Patented Dec. 10, 1946

2,412,543

UNITED STATES PATENT OFFICE

2,412,543

COATED ZINC ARTICLE AND METHOD OF MAKING SAME

Robert R. Tanner, Detroit, Mich., assignor to Parker Rust Proof Company, Detroit, Mich.

No Drawing. Application July 3, 1941, Serial No. 401,055

14 Claims. (Cl. 204—35)

1

This invention relates to an article having a zinc surface covered with a paint-holding coating formed by drying thereon a solution of chromic and phosphoric acids and/or their salts, and to a method of making the same, and is a continuation in part of my application for "Corrosion resistant ferrous sheet and process," Serial No. 252,389, filed January 23, 1939.

While the invention will probably find its widest use as applied to galvanized iron and ferrous sheets electroplated with zinc, its broader aspects include its application to any article having a zinc surface to which paint, varnish, lacquer or a like siccative coat is to be applied.

It has been known previously that a solution of chromic and phosphoric acids and/or their salts, when properly proportioned and applied and dried upon a ferrous surface, serves to increase corrosion resistance and increase the effective life of a subsequently applied coat of paint, varnish, lacquer or the like; but methods of proportioning, applying and drying which work well on ferrous sheets are not best adapted for use with zinc surfaces.

One species of this invention which is adapted for wide use is to apply to a sheet of iron or steel a thin electrolytic coating of zinc and thereafter apply to the zinc coated sheet a solution which may be designated solution No. 1, and which comprises approximately 6% H_3PO_4 and 3% CrO_3. A film of this solution is preferably baked upon the metal surface, and for this purpose may be subjected to a temperature of about 600° F. for one minute, which will render it dry and relatively insoluble.

A lesser baking temperature may be preferable, as the proper amount of baking can then be more readily controlled. Apparently the hexavalent chromium is reduced during the baking operation, and the baking may be continued until a large part, but preferably not all, of the hexavalent chromium has been reduced. It should not be continued at all after the reduction is complete.

The method is especially suitable for use with paints or lacquers which are baked on, and where some hexavalent chromium remains at the time the lacquer is applied, reduction continues during the baking of the lacquer.

As indicated above, salts of chromic or phosphoric acid may be used to replace part or all of the acids. Typical examples of such solutions follow.

2

	Per cent
Solution No. 2:	
$ZnCr_2O_7$	6
H_3PO_4	3
Solution No. 3:	
$ZnCr_2O_7$	6
$Zn(H_2PO_4)_2.2H_2O$	6
Solution No. 4:	
$ZnCr_2O_7$	3
H_3PO_4	1.5
Solution No. 5:	
$ZnCr_2O_7$	1.5
H_3PO_4	.5

These solutions applied by dipping and then passed between knurled rollers to remove any excess and render the remaining film uniform, and then baked from one to three minutes at 325° F. gave good satisfaction. The baking time and temperature may be varied quite widely, but at lower temperatures longer baking times are required than at higher temperatures. The baking should be continued until the coating is substantially insoluble in pure water, but should not be continued until all of the hexavalent chromium is reduced.

In each of the examples given, the solution is acidic. For best results, this condition is desired. The metal in the salts mentioned is zinc, but other metals may be employed. It is preferable to avoid alkali metals in the final coating, and therefore it is preferable to use salts of metals other than alkali metals. Salts of ammonium may be employed, if desired, if ammonium is driven off during the baking operation sufficiently so that the baked coating is substantially insoluble in water.

It will be noted that the concentration of the solutions given varies, but this does not indicate the limit of variation. In general, the thicker coating resulting from a more concentrated solution is more corrosion resistant, but is more brittle and is more easily injured by bending or working the metal. The thinner coating resulting from a weaker solution will better withstand bending, but does not furnish as much resistance to corrosion. Therefore, the concentration of the solution depends somewhat upon the conditions

which are to be encountered. However, it is generally preferable to produce a coating not thicker than will result from a solution containing not more than 10% chemicals in a film not greater than results from dipping the surface in the solution and allowing to drain.

