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ACCELERATION OF PHOSPHATE COATING WITH QUINONE

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This invention relates to the production of coatings on ferrous and zinc surfaces by chemical means. It relates more specifically to the formation of phosphate coatings that serve as a bonding coating for paints, lacquers, enamels and similar finishes.

It is well known that ordinary finishes do not adhere well to bare metal surfaces. Treatments of various kinds have been used for years in order to overcome this difficulty, and today the step of chemically forming a bonding coat is an integral part of the procedure with a large part of the metal fabricating industry.

The most widely used processes are those which form insoluble phosphate coatings by reaction when the metallic surfaces are subjected to acid phosphate solutions. The action of the coating bath is generally accelerated by the presence of an oxidizing agent in order to meet the demands of high speed production.

Phosphate coatings are produced on iron or zinc by solutions containing acid phosphates of certain metals which may be conveniently designated by the term "phosphate coating metals." The oxidizing agents most commonly used to accelerate the action of phosphate coating solutions have been nitrates and nitrites. When nitrates are used, it is found advisable to increase the amount of phosphate coating metal in the solution so as to increase the tendency of a less acid phosphate of the metal to precipitate out of the solution. A solution having this tendency will be hereinafter referred to as supersaturated. The amount of the phosphate coating metal in the solution has been increased in many instances by employing it as the base metal in nitrate added to the solution. As the nitrate ion is used up in the reaction, the phosphate coating metal ion adds to the supersaturation of the solution.

Nitrites, such as sodium nitrite, decompose quite rapidly when added to a phosphate coating solution. The base element has a neutralizing effect which adds to supersaturation.

While supersaturation aids in the production of a phosphate coating by facilitating precipitation of coating phosphates, it also increases the precipitation of sludge and the waste of chemicals in this way. Therefore, the supersaturation commonly employed with both nitrates and nitrites causes waste by creating sludge, and the decomposition of nitrite is a further source of waste.

An object of my invention resides in the use of a different type of oxidizing medium characterized by its occurrence in organic compounds.

A further object is the use of an oxidizing medium having certain desirable characteristics not ordinarily associated with the use of nitrate or nitrite, including a less wasteful use of coating chemicals.

These objects are accomplished by supplying the oxidizing medium by addition to the phosphate solution of substances derived from aromatic hydrocarbons by replacement of two hydrogen by two oxygen atoms and designated by the generic term, quinones.

These oxidizing agents in general are rapid in their action on ferrous iron. When such agents are added to a solution containing a material amount of ferrous phosphate, they convert the ferrous phosphate to ferric phosphate and free phosphoric acid. Ferric phosphate being substantially insoluble, is precipitated as sludge. This constitutes a waste of chemicals, and the free phosphoric acid remaining in the solution upsets the chemical balance suitable for best coating action. Therefore quinones generally are not useful for accelerating the coating action of phosphate solutions containing a material amount of ferrous phosphate.

I have discovered, however, that quinones may be successfully employed in solutions prepared with phosphates of metals that are not oxidized by them, provided the amount of quinone present in the solution is regulated within certain limits. Too little quinone of course will not have sufficient accelerating action. On the other hand, the presence of too much quinone first causes the appearance of wavy lines in the coating, while a still further increase in the amount of quinone results in the formation of a coating apparently containing oxide. When this stage is reached it occasionally happens that portions of the metal subjected to the solution will not be reacted upon sufficiently to produce more than a barely visible coating. Other areas will be covered with a white smudge.

Coatings having the appearance of containing oxide or those on which the white smudge is evident are not commercially acceptable.

The wavy lines referred to above make their appearance somewhat gradually, and may be taken as an indication that an excessive amount of quinone in the solution is being approached. When these lines are only present occasionally on the metal being treated, they are not particularly objectionable. However, sufficient quinone may be used to produce the desired acceleration without using an amount that produces any wavy lines.

Under favorable conditions good coatings are produced at temperatures as low as 100° F., but for best results at low temperatures somewhat higher concentrations of coating metal phosphate and a somewhat longer processing time is needed than where higher temperatures are employed.

