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COATING OF METALS

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ABSTRACT OF THE DISCLOSURE

A method for formulating a one step phosphate-lubricant composition for use in metal deforming processes wherein an aqueous zinc phosphate solution containing zinc ions and phospate ions is formed and to said phosphating solution there is added a solid, particulate mixture of a fatty acid lubricant and a water-soluble surface active agent, which solid, particulate mixture is then dispersed throughout the zinc phosphate phosphatizing solution.

This invention relates to an improved process for coating metal surfaces and more particularly it relates to a process for forming a lubricant coating on the surface of metals to be deformed.

In the cold forming of metal surfaces, such as wire drawing, tube drawing, cold extrusion, or the like, it is well known that it is often desirable to form a phosphate coating, such as zinc phosphate coating, on the surface of the metal article which is to be formed. Thereafter, the phosphate coated metal surface is normally rinsed, and a lubricant coating is applied thereto, for example, as from an aqueous solution of a long chain fatty acid soap.

Although, by this method, a satisfactory lubricant coating is formed on the metal surfaces which greatly facilitates the cold forming of the metal, in many instances it is desirable to form the zinc phosphate coating and lubricant coating in a single treatment, rather than in two separate operations, as is presently the practice. In many instances, it is even desirable to form the phosphate and lubricant coating in a single treatment even though the application of a further lubricant coating may still be necessary, where particularly severe deformations are being carried out. It is necessary, however, that the solution for the single application of the phosphate and lubricant be easily prepared, having a uniform concentration and composition throughout, and that it be capable of being replenished readily when it is used in a continuous process. The accomplishment of this, however, is made somewhat difficult in that the phosphate coating solutions which are normally used are dilute solutions, commonly prepared by dissolving a concentrate composition in water.

In the past, attempts have been made to form suitable phosphate and lubricant compositions either by using a preformed emulsion of the lubricant which is added to the phosphatizing bath or by emulsifying the lubricant in the cencentrated phosphate solution, which solution is then diluted with water to form the desired operating bath. These attempts have not, however, been completely successful in that it has been extremely difficult to obtain a stable, homogenous emulsion, which gives a consistent composition when diluted, as for example when poured from a drum into water to form the treating bath. Moreover, with these preformed emulsions, it is not possible to easily change to relative amounts of the various components in the coating bath or compensate for changing consumption of phosphate and lubricant, without formulating a new emulsified composition. This, of course, detracts greately from the flexibility of the process and its

ability to compensate for the changing conditions which are encountered on the processing line.

It is, therefore, an object of the present invention to provide an improved process for formulating a lubricant bath whereby a phosphate and lubricant coating may be applied to a metal surface to be deformed in a single operation.

A further object of the present invention is to provide an improved method for forming, in a single operation, a phosphate and lubricant coating on a metal surface to be deformed.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a process for formulating a solution for forming a phosphate coating and a lubricant coating on a metal surface in a single treatment, which process comprises forming an aqueous zinc phosphate solution, which solution contains zinc ions and phosphate ions in an amount suitable for forming a phosphate coating on a metal surface treated therewith and, thereafter, adding to the zinc phosphate solution a solid particulate mixture of a fatty acid lubricant and a water-soluble surface active agent, the amount of the surface active agent in the mixture being sufficient to effect dispersion of the fatty acid throughout the zinc phosphate solution. The treating solutions thus-formulated may be used to treat metal surfaces which are to be deformed, to produce thereon a combined phosphate and lubricant coating which, in many instances, will provide sufficient lubrication of the metal surface during the deformation without the application of additional lubricant material.

