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[54] **METAL PHOSPHATIZING
COMPOSITION AND PROCESS**

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[56] **References Cited**

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[57] **ABSTRACT**

In a phosphating process in which the metal surface is treated with a solution of phosphoric acid, a dibasic phosphate and an accelerator which is a nitrated aromatic derivative having at least one free phenol radical, the nitrated organic derivative is dissolved in a nonionic surfactant which is the reaction product of ethylene oxide and a hydrophobic base, before being combined with the phosphoric acid and dibasic phosphate to form the phosphating solution. In this manner, a more homogeneous composition is obtained than has heretofore been possible when the nitrated organic derivative per se, has either been mixed with the phosphated compounds to form a concentrate composition or has been added to the aqueous phosphating solution.

2 Claims, No Drawings

METAL PHOSPHATIZING COMPOSITION AND PROCESS

This invention relates to an improved composition and process for the phosphate coating of metal surfaces and more particularly it relates to the phosphate coating of metal surfaces using an aqueous acidic phosphating solution which contains nitrated phenolic compounds as accelerators.

Heretofore, it has been known to apply phosphate coatings to metal surfaces using aqueous acidic phosphate solutions which contain nitrated phenolic compounds as accelerators. Compositions and processes of this type are described in French Pat. No. 1,123,368. Generally, however, the nitrated phenolic compounds are in the form of relatively coarse crystals which make it very difficult to blend these materials with the phosphated components of the composition, such as monosodium phosphate or phosphoric acid, to form a homogeneous concentrate composition which is ready for use after dilution with water. Additionally, these nitrated phenolic compounds are sufficiently insoluble in the aqueous acidic phosphating solutions that it has frequently been necessary to modify the nitrated phenolics with radicals of a hydrophilic solvent, such as for example the sulfonic radical, to impart the necessary solubility. Generally, this has been found to be necessary even where the phosphating solutions have themselves contained various solubilizing, wetting, and/or surface active agents.

It is, therefore, an object of the present invention to provide an improved concentrate composition from which aqueous acidic phosphating solutions can be formulated.

Another object of the present invention is to provide an improved aqueous acidic phosphating composition for the phosphate coating of metal surfaces.

A further object of the present invention is to provide an improved method for formulating a concentrate composition for use in making up aqueous acidic phosphating solutions.

A still further object of the present invention is to provide an improved process for forming phosphate coatings on metal surfaces.

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

Pursuant to the above objects, the present invention includes a concentrate composition, useful when diluted with water for the phosphate coating of metal surfaces, which comprises a dibasic phosphate, phosphoric acid, and an accelerator composition, which accelerator composition is comprised of a nitrated aromatic compound having at least one free phenol radical, dissolved in at least one nonionic surface active agent which is the condensation product of ethylene oxide with a hydrophobic base. This concentrate composition is found to be a substantially uniform, homogeneous mixture which is readily dissolved in water to form the aqueous phosphating solution.

More specifically, in the practice of the present invention, the concentrate composition contains the phosphated materials, i.e., the diacid phosphates and phosphoric acid, in an amount within the range of about 80 to 95 percent by weight and the accelerator composition in an amount within the range of about 5 to 20 percent by weight. In a preferred embodiment, however, the accelerator composition is present in an amount within the range of about 8 to 12 percent by weight of the concentrate composition.

Desirably, the phosphated materials are a mixture of one or more diacid phosphates and phosphoric acid, the diacid phosphates constituting the major portion of the phosphated materials. Thus, for example, in many instances, it is preferred that the concentrate composition contain one or more diacid phosphates in an amount within the range of about 70 to 94 percent by weight of the concentrate composition and the phosphoric acid in an amount within the range of about 1 to 10 percent by weight of the concentrate composition.

In referring to the phosphated materials in the concentrate composition, it has been noted that these are made up of one

or more diacid phosphates and phosphoric acid. Various diacid phosphates may be used in the composition, such as the alkali metal diacid phosphates, as well as other metal diacid phosphates, such as zinc diacid phosphate, and the like. Of the numerous diacid phosphates which may be used, the preferred are the alkali metal diacid phosphates and, particularly, monosodium phosphate. Accordingly, hereinafter, specific reference will be made to monosodium phosphate as being the preferred diacid phosphate material. This reference, however, is not deemed to be a limitation on the diacid phosphates which may be used but rather, merely as being exemplary thereof.

With regard to the phosphoric acid, this is desirably orthophosphoric acid and may be used in any suitable concentration. In many instances, however, for ease in handling and shipping the concentrate composition, it is preferred that the orthophosphoric acid used be 100 percent phosphoric acid, which material is in a dry, crystalline form. In this manner, the concentrate composition can be formulated as a homogeneous, substantially dry mixture which is readily dissolved in water to form the aqueous acidic phosphating solutions.