The concentrations of quinone which on one hand are required to produce a coating and on the other hand may be tolerated without obtaining oxide or smudge on the articles treated, vary both with the concentration of coating metal in the solution, and with the temperature. This is illustrated by the following:

Steel articles were first cleaned by spraying them for one minute at 140°–160° F. with a dilute kerosene emulsion, the cleaner being adjusted by the addition of phosphoric acid to produce a pH of approximately 8. After water rinsing they were then sprayed for one minute with acid zinc phosphate solutions of varying concentrations and temperatures. The zinc concentration was adjusted by adding the appropriate quantity of a concentrated solution prepared by using the following proportions of chemicals:

	Pounds
Zinc oxide	125
75% phosphoric acid	525
Water to make	1000

The values given for quinone in the table below were obtained by visual observation of the coatings obtained at the different temperatures and different concentrations of benzoquinone, the lower limit indicating the amount required to produce a visible improvement in the coating, the upper limit indicating the point at which excessive amounts of quinone are present because of the evidence of oxide, smudge or both, and the approximate optimum indicating an amount of quinone approximating that which produces the best results. It should be understood however that good coatings are obtained with amounts of quinone both above and below the optimum values.

Temperature	Percent zinc	Percent quinone		
		Lower limit	Approximate optimum	Upper limit
140° F.	.20	.024	.05	.072
	.40	.032	.092	.136
	.50	.036	.114	.174
	.60	.040	.136	.216
178° F.	.20	.026	.074	.116
	.40	.064	.148	.224
	.50	.082	.184	.280
	.60	.102	.216	.332

It will be seen that the amounts of quinone given in the table rise both with the increase of zinc and increase in temperature. This is true of the minimum required, the maximum permissible and the approximate optimum amount.

The above tests were made with solutions containing such a proportion of acid and zinc as to be substantially at equilibrium at the temperature at which they were used.

As the use of the solutions continues it will be found in some instances that not only the minimum amount of quinone required to show acceleration will rise somewhat but the amount required for optimum coating conditions will also increase and this should be taken into consideration in replenishing the solution. If inferior coatings are in evidence, the amount of quinone in the coating solution should be increased until the condition disappears.

Other soluble quinones may be used in place of benzoquinone. The most common quinones are those of benzene, naphthalene, anthracene and phenanthrene.

In many instances aromatic hydrocarbons have further substitutions than those required to produce simple quinones such as benzoquinone. These compounds, unless they contain an element or radical which is incompatible with the phosphate coating solution, are also effective in accelerating the coating action. For example, good results have been obtained with tetrachlorparabenzoquinone, (chloranil).

In figuring the quantity which should be used, the additions should be based on the equivalent weight of the substance under consideration. As an illustration, the molecular weight of benzoquinone is 108 while that of sodium anthraquinone sulfonate is 310. It is shown in the chart that, with .2% zinc and a temperature of 140° F., the optimum concentration of benzoquinone is .05%. Under like conditions the optimum concentration of sodium anthraquinone sulfonate is approximately .15%, which would be expected because of the difference in molecular weight of the two compounds. Of course, if the other portions of the molecule, aside from the oxygen atoms typical of quinone, are such as to affect the coating action, their influence must be taken into consideration. For example, some quinone compounds comprise nitro groups which have an accelerating oxidizing effect and so increase the effect of the molecule over that which the quinone group alone would have.

The solubility of the quinones varies considerably. For example, benzoquinone is readily soluble in sufficient amounts in ordinary phosphate coating solutions, while anthraquinone as such is practically insoluble. Therefore, the sulfonated anthraquinone or other soluble compound is used. The expedient of sulfonation can be resorted to in other instances where it is necessary to increase the solubility, and sulfonation also has a tendency to reduce the volatility of the quinone. It is wasteful and otherwise objectionable to employ quinones that are too volatile at the temperature at which the solution is used. The use of sulfonated quinones is therefore within the scope of the invention. Also quinones which are not sufficiently soluble in water may be employed by use of an added solvent which does not interfere with the coating action of the phosphate solution. Therefore, the term "soluble quinone" is employed in the claims to cover any quinone which is soluble in the proportion required in the particular solution being employed.

The quinone may be soluble enough to obtain an ample amount for acceleration in the coating solution while still being too slightly soluble to form a condensed solution suitable for shipping and using in replenishing. Such quinones are still "soluble" within the meaning of the claim, but are best furnished as solids. They can be mixed with acid phosphate powder to form a convenient replenishing material. When a quinone is employed which is sufficiently soluble in a concentrated phosphate solution, it may be mixed with a replenishing solution.