More specifically, in the practice of the present invention, the phosphate solutions used are desirably any of the zinc phosphate solutions which are commonly applied to provide a coating to assist in cold forming operations. Typically, these solutions are aqueous acidic solutions containing zinc ions and phosphate ions and may be formulated from zinc phosphate, zinc oxide, phosphoric acid, or other suitable sources of zinc ions and phosphate ions. Additionally, these solutions may also contain an accelerator or oxidizing agent, such as nitrate ions, nitrite ions, chlorate ions, and the like, as well as various mixtures of these accelerators. Additionally, organic accelerators or oxidizing agents, including aliphatic or aromatic nitro compounds, such as nitroguanadine and the like, as are known to those in the art, may also be used. Although the specific concentration of the components of the phosphate solutions will depend upon the specific operating conditions utilized, in general it has been found to be desirable that these solutions contain from about 0.5 to 3% by weight of phosphate (PO_4) and have a free phosphoric acid content within the range of about 0.3 to about 0.8%. Additionally, the accelerators are typically present in amounts within the range of about 0.0001 to about 5% by weight of the solution, depending upon the particular accelerating ions used. Typically, these working phosphate solutions are prepared by diluting a concentrate composition, containing the bath components, with water.

The lubricant material, which is added to the phosphatizing solution in combination with the surface active agent, may be any fatty acid or mixture of fatty acids, normally used in forming lubricant coatings, which is available as a solid. Additionally, the melting point of the fatty acid lubricant should be below the temperature at which the zinc phosphate solution is used, i.e., the fatty acid should have a melting point which is not in excess of about 100° centigrade, and preferably, should have a melting point below about 60° centigrade, which temperature is that at which the coating solutions are most generally used. Any solid form of the fatty acid lubricant,

as for example, powder, beads or flakes may be used. Typically, the lubricant may be a fatty acid or mixture of fatty acids wherein the acid contains from about 12 to 26 carbon atoms and may also be the mono-, di-, and/or tri-, glycerides of these fatty acids. In many instances commercial stearines have been found to be particularly suitable fatty acid lubricants for use in the present invention. Accordingly, hereinafter, primary reference will be made to the use of such materials.

The surface active agent which is admixed with the fatty acid lubricant material and added to the zinc phosphate solutions is also a solid and may be in any desired particulate form. Although any suitable surface active agent which will not interfere with the coating formation may be used, the preferred surface active agents are nonionic. Desirably, the surface active agents used have a cloud point which is above the temperature at which the resulting solution is used. Accordingly, for most applications, the solid nonionic surface active agents used will have a cloud point which is above about 60° centigrade. Typical of suitable surface active agents which may be used are ethylene oxide condensates with alkyl phenols or C_{16} to C_{18} fatty alcohols, wherein the ethylene oxide chain is made up of at least 20 units. Polyoxyethylene-polyoxypropylene compounds, such as are disclosed in U.S. Pat. No. 2,674,619, wherein the proportion of polyoxyethylene in the molecule is greater than 60%, may also be used. Other suitable surface active agents which may be utilized in the method of the present invention will be apparent to those in the art. In many instances, it has been found that rapid dispersion of the lubricant in the phosphate solution is facilitated if the surface active agent used has a melting point which is the same as or at least close to that of the lubricant. Accordingly, in choosing a suitable surface active agent and lubricant, this factor will also be taken into consideration.

It has been found that if the surface active agent and/or the lubricant which is to be added to the phosphatizing solution is sticky and/or waxy, it may be difficult to prepare a homogenous, free-flowing, particulate mix of the materials. When this occurs, the difficulty is often overcome by incorporating in the mixture an inert, particulate material, such as anhydrous sodium sulfate, boric acid, or the like. It is to be appreciated that by "inert" it is intended to mean that the particulate material does not react with either the surface active agent or the lubricant and that it has no adverse effect on either the coating action of the resulting lubricant containing solution or on the ultimate coating formed on the metal surface. Where such inert, diluent materials are used they preferably do not form more than about ⅓, i.e., about 33% by weight, of the mixture.

The solid, particulate mixture of the fatty acid lubricant material and the surface active agent is added to the phosphate solution in an amount which is suitable to provide a sufficient amount of the fatty acid to produce the desired lubricant coating on the metal surfaces treated. Desirably, the mixture of lubricant and surface active agent is added to the aqueous phosphate working solution in an amount sufficient to provide a concentration of fatty acid lubricant in the solution of from about 0.2 to about 20 grams per liter. It is to be appreciated, however, that both greater and lesser concentrations of the fatty acid lubricant in the phosphate solution may be used, depending upon the amount of lubricant which is desired on the metal surface. The mixture of the fatty acid lubricant and the surface active agent may be incorporated in the phosphating solution in any convenient manner, as for example, merely by scattering the mixture over the surface of the working phosphate solution and thereafter stirring the solution sufficiently to incorporate the lubricant therein. In most instances, it has been found that very little deliberate agitation of the solution is necessary before the fatty acid becomes emulsified and dispersed homogenously throughout the entire body of the treating solution.

