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METAL TREATMENT

Robert C. Gibson, Detroit, Mich., assignor to Parker Rust Proof Company, Detroit, Mich.

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This invention relates to the production of phosphate coatings on metal surfaces and relates more particularly to a method of replenishing the solutions which are used for that purpose.

Methods of coating metal surfaces with insoluble phosphates have undergone considerable evolution in recent years. One of the main points of progress has been the reduction in the treating time required to produce the desired results. This has been brought about in a large measure by employing suitable oxidizing agents to expedite the coating action. Among these, nitrite usually furnished as sodium nitrite, has found favtor because it is relatively cheap, only a small percentage is required in the solution, and very fine grained coatings are produced by solutions containing it. On the other hand, there are disadvantages connected with its use. In acid solutions, such as phosphate coating solutions, sodium nitrite is unstable. Its decomposition results in the loss of certain volatile constituents while the sodium remains in solution and acts as a neutralizing agent forming sodium dihydrogen phosphate. The resultant loss of acidity causes a wasteful precipitation of coating phosphates from the solution. For example, if zinc dihydrogen phosphate is employed, the neutralization will result in the precipitation of normal zinc phosphate as sludge. The recovery of this sludge and its conversion to the soluble dihydrogen phosphate on a commercial scale is impractical.

The presence of sodium dihydrogen phosphate also has disadvantages. The coating efficiency of the solution will be impaired by the accumulation of an appreciable amount of sodium phosphate because it increases the solubility of normal zinc phosphate which comprises the bulk of the coating formed on the metal surface. Also, unless care is used in analyzing the solution, the sodium phosphate will be calculated as a coating material along with zinc phosphate. This will occur whenever the usual titrating methods are employed. The true coating phosphate content of the bath, therefore, must be determined by other less convenient means whenever an appreciable amount of sodium phosphate is present.

The addition of phosphoric acid in sufficient amounts will offset the neutralizing effect of the sodium nitrite, but facilitates the formation of the sodium salt. Furthermore, it becomes increasingly difficult to maintain a given acidity (pH) in the processing bath as the amount of sodium phosphate rises. Therefore, the addition of increasingly large quantities of phosphoric acid is required.

An object of this invention is a method of using a nitrite, such as sodium nitrite, or any similar nitrite which by decomposition in an acid phosphate solution results in a neutralizing action, as an accelerator and at the same time avoid the build up of more than insignificant amounts of the objectionable sodium salt, and at the same time avoid the neutralizing effect which would otherwise be obtained.

Another object is the avoidance of sludge formation and the consequent loss of coating chemicals such as occurs in phosphate solutions when the neutralizing effect of a nitrite is not counteracted.

A further object is to enable the operator of a solution to determine by a simple titration the true coating strength present.

These objects are accomplished by replenishing the solution as required, with a coating dihydrogen phosphate, such as zinc phosphate, a nitrite, such as sodium nitrite, and an acid with which the nitrite will react with the liberation of nitrous acid, and in amount at least equivalent to that required to form a substantially neutral salt by reaction with the nitrite present. It is preferable when any replenishing is done that the coating metal and the phosphate content of the replenishing materials be added in substantially the proportions to form zinc dihydrogen phosphate. Less phosphate (phosphoric acid) would, of course, result in the presence of sludge, while more than is required would be available to form sodium phosphate.

Sodium nitrite, being unstable in the presence of acid, must be added separately from the acid phosphate. The nitrite will vary in efficiency within limits, with the rate of production, that is, the greater the amount of surface treated in a given time, the less the amount of nitrite required for a given area coated, because there is less chance for decomposition to occur in the absence of coating formation. It can be seen, therefore, that the amount of acid to be added to combine with the sodium of the sodium nitrite will vary somewhat depending on operating conditions. To a degree, this factor is compensated for by a more or less corresponding change in consumption of coating chemicals, and for variations ordinarily encountered the acid may be incorporated with the coating phosphate material so that the addition of the acid as a separate ingredient is avoided. However, in extreme cases, it may become necessary to add

the acid separately to be certain that the proper quantity is present on the one hand and on the other, that an undesirable excess is not introduced.

I have found that nitric acid is a very suitable material for the purpose of the invention. This may be added along with the acid phosphate as a single mixture.

When preparing a coating solution, the water in the tank is first heated to 110–130° F. The processing bath may be prepared by adding in the proportion of 40 pounds to 100 gallons of water a concentrated solution of the following composition:

	Pounds
42° Bé. nitric acid	200
75% phosphoric acid	1,335
Zinc oxide	400
Water to make	4,900

To the bath is also added 0.3 pound of sodium nitrite for each 100 gallons. This is conveniently added in the form of a 20% solution. The solid material may be added if desired, but excessive decomposition of the nitrite takes place.