Zinc acid phosphate was specifically mentioned in connection with the table of limits, but other acid phosphates of coating metals such as manganese, cadmium and calcium, which are not oxidized by the quinones, may be used.

The quinones may be used for acceleration where the metal is coated by immersion as well as where the solution is sprayed on the surface, recirculated and resprayed. Where the immersion method is employed the optimum concentration of quinone is somewhat lower than that given for any particular set of conditions in the table, since a longer processing time is usually permissible.

Zinc as well as ferrous metals is successfully coated by quinone-accelerated solutions.

A quinone may be chosen which will be partially reduced in the coating reaction and will be re-oxidized or regenerated by oxidation in the air during the spraying operation, so as to reduce the amount of oxidizing agent which must be added during replenishing to maintain the coating action of the bath. No claim is made in this application to the regeneration of the oxidizing agent.

It will be seen that the use of quinone as an oxidizing agent, within proper limits, accelerates the action of a phosphate coating solution without necessitating supersaturation, and consequently obtains the desired result by a very economical use of chemicals, especially where regeneration of the quinone is employed.

What I claim is:

1. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble quinone.

2. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble sulphonated quinone.

3. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble non-volatile quinone.

4. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is metal in the coating phosphate.

5. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 15% to 40% as much benzoquinone as there is metal in the coating phosphate.

6. The method of producing a phosphate coat upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone and accelerating the coating action of the solution by including in the solution a compatible soluble quinone and maintaining the solution in contact with the surface at a temperature of from 100° F. to 180° F.

7. The method of producing a phosphate coating upon the surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of an acid phosphate of a coating metal capable of resisting the oxidizing action of quinone, maintaining the solution in contact with the surface at a temperature of from 100° F. to 180° F., and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is metal in the coating phosphate.

8. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accelerating the coating action of the solution by including in the solution a compatible soluble quinone.

9. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is zinc in the solution.

10. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is zinc in the solution and maintaining the solution in contact with the surface at a temperature of from 100° F. to 180° F.

11. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accelerating the coating action of the solution by including in the solution a compatible soluble quinone and maintaining the proportion of metal to phosphoric acid in the solution at approximate equilibrium for the solution and temperature being employed.

12. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accel-

erating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is zinc in the solution and maintaining the proportion of metal to phosphoric acid in the solution at approximate equilibrium for the solution and temperature being employed.

13. The method of producing a phosphate coating upon a surface composed principally of metal of the group consisting of iron and zinc which comprises subjecting the surface to the action of a solution of zinc acid phosphate and accelerating the coating action of the solution by including in the solution a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is zinc in the solution and maintaining the solution in contact with the surface at a temperature of from 100° F. to 180° F. and maintaining the proportion of metal to phosphoric acid in the solution at approximate equilibrium for the solution and temperature being employed.

14. A solution for coating metal which comprises as its principal coating chemicals an acid phosphate of a phosphate coating metal capable of resisting the oxidizing action of quinone and compatible soluble quinone in an amount sufficient to accelerate the coating action of the solution.

15. A solution for coating metal which comprises as its principal coating chemicals an acid phosphate of a phosphate coating metal capable of resisting the oxidizing action of quinone and compatible soluble sulphonated quinone in an amount sufficient to accelerate the coating action of the solution.

16. A solution for coating metal which comprises as its principal coating chemicals an acid phosphate of a phosphate coating metal capable of resisting the oxidizing action of quinone and compatible soluble non-volatile quinone in an amount sufficient to accelerate the coating action of the solution.

17. A solution for coating metal which comprises as its principal coating chemicals an acid phosphate of a phosphate coating metal capable of resisting the oxidizing action of quinone and compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is metal in the coating phosphate.

18. A solution for producing a phosphate coating on metal which comprises as its principal coating chemicals an acid zinc phosphate and a compatible soluble quinone.

19. A solution for producing a phosphate coating on metal which comprises as its principal coating chemicals an acid zinc phosphate and a compatible soluble quinone in an amount to constitute the molecular equivalent of from 10% to 50% as much benzoquinone as there is zinc in the solution.

20. Powders for use in a phosphate coating solution, said powders comprising a mixture of acid phosphate coating material and soluble non-volatile material containing quinone.

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