When using the thus-formulated treating solution, a lubricant coating is formed on the metal surfaces to be treated by bringing these surfaces into contact with the treating solution. The desired contact may be effective in any suitable manner, for example by spraying the treating composition on the metal surface or by immersing the metal surface in the composition. During the time of treatment, the temperature of the treating solution may be from about room temperature, e.g., 20° centigrade up to the boiling point of the solution, e.g. about 100° centigrade. Generally, it is preferable that the solution is used at a temperature within the range of about 50 to 70° centigrade. The contact times between the treating solution and the metal surfaces to be treated may also vary, depending upon the application techniques used and the amount of coating which is desired on the metal. Typically, these contact times will vary from several seconds up to five or more minutes.

Following the formation of the desired lubricant coating on the metal surfaces treated, the coated surfaces may then be subjected to the desired cold forming operation. In some instances, particularly where accelerating agents have been used in the phosphatizing bath which leave a corrosive residue on the metal surface, it may be desirable to rinse the coated surfaces prior to carrying out the deformation process. Additionally, where a particularly severe deforming operation is to be effected, it may also be desirable to apply a further lubricant film to the coated metal surfaces, as for example, by treating these surfaces in aqueous solution of an alkali metal soap of the same fatty acid used in the initial treating solution. Suitable lubricant solutions which may be used for this purpose are well known to those in the art, such solutions being those which are normally used in treating a chemically coated metal surface to impart a lubricant layer thereto, when the chemical coating and lubricant are applied in two separate operations.

As the treating solutions of the present invention are used to treat a succession of metal surfaces, replenishment of the solution becomes necessary. It is to be appreciated, that the phosphating components of the treating solutions may be replenished in the normal manner, by adding the usual, appropriate phosphating replenishing solution. Additionally, the lubricating components of the treating solution may be replenished in accordance with the present invention by adding the solid, particulate mixture of the fatty acid lubricant and the surface active agent. The need for replenishment of the solution by addition of the mixture of the lubricant and the surface active agent can be based on visual observation of the appearance of the article that results from the treatment with the solution. Alternatively, the content of the lubricant or surface active agent in the solution can be estimated or preliminary tests may be made to determine the rate at which the lubricant is consumed in relation to the consumption of the phosphate and thereafter the phosphate consumption can be measured.

The coated surfaces produced in accordance with the present invention may then be subjected to various cold forming operations such as wire drawing, tube drawing, cold extrusion or the like. It is to be appreciated that by formulating the treating solutions in accordance with the method of the present invention that has been described hereinabove, the prior art difficulties of achieving a homogenous distribution of the fatty acid lubricant in, first, a concentrated aqueous solution and then a dilute solution are overcome, while still making it possible to supply the ingredients of the treating solution in a relatively simple form. Additionally, by replenishing the treating solutions with a particulate mixture of the lubricant and surface active agent, additions of the lubricant can be made as they are needed without effecting the strength or concentration of the phosphate solution.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, parts and percent are by weight and temperatures are in degrees centigrade. It is to be appreciated, however, that these examples are merely exemplary of the present invention and are not to be taken as a limitation thereof.

EXAMPLE 1

An aqueous phosphating solution was prepared containing the following components in the amounts indicated:

Components:	Grams per liter
Zinc	3.9
Sodium	4.9
Phosphate	11.6
Nitrate	6.1
Chlorate	3.7