As has been noted hereinabove, the accelerator composition which is present in an amount within the range of about 5 to 20 percent by weight and preferably 8 to 12 percent by weight of the concentrate composition, is formed by dissolving the nitrated aromatic compound containing at least one free phenol radical in the nonionic surface active agent. In general, it has been found to be desirable if the nitrated aromatic compound containing the free phenol radical is present in amounts within the range of about 0.5 to 50 percent by weight of the accelerator composition, although in some instances, amounts outside of this range may also be used, depending upon the nature of the particular nitrated aromatic and nonionic surfactant which are used. Moreover, the particular specific proportion of these materials which are used in any particular instance will vary depending upon both the materials themselves, the characteristics of the solutions in which they are used and the operating conditions under which the compositions are utilized.

It is believed that those in the art are familiar with the various different nitrated aromatic compounds containing at least one free phenol radical which are effective as accelerators in the present types of phosphating baths. Such accelerator materials are frequently coarsely crystalline in form, having limited solubility in aqueous solutions and, in general, any of the nitrated aromatic compounds containing at least one free phenol radical, having these characteristics, which have heretofore been known as accelerators for phosphating baths, may be used in the present composition. Exemplary of specific nitrated accelerator materials of this type are orthonitrophenol, metanitrophenol, paranitrophenol, 2,4-dinitrophenol, 2,6-paradinitrocresol, 2-nitro-1-naphthol, 1,6-dinitro-2-naphthol and the like. In general, these compounds may be characterized as being aromatic compounds having a benzene or naphthalene nucleus which contains from 1 to 2 nitro groups, 0 to 1 alkyl groups containing from 1 to 3 carbon atoms and at least one OH group, all of said substituent groups being attached to the benzene or naphthalene nucleus.

The nonionic surfactants which are used in the present composition are the condensation products of ethylene oxide and a hydrophobic base. The surfactants used should be stable in the phosphating solution and compatible with this solution and the conditions under which it is used. The surfactant should be either soluble or dispersible in aqueous medium and be low foaming while still having good detergent and wetting characteristics. Additionally, it is preferable if the surfactants used substantially reduce the surface tension of the aqueous phosphating solution so that a degreasing of the metal surface is also effected during treatment with the solution.

Exemplary of the nonionic surfactants which may be used are the alkyl phenol oxyethylenes such as the oxyethylenes of octylphenol, nonylphenol, tributylphenol, and the like; the oxyethylenic alcohols containing straight or branched hydrocar-

bon chains, particularly those which have been modified to reduce their foaming tendencies; polyoxypropylenes; polyoxypropylene glycols; condensates of ethylene oxide and propylene oxide; condensates of ethylene oxides with fatty acids, fatty amines, fatty amides and the like. Typically, these surfactants will contain from about 5 to 10 moles of ethylene oxide per mole of surfactant, although the particular nonionic surface active agent used in each instance may vary, depending upon the particular nitrated aromatic accelerator compound which is used. Similarly, although the accelerator compound has heretofore been indicated as containing from about 0.5 to 50 percent by weight of the nitrated aromatic material and from about 50 to 99.5 percent by weight of the nonionic surface active agent, the specific amounts of these components which are used may be varied in each instance, depending upon the particular materials and conditions of use which are utilized.

In formulating the compositions of the present invention, the nitrated aromatic compound is incorporated into the nonionic surfactant, desirably, using moderate agitation. The dissolution of the nitrated aromatic in the surfactant may be facilitated by raising the temperature of the mixture, although, preferably, the temperature should not be in excess of about 50° C. The resulting compositions, which are in the form of a viscous, clear, homogeneous liquid, the color of which varies from clear yellow to dark brown, may then be added as such to the aqueous phosphating solution or may be mixed with the diacid phosphate and phosphoric acid to form a concentrate composition which may subsequently be diluted with water to form the final phosphating solution. As has been noted hereinabove, in forming the concentrate compositions, the accelerator composition of the nitrated aromatic accelerator, dissolved in the nonionic surfactant, is admixed with the dibasic phosphate and phosphoric acid in amounts of from about 5 to 20 percent by weight and preferably from about 8 to 12 percent by weight of the final concentrate composition. In this manner, there is obtained a substantially dry concentrate composition which is substantially homogeneous and which is readily dissolved in water to form the phosphate treating solution.

Where the aqueous phosphatizing solution is formulated by dissolving the concentrate composition in water, the concentrate material containing the diacid phosphate, phosphoric acid and the accelerator composition are desirably dissolved in the water in a concentration within the range of about 5 to 25 grams per liter and preferably within the range of about 9 to 13 grams per liter. The resulting aqueous phosphating solution, which desirably has a pH within the range of about 4 to 6 and preferably within the range of about 4.5 to 5.5, is then applied to the metal surfaces to be treated, such as ferrous metal surfaces, preferably by spraying. By the use of the solutions in this manner, there is obtained both a degreasing of the metal surface treated as well as a phosphatizing and passivating of the metal.