With the thin coating of a weak solution the baking effect is achieved more quickly than with the thicker coating of a stronger solution. Likewise, a greater degree of acidity requires more baking than a less acid solution. The solution reacts with the zinc surface during the baking to reduce its acidity, and it is preferable that the coating shall be still slightly acid at the conclusion of the baking.

Where the solution is employed to coat a thin layer of zinc, such as may be electrolytically deposited on iron, it is preferable to employ a quantity and kind of material in the solution which will not react with all of the zinc, but will leave a layer of zinc on the iron beneath the baked coating.

The proportion of PO_4 to hexavalent chromium in the solution may be varied, as indicated by solutions Nos. 1 and 2, for example, but these examples do not indicate the permissible limits of the proportions. The reactions taking place during the baking which may be employed as tests of proper baking are the reduction of hexavalent chromium and the reduction in acidity. Where there is a large proportion of hexavalent chromium, the test may be employed that some hexavalent chromium should be left. Where PO_4 largely predominates, the criterion of some remaining acidity may be employed. In all cases, the baking should render the coating substantially insoluble in pure water, but should not be continued until all possible chemical reaction is completed. In other words, some unreacted chemical should remain in the baked coating.

Ingredients other than those named above may be included in the solution so long as the other ingredients do not interfere with the essential coating action of the solution; and in the appended claims, where the solution is stated to consist essentially of certain ingredients, it is to be understood that the ingredients named give the essential characteristics to the coating and to the reactions taking place during its production, but that the presence of other ingredients not materially affecting these essential results is within the scope of the invention.

What I claim is:

1. An article of manufacture having a zinc surface with a thin, adherent, continuous coating containing chromium and PO_4 and formed by drying on said surface an acidic solution consisting essentially of water, a compound containing hexavalent chromium, and a compound containing PO_4, the coating being substantially insoluble in water and containing some unreacted chemical.

2. An article in accordance with claim 1 and in which the material in the coating is not greater than results from a solution, containing not over 10% of material other than water, dried on the surface in a layer not greater than that which will cling to the surface and not drain therefrom.

3. An article in accordance with claim 1 and in which the zinc surface is of a layer of zinc applied to a ferrous sheet.

4. An article in accordance with claim 1 and in which the zinc surface is that of a galvanized sheet.

5. An article in accordance with claim 1 and in which the zinc surface is that of a coating of zinc electroplated upon a ferrous sheet.

6. An article in accordance with claim 1 and in which the dried coating contains hexavalent chromium.

7. An article in accordance with claim 1, and in which the coating is acidic.

8. The process of coating a zinc surface which comprises applying to said surface an acidic solution consisting essentially of water, a compound containing hexavalent chromium, and a compound containing PO_4, drying a film of the solution on the surface, continuing the drying action until the dried coating is substantially insoluble in water, and stopping the drying action before the reaction of the ingredients caused by the drying step is entirely complete.

9. A process in accordance with claim 8, and in which the solution contains not over 10% of the combined compounds named.

10. A process which comprises applying to a ferrous sheet a layer of zinc and then applying to said surface an acidic solution consisting essentially of water, a compound containing hexavalent chromium, and a compound containing PO_4, drying a film of the solution on the surface, continuing the drying action until the dried coating is substantially insoluble in water, and stopping the drying action before the reaction of the ingredients caused by the drying step is entirely complete.

11. A process which comprises electroplating a thin layer of zinc on a ferrous sheet, then applying to said surface an acidic solution consisting essentially of water, a compound containing hexavalent chromium, and a compound containing PO_4, drying a film of the solution on the surface, continuing the drying action until the dried coating is substantially insoluble in water, and stopping the drying action before the reaction of the ingredients caused by the drying step is entirely complete, and regulating the amount of acid in the film in proportion to the thickness of the layer of zinc so that a layer of metallic zinc remains between the iron and the dried coating at the conclusion of the drying.

12. A process in accordance with claim 8 and in which the drying step is effected at not over about 325° F.

13. A process in accordance with claim 8, and in which the drying is stopped while there is still hexavalent chromium in the dried coating.

14. A process in accordance with claim 8, and in which the drying is stopped while the coating is still acidic.

ROBERT R. TANNER.