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COATED ARTICLE AND METHOD OF
MAKING THE SAMEJohn S. Thompson, Detroit, Mich., assignor to
Parker Rust Proof Company, Detroit, Mich.No Drawing. Application March 9, 1939,
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4 Claims. (Cl. 148—6)

This invention relates to an article having a surface of iron, steel, zinc or other alloys and protected by a coating suitable for bonding paint or the like to the surface.

More particularly, the invention relates to such a coating composed essentially of an oxide of the metal which is coated and an oxide of another metal with or without the inclusion of the PO_4 radical and/or chromium compounds. The invention also relates to a method of making such a coating.

The invention claimed in the application is specific to the method wherein a nitrate is employed in producing the coating and to the article resulting from that method. Broader claims and alternative specific claims are made in my co-pending application for Coated metal article and method of making the same, filed April 25, 1941, Serial No. 390,337, which eventuated May 11, 1943, in Patent Number 2,318,642.

The following examples will serve to illustrate the invention, although as will be explained below, the specific examples do not exhaust the possible variations which may be employed within the scope of the invention.

Example 1

Steel panels sprayed with a zinc nitrate solution ranging from 10 to 30 points, (this means that a 2 cc. sample titrated against N/50 NaOH using phenolphthalein indicator requires from 10 to 30 cc. of the alkali) the spraying being applied for about two minutes at 160° F., have produced thereon a satisfactory bonding coat. It will be seen that the solution is definitely acid, but this acidity may result from the hydrolyzation of the zinc nitrate.

Example 2

A bonding coat may be produced upon iron or steel by immersing it for about five minutes in an aqueous solution containing $2\frac{1}{2}$ to 10 grams of manganese nitrate to 100 cc. volume of the aqueous solution. Manganese nitrate does not hydrolyze to as great an extent as zinc nitrate, and the action can be speeded up by additional acidulation. This may be obtained by any compatible acid, but as one example there may be employed sufficient nitric acid to bring the points, as explained in connection with Example 1, to from 10 to 30.

Example 3

Iron or steel articles immersed for five minutes in a solution at approximately boiling temperature containing 1, $2\frac{1}{2}$, 5 and 10 grams, respec-

tively, of chromium nitrate to 100 cc. of water in each case obtain good protective and bonding coats.

Example 4

Likewise, steel and iron articles may be coated satisfactorily by five minute immersion in a substantially boiling aqueous solution of aluminum nitrate, a satisfactory strength being from $2\frac{1}{2}$ to 5%.

Example 5

Articles having zinc or zinc alloy surfaces may be coated satisfactorily by five minute immersion in an approximately boiling solution of a $2\frac{1}{2}$ to 5% solution of aluminum nitrate or a similar solution of zinc nitrate, manganese nitrate or chromium nitrate.

When the solution is applied to the metal to be coated, some of that metal enters the solution as nitrate. When coating zinc, nitrate of iron may be employed.

It is desirable that the solution shall be sufficiently acid to attack the metal. This may be accomplished by the hydrolyzation of the salt where that results inconsiderable acid, but generally speaking, the addition of a small amount of acid accelerates the action and this is particularly true with salts which do not hydrolyze to produce as much acid as is the case with zinc nitrate, for example. Other nitrates may be employed in suitable proportions and with suitable acidulation. The nitrates of magnesium, calcium, strontium, barium, cadmium, cobalt and nickel have been employed with success. None of these hydrolyze sufficiently to obtain the best results and, therefore, added acidulation is preferable in each case.

While it has been suggested that the added acidulation may be obtained by nitric acid, it also may be obtained by other acids, if preferred.

If desired, phosphoric acid may be employed with the nitrates mentioned and may be used, if desired, in considerable strength. A good coating may be produced in the cold on iron or steel by spreading thereon a 10% solution of 75% phosphoric acid containing $2\frac{1}{2}$ to 5% of manganese nitrate or zinc nitrate. Similar results can be obtained by a similar phosphoric acid solution with 1 to 2% of potassium permanganate therein. Likewise, a good gray coating can be obtained by applying to steel a 10% solution of phosphoric acid having added thereto 5% of potassium dichromate. It will be readily understood that the manner of applying the solution to the surface to be coated may be modified

in accordance with convenience, with appropriate modification of the strength of the solution. Likewise, the duration of treatment and the temperature at which the treatment takes place are related variables which also affect the concentration and the acidity of solution which is necessary. The hydrolyzation and consequent acidity of a zinc nitrate solution increase with temperature, for example, so that added nitric acid is more desirable when the solution is employed cold than when it is employed at a higher temperature.

In all the above indicated operations, the coating produced upon the surface of the metal is largely oxide. This comprises oxide of the metal which is being coated and of the metal included in the salt employed. Where phosphoric acid is used, either in the amount specified or in lesser amounts, there are compounds of the PO_4 radical in the resultant coating even though the coating still is largely oxides. Where potassium permanganate or chromate is employed, there will be resultant manganese and chromium compounds, respectively, in the coating. In each case, there is a thin, continuous, adhesive coating produced which is protective against immediate weathering and also acts as a bond for a siccative coat, insuring much better adherence of such siccative coat than would result from its application upon the bare metal.

In the reaction of the solutions mentioned with the metal, the NO_3 radical acts as the oxidizing agent in each case where a nitrate and/or nitric acid is employed. Similar results may be obtained by employing nitric acid or other compatible oxidizing agents with other soluble salts of the metals which are enumerated above as being employed as nitrates. In the examples where potassium permanganate and potassium chromate are employed, these compounds act at once as oxidizing agents and as carriers of the desired manganese and chromium.

While several specific formulas have been given and certain possible variations indicated, it will be understood that no attempt has been made

to indicate as specifically all the variations permissible within the general principles stated in the foregoing description.

What I claim is:

5 1. An article of metal of the class consisting of iron, steel, zinc and their alloys having formed thereon a thin, continuous, adherent, protective and bonding coating composed essentially of an oxide of the metal and an oxide of a metal from magnesium to nickel, inclusive, in the electro-
10 motive series, said coating being formed by reaction of the metal of the article with an acidulous, aqueous solution containing, as its chief coating chemicals, the NO_3 radical and said metal from magnesium to nickel, inclusive, in the electro-
15 motive series.

2. A method of coating a surface of metal of the class consisting of iron, steel, zinc and their alloys which consists in applying to the surface
20 to be coated an acidulous, aqueous solution containing the NO_3 radical and a metal from magnesium to nickel, inclusive, in the electromotive series as its chief chemicals and continuing the application of the solution to the surface until
25 a visible, continuous, bonding coating is formed thereon composed essentially of oxides of the metal being coated and said metal from magnesium to nickel, inclusive, in the electromotive series.

3. A method of coating a surface of iron, or steel, which consists in applying to said surface
30 an acidulous aqueous solution having the composition resulting from dissolving zinc nitrate in water and treating a ferrous surface therewith, and continuing the application of the solution until a visible continuous bonding coating is
35 formed on said surface consisting essentially of oxides of iron and zinc.

4. An article of iron or steel having formed thereon a thin, continuous adherent protective and bonding coating composed essentially of
40 oxide of iron and oxide of zinc, said coating being formed by reaction of the metal of the article with an acidulous aqueous solution of zinc nitrate.

JOHN S. THOMPSON.