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METAL COATING METHOD AND ARTICLE PRODUCED THEREBY

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This invention pertains to increasing the adhesion of paint to metal surfaces. It also pertains to steel articles, and more especially steel sheets carrying a coating containing at least two other metals and a phosphate.

Zinc coated steel sheets such as galvanized and galvanneal have been known for many years to possess corrosion resistance superior to that of steel itself. These coated sheets have been highly successful when fabricated into objects where only a small amount of forming or drawing is required. However, the effectiveness of the product, especially in the case of galvanized sheets, is impaired by severe forming or drawing because the zinc coating is brittle and scales away from the base metal leaving unprotected areas.

This invention concerns a new steel article or sheet which possesses corrosion resistance, drawing and paint-holding properties, believed to be superior to those of galvanized sheets. The new article, in brief, is produced by coating the steel first with a thin layer of nickel, then with a layer of zinc over the nickel, and thereafter treating the article to obtain a phosphate coating on the surface.

The coatings of nickel and zinc may be obtained by electrolytic methods for the best results. Prior to the application of the phosphate coating, the steel sheet which is coated with the nickel and zinc may be heated, and this seems to be desirable for best results. Heating for a relatively long period at a temperature slightly below the melting point of zinc, or for a relatively short period at a temperature slightly above the melting point of zinc, has been found to be satisfactory. A temperature of 675° F. applied for a period of 5½ hours is sufficient. After the sheets have cooled, a thin film of oxide is usually discernible on the surface.

Some coatings obtained after heating when examined under the microscope show a layer of nickel next to the steel, a layer of nickel-zinc alloy, and then a layer of zinc beneath the thin oxide layer. Chemical analysis discloses the presence of nickel at the surface even when the microscopic appearance is as described in the last sentence. After treatment with the phosphate coating solution the article will, of course, be covered with a phosphate coating.

The article obtained without the phosphate coating possesses satisfactory corrosion-resistance. It also has some drawing properties. However, adhesion of paint to the article is poorer. A handicap of this nature obviously places a limitation on the use of this kind of sheet because the great majority of articles which in their fabrication require the properties inherent in the described sheet, are usually painted.

I have found that if the surface of the article after the treatment previously described, is treated with an acid phosphate solution for even a very short length of time, the paint adhesion is decidedly increased, as shown by a comparison between treated and untreated metal which was painted and subjected to salt spray. The steel article, after having been coated with nickel and zinc, then heated and cooled, may be immersed in a solution made up as follows:

Solution #1	Parts	Solution #2	Parts
Zinc metal	.75	Anhydrous zinc nitrate	25
Iron	5.5	Zinc dihydrogen phosphate	16
Phosphoric acid (75%)	33.3	42° Bé. nitric acid	4
Water to make	100	Water to make	100

To 100 gallons of water 25 pounds of solution #1 and 35 pounds of solution #2 are added. Solution is heated to 170° F. and the articles are immersed for five seconds or longer. A phosphate coating is obtained on the surface of the articles. The articles are then rinsed with water and then given a final rinse in a solution of chromic acid of the concentration of two grams per gallon of water for ten seconds at 175° F. The articles thus obtained possess good corrosion resistance and provide improved paint adhesion.

In one test, the articles were painted with a synthetic enamel, scratched diagonally across the face to expose bare metal thru the paint and subjected to salt spray test. At the end of 160 hours the metal showed no creepage of the paint from the scratch. At the end of 763 hours the paint on the treated metal was still in excellent condition.

While the phosphate coating step was exemplified above by use of a solution containing zinc dihydrogen phosphate and ferrous phosphate, it is understood that this is by way of example only and other phosphate coating solutions may be employed. For example, solutions of ferrous phosphate alone have been found to give very satisfactory results and this is true also of zinc and manganese dihydrogen phosphates. Where use is not made of an oxidizing agent such as nitrate, the processing time for producing the same amount of coating will be longer than that given in the example. Where use is made of phosphates other than ferrous phosphate, accel-

erating salts of metals below iron in the electromotive series may be used, such as nickel and cobalt. Other suitable oxidizing agents besides nitrate may be used providing they are compatible with the solution. Likewise the coating solution may be applied hot or cold and by brushing or spraying as well as immersing.

If the nickel and zinc coated sheet is heated sufficiently so that some nickel is alloyed with the zinc coat, or if the nickel is otherwise contacted by the phosphate solution, the nickel of the article tends to accelerate the coating action of the phosphate solution.

The chromic acid rinse treatment acts to reduce to a minimum any blistering which may be caused by soluble salts left in the coating by improper water rinsing or by hard water salts present in the water rinse itself which follows the phosphate treatment. If after the coating operation a thorough rinse with clean water is used, the chromic acid treatment may be dispensed with and excellent paint adhesion will still be obtained but for practical commercial operation the chromic acid treatment is recommended.

Steel sheets carrying the coatings obtained in accordance with this invention may be manufactured into fabricated articles by steps such as drawing, welding, stamping, forming, etc. In this case the phosphate coating should be extremely thin and for best results there should not be over .03 ounce per square foot of surface. Of course the coatings may be obtained upon articles that already have been fabricated if desired.

What I claim is:

1. An article of manufacture comprising a sheet having a ferrous base and carrying a coating containing metallic zinc, metallic nickel, nickel-zinc alloy and a phosphate coating chemically formed on the metal.

2. An article of manufacture comprising a sheet having a ferrous base, said sheet carrying a coating of several layers, said layers appearing under the microscope to comprise, from the inner side outward in the order named, a layer of metallic nickel, a layer of nickel-zinc alloy, a layer of metallic zinc, and a layer comprising zinc phosphate chemically formed on the metal.

3. A process which comprises applying electrodeposited metallic nickel to a sheet of steel, electro-depositing metallic zinc onto the nickel coating, heating sufficiently to produce some alloying of the nickel and zinc, and thereafter chemically forming a phosphate coating on the zinc.

4. A process which comprises plating nickel on a ferrous surface, plating zinc on the nickel, subjecting the plated surface to heat until the exposed surface contains some nickel, and thereafter treating said exposed surface with a phosphate coating solution until a substantially integral phosphate coating is produced.

5. A process which comprises applying electro-deposited metallic nickel to a sheet of steel, electro-depositing metallic zinc on to the nickel coating, heating sufficiently to produce some alloying of the nickel and zinc, and thereafter chemically forming a phosphate coating on the metal, then treating the phosphate coating with a solution of chromic acid.

6. A process which comprises applying electro-deposited metallic nickel to a sheet of steel, electro-depositing metallic zinc onto the nickel coating, heating sufficiently to result in the presence of nickel in the exposed surface, treating the exposed surface with a coating phosphate solution until a substantially integral phosphate coating is formed thereon, and then treating the phosphate coating with a solution of chromic acid.

7. A process which comprises producing on a ferrous article a coating comprising an alloy of nickel and zinc, and thereafter applying a phosphate coating solution to said alloy coating.

8. A process which comprises producing on a ferrous article a coating consisting essentially of metallic nickel and zinc with both zinc and nickel present in the exposed surface, and thereafter treating the exposed surface with a phosphate coating solution until a substantially integral coating is formed thereon.

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