This solution had a pointage of 20.5, the points being the number of milliliters of 0.1 normal sodium hydroxide needed to titrate a 10 milliliter sample of the solution to the phenolphthalene end point. To this solution was added one gram per liter of a dry mixture containing equal weights of commercial stearine having an iodine value of 8, an acid value of 20.5, a melting point of 53° centigrade and a nonionic surface active agent which is a condensate of C_{16} to C_{18} fatty alcohols with 80 moles of ethylene oxide, and having a cloud point above about 100° centigrade and a melting point of 53° centigrade. This dry mixture was scattered over the surface of the phosphating solution and then agitated slightly to effect dispersion of the mixture throughout the solution. The resulting solution was maintained at a temperature of 60° centigrade and pickled carbon-steel tubes were immersed therein to form a lubricant coating on the surface of the tubes. The thus-treated tubes were then rinsed and lubricated by immersion in a 10% aqueous solution of the sodium soap of the same fatty acid used hereinabove as an additive for the original phosphate processing solution. The tubes were then dried and subjected to a rather severe drawing operation. It was found that all of the tubes drew satisfactorily with a complete absence of any tube failing and there was appreciably less chattering of the tubes during the drawing, as compared to similar operations carried out on tubes which had been coated only with a phosphate coating, which contained no lubricant material, and then given a lubricant coating in a separate operation. Additionally, the drawn tubes had a uniform dark and pleasing appearance and it was found that the phosphate containing processing solution containing the lubricant additives could be used for longer periods of time before desludging became necessary than could similar phosphate solutions without the lubricant additive.

EXAMPLE 2

The procedure of Example 1 is repeated with the exception that after treating the tubes in the phosphate solution containing the lubricant additive, the tubes are dried and then subjected to a somewhat less severe drawing operation. In this less severe drawing operation, it was found that satisfactory drawing of the tubes is obtained without the application of a further lubricant coating on the metal surface.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible and it is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A process for formulating a metal treating solution suitable for forming a phosphate coating and lubricant coating on a metal surface in a single treatment, which process comprises forming an aqueous zinc phosphate solution containing zinc ions and phosphate ions in an amount suitable for forming a phosphate coating on the metal surface treated therewith, adding to said zinc phosphate solution a solid, particulate mixture of a fatty acid lubricant and a water-soluble surface active agent, the amount of the surface active agent in the mixture being sufficient to effect dispersion of the fatty acid lubricant throughout the zinc phosphate solution and thereafter, dispersing said fatty acid lubricant throughout the zinc phosphate solution.

2. The method as claimed in claim **1** wherein the particulate mixture of the fatty acid lubricant and the surface active agent is added to the phosphate solution in an amount to provide from about 0.2 to 20 grams per liter of fatty acid lubricant in the resulting solution.

3. The method as claimed in claim **2** wherein the lubricant and surface active agent used both have a melting point which is not substantially in excess of about 100 degrees centigrade.

4. The method as claimed in claim **3** wherein the fatty acid lubricant is a commercial stearine and the surface active agent is a condensate of ethylene oxide with a C_{16} to C_{18} fatty alcohol, wherein the ethylene oxide chain contains at least 20 units.

5. A method of deforming ferrous metal surfaces which comprises formulating an aqueous acidic zinc phosphate solution containing zinc ions and phosphate ions in an amount suitable for forming a phosphate coating on a ferrous metal surface treated therewith, adding to said zinc phosphate solution a solid, particulate mixture of a fatty acid lubricant and a water-soluble surface active agent, the amount of the surface active agent being sufficient to effect dispersion of the fatty acid throughout the zinc phosphate solution, effecting dispersion of the fatty acid lubricant throughout the zinc phosphate solution, contacting the ferrous metal surfaces to be deformed with the thus-formulated treating solution for a period sufficient to form a combined phosphate and lubricant coating thereon, and thereafter, deforming the thus-produced coated ferrous metal surface.

6. The method as claimed in claim **5** wherein the mixture of the fatty acid lubricant and the surface active agent is added to the zinc phosphate solution in an amount sufficient to provide from about 0.2 to 20 grams per liter of the fatty acid lubricant in the phosphate solution.

7. The method as claimed in claim **6** wherein the fatty acid lubricant and the surface active agent used both have a melting point which is not substantially in excess of 100 degrees centigrade.

8. The method as claimed in claim **7** wherein the fatty acid lubricant is commercial stearine and the surface active agent is a condensate of ethylene oxide with a C_{16} to C_{18} fatty alcohol, wherein the ethylene oxide chain contains at least 20 units.

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