The coating solution may be applied to the metal to be coated by any of the usual methods, for example by immersing the metal, by flowing the solution over the surface, or by spraying the solution. In the latter two cases the solution is ordinarily recirculated.

If the metal, for example, fenders, wheels, or other automotive steel parts, is to be coated by spraying, the other steps incident to this coating operation, that is, the necessary cleaning and rinsing operations, are also carried out by the spray method. The metal is carried on a conveyor through a tunnel in which the various steps are performed. A spraying time of approximately one minute in the coating section is usually sufficient to cause a uniform conversion of the steel surface to an insoluble phosphate.

Since a continual consumption of chemicals occurs during the coating operation, these must be replaced. I have found that the solution may be operated over long periods without encountering an accumulation of sodium phosphate in the bath if, in addition to nitrite, the solution is replenished as required with the following composition:

	Pounds
42° Bé. nitric acid	800
75% phosphoric acid	1,900
Zinc oxide	575
Water to make	5,400

This is advantageously added by supplying a continuous stream to the processing bath and regulating the size of the stream in relation to the increase or decrease in production rate.

The sodium nitrite is preferably added in the same manner. The amount reqired in the solution will vary not only with the rate of production, as has been pointed out, but also to some extent with the ease with which any given kind of steel is coated. Where the processing time is standardized as it is in the usual spraying installations, it is sometimes necessary to slightly increase the amount of nitrite in order to obtain a satisfactory coating in a given time, since it is impractical to increase the processing time. I have found, however, that for the great majority of metal encountered, a range of nitrite, calculated as NO_2, from .006 to .05% is very satisfactory. The nitrite content of the solution can easily be determined by titrating a sample with permanganate in accordance with usual methods. The amount of NO_2 required varies with the temperature, that is, .006% is satisfactory when operating at around 130° F., while approximately .02–.05% is required at a temperature in the neighborhood of 110° F.

The amount of nitric acid in the above replenishing formula is sufficient to avoid the formation of sodium dihydrogen phosphate when the higher amounts of nitrite are used and, at the same time, there is insufficient to cause excessive acidity when only small amounts are employed.

The use of nitric acid has been dealt with somewhat in detail. However, it is to be understood that other acids may be used in place of it. For example, sulfuric and hydrochloric acid are also capable of counteracting the neutralizing effect resulting from the decomposition of sodium nitrite without the building up of sodium phosphate. Nitric acid, however, is preferred. The nitrite appears to have some catalytic action on the nitrate with the formation of some additional nitrite which also aids in accelerating the coating action.

The principle of the invention may be employed in connection with any phosphate solution whose coating action is accelerated by nitrite and is not restricted to instances where ferrous surfaces are coated, since various non-ferrous metals, such as zinc, cadmium, magnesium, copper, and aluminum may also be phosphate coated with the aid of nitrite. The invention is also applicable to other metallic phosphate solutions; for example, dihydrogen phosphates of manganese, cadmium, and calcium may also be accelerated by a nitrite.

What I claim is:

1. In the process of coating metal surfaces by an acidic phosphate coating solution accelerated by a nitrite, the step of including in the solution an acid which does not add to the PO_4 in the solution, and including said acid in an amount sufficient to counteract neutralization by the nitrite.

2. In the process of coating metal surfaces by an acidic phosphate coating solution accelerated by a nitrite which, by decomposition in the acid phosphate solution, results in neutralizing action, the step of including in the solution an acid with which the nitrite will react with the liberation of nitrous acid and which does not add PO_4 to the solution, and including said acid in an amount sufficient to counteract neutralization by the nitrite.

3. In the process of coating a metallic surface by means of an acidic phosphate coating solution accelerated by a nitrite, the step of including in the solution nitric acid in an amount sufficient to counteract neutralization by the nitrite.

4. In the process of coating a metallic surface by means of an acidic phosphate coating solution, the combination of steps comprising introducing sodium nitrite into the solution in an accelerating amount, and introducing into the solution nitric acid in an amount sufficient to form sodium nitrate with all of the sodium introduced in the sodium nitrite.

5. In the process of coating a metallic surface with an acidic phosphate coating solution, the combination of steps which comprises accelerating the action of the solution by the addition of sodium nitrite and replenishing the solution with chemicals including nitric acid in an amount at least sufficient to form sodium nitrate with the sodium in the sodium nitrite.

6. In the process of coating a metallic surface by an acidic phosphate coating solution, the steps of accelerating the coating action of the solution by adding sodium nitrite and introducing in the solution at least sufficient nitric acid to form sodium nitrate with the sodium in the added sodium nitrite.

7. In the process of coating a metallic surface by an acidic zinc phosphate coating solution, the steps of accelerating the coating action of the solution by adding sodium nitrite and introducing in the solution at least sufficient nitric acid to form sodium nitrate with the sodium in the added sodium nitrite.

ROBERT C. GIBSON.