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METHOD OF TREATING CHROMIUM SURFACES

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13 Claims. (Cl. 117—71)

This invention relates to the treatment of metal articles to prevent or retard corrosion, and more particularly to the treatment of articles formed of ferrous metals and having nickel and chrome plate coatings thereover. This application is a division of our earlier file copending application entitled Metal Treatment and Article, Serial #251,462, filed October 15, 1951, now Patent No. 2,746,915.

Difficulty has been experienced in the past with articles of this type due to the formation of numerous rust or corrosion spots on the surface thereof after a short period of time. Although the reasons for this corrosion are not too well established, there are, particularly in the case of nickel plating, two schools of thought at the present time, one assuming that there are pores present in the plating itself which expose the base metal and thus permit corrosion thereof, and the other holding that the plating is initially substantially continuous but subject to a pit type of corrosion which rapidly penetrates the coating, with resultant corrosion of the base metal. Previous attempts to eliminate corrosion of such plated articles have been directed toward elimination of the initial pores in the plating, while one of the primary objects of the present invention is the provision of a coating which will minimize either the pit type of corrosion or corrosion due to initial pits in the plating.

Another object of the invention is the provision of a substantially invisible corrosion inhibiting coating on the plated surface of a metal article.

Still another object is to provide a corrosion inhibiting coating on the plated surface of the article which is anodic to the plating.

A still further object is to provide a corrosion inhibiting coating on the plated surface of the article which is anodic to the base metal portion of the article.

Yet another object is the provision of a process for economically and efficiently forming a corrosion inhibiting coating on a plated metal article.

Still another object is the provison of an abrasion resistant corrosion inhibiting coating on an article of the above type.

These and other novel objects and features of the invention will be apparent to those skilled in the art in the light of the following description, but it is to be understood the description is not to be considered as defining the limits of the invention, reference being had for this purpose to the appended claims.

Although the invention is more particularly directed toward the inhibiting of rust and corrosion on steel articles having a layer of nickel plate thereon and a layer of chromium plate over the nickel, it is also applicable to steel articles having chromium plated directly thereon, and is in fact applicable to numerous metal base articles plated with chromium or nickel and chromium, or plated with chromium or nickel and chromium over platings of other metals. In the preferred form the coating is invisible in the sense that it does not appreciably alter the appearance of the outer plate, and the methods

used to obtain the corrosion inhibiting coating may be so controlled as to attain this result.

While opinions vary as to the nature of the action which results in the formation of corrosion, and particularly of rust spots on steel articles plated with nickel followed by a plate of chromium, it is generally agreed that in chromium plate, there are a large number of cracks or pores. These cracks or pores apparently expose the nickel underneath, and it has been determined by tests that in untreated articles, corrosion of the nickel occurs at these cracks and eventually extends underneath the chromium plate. This corrosion forms holes in the nickel plate, the steel is attacked, and rust spots appear on the article. Thus it is apparent that as long as the plating is protected against the formation of corroded holes by the coating, the base metal regardless of its nature, is also protected.

It has been found that untreated nickel and nickel chromium plated steel articles are normally cathodic to steel when immersed in a sodium chloride solution, and it was reasoned that a coating on the article which rendered the latter anodic to steel, might, under the influence of corrosive agents, reduce corrosion forming galvanic action, or be eaten away in preference to the other metals present, thus protecting the articles against corrosion. It was found that through the means to be described, substantially invisible and apparently anodic chromium compound coatings having the above characteristics could be formed on articles of the above type, and that these coatings were apparently anodic to steel and very effective in preventing corrosion of the articles, due to sacrificial or other inhibiting action. While the exact nature of the coating is not definitely known, it is reasoned that it is probably chromium chromate, or that it includes chromium chromate, and is not a conversion coating, but rather one that is formed entirely from the ingredients of a treating bath.

In general, the invention contemplates treatment of articles of the above type in hexavalent chromium containing solutions, and preferably solutions having a pH below 7. More specifically, chromic acid baths, and dichromate solutions such as sodium dichromate, potassium dichromate, nickel dichromate, ammonium dichromate, copper dichromate, zinc dichromate, and calcium dichromate were found to provide satisfactory coatings, although some of these materials are more satisfactory than others from an economic standpoint.

