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 thereon.

Difficulties have been experienced in the past with articles of this type due to the formation of rust 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.

Another object is to provide a process for electroforming a substantially invisible protective coating on a plated metal article.

Yet another object is the provision of a process for economically and efficiently forming a corrosion inhibiting coating on articles of the above type.

A further object is the provision of an electroplated ferrous metal article, having an invisible corrosion inhibiting coating thereon.

Still another object is the provision 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 from the following description, but it is 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 if it includes chromic acid 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 aqueous 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.

In the preferred form of the invention, the article to be treated is placed in the bath chosen, and the bath is then electrolyzed with the article as the cathode. The concentration of the bath, the current density, the pH of the bath, the bath temperature, and the time of immersion are controlled as will be described in order to obtain the desired results, as will be set forth more fully hereinafter. The time period required for this type of treatment is normally of the order of two minutes, and this cathodic treatment is therefore well adapted to production requirements. The details of the cathodic process using hexavalent chromium-containing solutions such as dichromate and chromic acid solutions will be more fully described hereinafter. It has also been found that corrosion inhibiting coatings of the above type can be applied to chromium and nickel and chromium plated articles, for example, by immersion in baths of various hexavalent chromium-containing solutions such as those containing various dichromates, without the application of electric current to the article as a cathode, this modification of the process requiring a longer treatment period than is necessary.
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when current is applied to the article. Here again, 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. The coating formed results in an article having the above characteristics regardless of whether the article is treated by simple immersion or by immersion in an electrolyzed bath of the above type as a cathode, although tests have indicated that articles treated by the immersion process have coatings which appear to be more resistant to abrasion.

Numerous exposure tests were made on test pieces treated both by the cathode treatment and by immersion only. 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 of the tests given, and the thickness of the chromium was on the order of .0001 inch.

Test pieces having .0003 nickel plate with chromium plate thereover were treated as cathodes in an electrolyzed bath of sodium dichromate solution having a concentration of 30 gm. per liter for 2 minutes at 200° F. at a current density of 3 to 4 amperes per square foot, using steel anodes. The above treat test pieces, and an equal number of like untreated pieces, were cleaned with magnesium oxide and then placed in a salt spray cabinet. The number of rust spots visible was counted at intervals during the salt spray tests. The untreated pieces having .0003 nickel plate thereon showed 30 rust spots after 6 hours and over one hundred at the end of 24 hours. The treated articles showed no spots after 24 hours and 16 after 72 hours. Articles having .0008 nickel plate and the same chromium plate gave results of 60 spots after 48 hours for untreated articles and 3 spots after 120 hours for treated articles.

Tests of pieces like the above were also made using the immersion treatment only. All the treated pieces were immersed in a 3 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. Untreated pieces and cathodically treated pieces were placed in a salt spray cabinet for 120 hours, and the treated pieces in both instances showed corrosion resistance much better than that of the untreated pieces. The treated pieces in the above tests were subjected to a current having a density of 3 and 4 amperes per square foot in a 200° F. solution having a hexavalent chromium concentration of 50 gm. per liter and a pH of about 4.5. The treatment time was 2 minutes, and all of the pieces were cleaned with light magnesium oxide before being placed in the salt spray.

Tests were also conducted with both the cathodic and immersion methods of treatment to determine the conditions of operation required for satisfactory treatment, these tests relating to time of treatment, solution concentration, pH of the bath, solution temperature, and current density.

In the cathodic treatment, it was found that a 2 minute treatment gave satisfactory results, although shorter and longer time periods were successfully used. A 1 minute time period was successfully used, but results obtained when the time was materially increased over the 2 minute period did not give results that justified the increase in treatment time. With regard to solution concentration, baths containing from 1 gm. per liter to 200 gm. per liter of hexavalent chromium were successfully used. The pH values were not at all critical from the standpoint of successful treatment, best results being obtained with a bath having a pH below 7, however. In sodium dichromate baths, a sodium dichromate concentration of 50 gms. per liter was found to give a more stable and more easily maintained solution than lower concentrations.

Steel electrodes were found to be more satisfactory than lead, although lead could be used, and at low pH values, some difficulty was experienced with iron in the bath, this tending to cause discoloration. At pH values above 2.5, the iron apparently separated out in insoluble compound form, and no difficulty was experienced.

Treatment time varied with the solution temperature, and although much lower temperatures have been used, a solution temperature of about 200° F. has been found to give good results. This temperature is high enough to provide a short treatment period of around 2 minutes or less, and low enough to minimize excessive losses of solution due to evaporation. The most important variable appears to be current density, although this variable is of course affected by the other variables. A density of 3 amperes per square foot gives excellent results, but satisfactory treatment has been obtained at densities ranging from 1 ampere to 15 amperes per square foot. It has been found that excessively high current densities tend to produce discoloration of the work at high solution temperatures. At lower temperatures the higher current densities can be used.

In the immersion treatment, 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 treat-
ment 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 consid-
erable 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 ap-
pended 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 connecting
the article as a cathode in an aqueous electrolyte con-
sisting essentially of a hexavalent chromium-containing
compound, passing an electric current through said elec-
trolyte having a current density of about 3 to 4 amperes
per square foot of cathode for a time period of from
about 1 to 2 minutes, and maintaining the temperature
of the electrolyte about 200° F.

2. The method as set forth in claim 1, wherein the pH
of the electrolyte is maintained below 7.

3. The method as set forth in claim 1, wherein the
electrolyte consists essentially of a sodium dichromate
solution having a concentration of 50 grams per liter.

4. A corrosion resistant chromium plated steel article
made in accordance with the method set forth in claim 1.

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 com-
prises forming a coating over the chromium plating
which is anodic to the steel of the article by connecting
the article as a cathode in an aqueous electrolyte con-
sisting essentially of a hexavalent chromium-containing
compound, passing an electric current through said elec-
trolyte having a current density of from about .1 to 15
amperes per square foot of cathode, and maintaining the
temperature of the electrolyte not in excess of about
200° F.

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