisting essentially of sodium acid pyrophosphate obtained by the method of claim 3.

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