It has been found that corrosion inhibiting coatings of the above type can be applied to chromium and to nickel and chromium plated articles by immersion in baths of various hexavalent chromium containing solutions such as those containing various dichromates. Here as will be noted from the examples to be given, factors such as solution concentration, pH, bath temperature, and time, are all controlled in such a manner as to give the desired result. The immersion process can also be so controlled as to produce corrosion inhibiting chromium compound coatings which are substantially invisible and which do not appreciably change the normal appearance of the plating. No complicated or expensive apparatus is required for the practice of this process, and it is therefore particularly adapted to the treatment of articles in small lots.

As indicated heretofore, the composition of the coating is not definitely known, but it has been found, for example, that the effectiveness of the coating is unaffected by dipping for 1 minute, after treatment in a 10 gm. per liter solution of chromic acid, while dipping for 1 minute in a concentrated chromic acid solution destroys the effectiveness of the coating, and presumably destroys the coating itself. Also the coating is subject to removal or partial removal when subjected to vigorous scrubbing with fine

abrasive cleaners such as light magnesium oxide, but as will be shown by tests to be described hereinafter, treated articles cleaned with light magnesium oxide were found to be far more resistant to corrosion than similarly cleaned untreated articles. It is also noted that ferrous base articles plated with nickel and thereafter with chromium and subsequently treated as above are anodic to steel, and that the articles maintain this anodic characteristic over long periods of time. Test pieces aged for six months after treatment were still anodic. On the other hand, articles which have been subjected to salt spray tests gradually lose this characteristic. Tests have indicated that articles treated by the immersion process have coatings which appear to be highly resistant to abrasion.

Numerous exposure tests were made on test pieces treated. In the tests to be described by way of example, all of the test pieces were of steel, and were plated first with bright nickel and then with bright chromium. Nickel plate thicknesses of about .0003 and about .0008 inch were included in the tests. The chromium plating conditions were the same for all the tests given, and the thickness of the chromium was on the order of .00001 inch.

Test pieces having .0003 nickel plate with chromium plate thereon are given the immersion treatment. All the treated pieces were immersed in a 5 gm. per liter sodium dichromate solution at 200° F. for 2 hours. Untreated pieces having .0003 nickel plate and chromium plate thereover showed over 100 rust spots after 24 hours in the salt spray. The treated pieces showed 6 spots at the end of 120 hours. Like untreated pieces having an .0008 nickel plate showed 60 spots at the end of 48 hours in the salt spray while like pieces treated as above showed no spots after 48 hours and 3 spots after 120 hours. All of these test pieces were also cleaned with magnesium oxide prior to the salt spray test.

Test pieces of steel having .0003 nickel plate and chromium plate thereover were treated by immersion in a 5 gm. per liter solution of sodium dichromate at 200° F. for 2 hours, and tested in comparison with like untreated pieces by exposing them to the weather on the roof of a building for 6 months. At the end of 10 weeks the untreated pieces showed over 100 rust spots. No spots appeared on the treated pieces. At the end of 6 months the untreated pieces were in very bad condition, while an average of 1 rust spot was found on the treated pieces. In this test none of the pieces were cleaned with abrasive cleaner prior to exposure.

Tests were also made on similar test pieces of steel plated with copper and then with chromium, as well as with copper, nickel and chromium in the order named.

Tests were also conducted to determine the conditions of operation required for satisfactory treatment, these tests relating to time of treatment, solution concentration, pH of the bath, and solution temperature.

It was found desirable to use a treatment time of about 2 hours for good results in a 50 gm. per liter sodium dichromate solution at 190 to 212° F. having a pH of about 4.5. However, articles were successfully treated in solutions having pH values of from 2.5 to 7. The use of lower temperatures results in satisfactory coatings but the time required for treatment is materially increased. It was found, however, that the corrosion inhibiting films could be formed in solutions having a hexavalent chromium concentration of .1 to 150 gm. per liter, and temperatures as low as 70° F. could be used.