Additionally, it is to be appreciated that these aqueous phosphating solutions may be made up without the addition of the accelerator composition, by admixing the diacid phosphate and phosphoric acid in water in amounts sufficient to form the phosphating solution having the desired concentration of phosphating materials and pH, and that the accelerator material may then be added to this aqueous phosphating composition, desirably in amounts within the range of about 0.25 to 5 grams per liter, to give the final working phosphatizing bath.

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.

The following concentrate compositions were formulated by dispersing the nitrated aromatic compound in the nonionic surfactant, using moderate agitation:

1	orthonitrophenol	21
	oxyethylene nonylphenol	
	containing an average	
	of 6 moles of ethylene	
	oxide per mole	79
5	2 meta-nitrophenol	19
	oxyethylated nonyl	
	phenol containing	
	an average of 6	
	moles of ethylene	
	oxide per mole	81
10	3 para-nitrophenol	30
	oxyethylated	
	nonylphenol containing	
	an average of 6 moles	
	of ethylene oxide per	
	mole	70
15	4 2,4-dinitrophenol	16
	oxyethylated straight	
	chain alcohol, obtained	
	from a C ₈ -C ₁₀ fraction	
	and containing an	
	average of 5 moles of	
	ethylene oxide per mole-	84
20	5 2,6-para-dinitroresol	11
	condensation product	
	of ethylene oxide and	
	propylene oxide contain-	
	ing an average of 40%	
	by weight ethylene oxide	
	per mole	89
25	6 para-nitrophenol	25
	oxyethylated straight	
	chain alcohol obtained	
	from a C ₈ -H ₁₀ fraction,	
	containing an average	
	of 10 moles of ethylene	
	oxide per mole	75
30	7 para-nitrophenol	27
	condensation product	
	of ethylene oxide and	
	propylene oxide containing	
	an average of 40% by weight	
	of ethylene oxide per mole-	73

Concentrate compositions, suitable for dilution with water to form aqueous phosphating solutions, were formulated by admixing the accelerator compositions of the types described above with the phosphating chemicals, to form the following homogenous, substantially dry compositions:

Example	Components	Percent by weight
8	anhydrous monosodium phosphate	88
	crystalline phosphoric acid, (100%)	3
	accelerator composition of Example 3	9
9	anhydrous monosodium phosphate	88
	crystalline phosphoric acid (100%)	2
	accelerator composition of Example 6	10
10	anhydrous monosodium phosphate	88.5
	crystalline phosphoric acid (100%)	3.5
	accelerator composition of Example 7	8.0

Aqueous phosphating solutions were prepared by dissolving concentrate compositions of the type described above in water to form aqueous acidic phosphating solutions having a pH within the range of about 4 to 6 and containing the phosphating and accelerating components as follows:

11	monosodium phosphate	8.8
	phosphoric acid (100%)	0.3
	accelerator composition of Example 3	0.9
12	monosodium phosphate	8.8
	phosphoric acid (100%)	0.2
	accelerator composition of Example 6	1.0
13	monosodium phosphate	8.85
	phosphoric acid (100%)	0.35
	accelerator composition of Example 7	0.8

The aqueous phosphating solutions of the preceding examples 11 through 13 are applied by spraying to a ferrous metal surface and by this treatment the metal surface is degreased and a passivated phosphate coating formed on the ferrous metal surface. The phosphating solutions used were found to be substantially free of undissolved solution components, including both the phosphating materials and the accelerating materials. Additionally, in formulating these solutions, by dissolving the concentrate composition in water, it was found that the concentrate materials dissolved readily with only moderate agitation required.

While there have been described various embodiments of the invention, the composition and methods described are not intended to be understood as limiting the scope of the invention as 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 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. An aqueous phosphatizing solution which comprises

water and from about 5 to 25 grams per liter of a concentrate composition comprising, (1) a dibasic phosphate present in an amount within a range about 70 to 94 percent by weight of the concentrate composition, (2) phosphoric acid present in an amount within a range of about 1 to 10 percent by weight of the concentrate composition, and (3) an accelerator composition present in an amount within a range of about 5 to 20 percent by weight of the concentrate composition being comprised of a nitrated aromatic compound having at least one free phenol radical, present in an amount of about 0.5 to 50 percent by weight of the accelerator composition, dissolved in at least one nonionic surface active agent which is the condensation product of ethylene oxide and a hydrophobic base, said surface active agent present in an amount of about 50 to 99.5 percent by weight of the accelerator composition.

2. A method for treating ferrous metal surfaces which comprises spraying the aqueous phosphating solution as claimed in claim 1 on the ferrous metal surface to be treated, and maintaining the aqueous solution in contact with the metal surface for a period sufficient to effect degreasing thereof and the formation of a phosphate coating thereon.

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