While the invention has been described with considerable particularity, it is to be understood that variations and modifications will suggest themselves to those skilled in the art, and reference is accordingly had to the appended claims for a definition of the limits of the invention.

What is claimed is:

1. The method of increasing the corrosion resistance of a steel article having a plating of chromium thereon which is normally cathodic to the steel of the article when immersed in a sodium chloride solution, which comprises forming a coating over the chromium plating which is anodic to the steel of the article by immersing the article in a solution containing hexavalent chromium until a coating of chromium compound is formed thereon.

2. The method as set forth in claim 1, wherein the hexavalent chromium concentration of the solution is of the order of .1 to 150 gm. per liter.

3. The method as set forth in claim 1, wherein the pH of the solution is maintained between 2.5 and 7.0.

4. The method set forth in claim 1, wherein the solution is maintained within a temperature range of approximately 70 to 212° F. and the article is immersed in the solution for at least 30 minutes.

5. The method of increasing the corrosion resistance of a steel article having a plating of chromium thereon which is normally cathodic to the steel of the article when immersed in a sodium chloride solution, which comprises forming a coating over the chromium plating which is anodic to the steel of the article by immersing the article in a solution containing hexavalent chromium until a coating of chromium compound is formed thereon, and rinsing the article to remove the hexavalent chromium containing solution therefrom.

6. The method as set forth in claim 5, wherein the hexavalent chromium concentration of the solution is of the order of .1 to 150 gm. per liter.

7. The method as set forth in claim 5, wherein the pH of the solution is maintained between 2.5 and 7.0.

8. The method set forth in claim 5, wherein the solution is maintained within a temperature range of approximately 70 to 212° F. and the article is immersed in the solution for at least 30 minutes.

9. The method of increasing the corrosion resistance of a steel article having a layer of nickel plate thereon and a layer of chromium plate on the nickel layer, the layer of chromium being normally cathodic to the steel of the article when immersed in a sodium chloride solution, which comprises forming a coating over the chromium plating which is anodic to the steel of the article by immersing the article in a bath containing hexavalent chromium in solution until the coating is formed thereon and thereafter removing the article from the bath and rinsing the article to remove the hexavalent chromium containing solution therefrom.

10. The method of increasing the corrosion resistance of a steel article having a layer of nickel plate thereon and a layer of chromium plate on the nickel layer, the layer of chromium being normally cathodic to the steel of the article when immersed in a sodium chloride solution, which comprises immersing the article in a hexavalent chromium solution until a coating of chromium compound is formed thereon, and thereafter removing and rinsing the article to remove the hexavalent chromium solution therefrom, the article being removed from the bath prior to the formation of an appreciable visible film of said compound thereon.

11. The method of forming a corrosion inhibiting coating on an article having a base member of ferrous metal and a layer of chromium plate thereover, which comprises immersing the article in a solution containing hexavalent chromium until a coating of chromium compound is formed thereon, and thereafter removing the article from the bath and rinsing the article to remove the hexavalent chromium solution therefrom.

12. The method of forming a corrosion inhibiting coating on an article having a base member of ferrous metal, a layer of nickel plate on the base member and a layer of chromium plate on the nickel layer, which comprises immersing the article in a bath containing hexavalent chromium in solution until a coating is formed thereon which is anodic to the chromium layer, the nickel layer, and the base metal, and thereafter removing the

article from the bath and rinsing the article to remove the hexavalent chromium containing solution therefrom.

13. The method of forming a corrosion inhibiting coating on an article having a base member of ferrous metal, a layer of nickel plate on the base metal, and a layer of chromium plate on the nickel plate layer, which comprises immersing the article in a hexavalent chromium

solution until a coating of a chromium compound is formed thereon, and thereafter removing and rinsing the article to remove the hexavalent chromium solution therefrom, the article being removed from the bath prior to the formation of an appreciably visible film of said compound thereon.

No references cited.