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ELECTROPLATING METHOD

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The invention relates to the production of corrosion-resistant coatings in which the outer surface is composed of electrolytically deposited metallic chromium. Electrolytic deposits of chromium have come into quite general use of recent years particularly as a decorative and protective finish for automobile parts. Such coatings are usually produced with a brilliant surface either by plating the chromium with a "mat" surface and then buffing it or by maintaining such conditions of temperature, current density, etc., in the bath that the metal is deposited in a brilliant form.

Chromium coatings have proven quite resistant to corrosion by atmospheric agencies, although the resistance depends to a large degree upon the character of the base metal or the sub-coatings applied to the base metal under the chromium deposit. One of the most serious defects of the chromium coating, however, resides in its peculiar susceptibility to attack by solutions of calcium chloride. In the presence of such solutions, which, when exposed to the air, develop an acid condition, chromium is attacked or corroded so readily that the whole protective coating may be quickly destroyed. The common and constantly increasing use of calcium chloride as a road dressing in summer and to dissolve ice and snow in winter constitutes, therefore, a serious menace to the durability of chromium plated articles, such as the parts of automobiles, which are unavoidably subjected to contact with solutions of the salt in question.

In the study of this problem and in efforts to alleviate the situation we have tried numerous expedients and many variations in the character of coatings and treatments thereof, testing the results by subjecting coated articles to calcium chloride spray as well as to the usual sodium chlorite or "salt spray". As a result of these investigations we have found that the resistance of the chromium coating to attack by calcium chloride solutions may be greatly increased by subjecting the coated article to certain heat treatments hereinafter described in detail. The principal object of the invention, therefore, is to provide a method of producing metallic coatings, the outer surface of which is composed of electrodeposited chromium, which shall be highly resistant to attack by acid solutions of calcium chloride.

The invention is of especial utility in connection with coatings applied to ordinary steels, which coatings usually comprise copper, nickel and chromium in the order named. It is also appli-

cable, however, to other ferrous metals such special steels or irons of high chromium content, as, for example, those containing from 8 to 30% of chromium, and to other metals or alloys subject to corrosion by calcium chloride solution and over which chromium plating is employed as a decorative or protective finish, such, for example, as Monel metal and white brass, which are characterized by a high nickel content.

The special heat treatment comprises subjecting the coated article to an elevated temperature which we have found to range preferably from 250° to 500° F. The period during which the treatment should be continued varies inversely with the temperature employed and ranges from at least one hour at 250° F. to at least twenty minutes at 500° F. It will be understood that the figures given are approximate and merely define the limits of time and temperature within which optimum results have been secured. For example, some improvement may be noted by treatment at 250° for less than an hour but optimum results would not be obtained. The treatment may be applied preferably by merely exposing the surfaces to be treated to air heated to the desired temperature.

The heat treatment preferably should not greatly exceed 500° F. for the reason that the brilliance of the chromium surface may be deleteriously affected by such temperature. This is particularly true where the chromium has been applied over composite coatings of other metals as is the usual practice. The desirable temperatures are also below those at which alloying of the chromium deposit with the subjacent metal may take place.

In applying the treatment to coatings including other electrolytic metallic deposits beneath the chromium, some difficulty is encountered due to the tendency of the underlying layers to blister or become loosened from the base metal when subjected to the heat treatment. In such cases we have found it desirable to avoid the use of alkaline baths in the deposition of the underlying metal or metals. In the particular instance at present of most especial interest to the automobile industry, namely, the application of bright chromium over nickel over copper as a decorative and protective covering for steel, we apply all of the coatings from acid baths. Since the deposition of copper directly upon iron from an acid bath is not practicable we apply first to the iron or steel surface a coating of nickel.

A recommended procedure is as follows: The ferrous surface, after being suitably cleaned, is

coated with a thin deposit of nickel from an acid nickel sulphate bath. This is followed by a relatively heavy deposit of copper from an acid copper sulphate bath. After buffing the copper it is covered by a second nickel deposit from the acid sulphate bath, and, after further buffing or coloring to produce the desired base for the chromium coating, the latter is deposited preferably from a chromic acid bath. A relatively high bath temperature is desirable in applying all of the coatings. The temperature of the copper and nickel baths may advantageously be maintained above 125° F. and preferably in the neighborhood of 150° F. and the chromium bath temperature recommended is around 125° to 150° F. The coated article may then be subjected to the heat treatment without danger of deleteriously affecting either the appearance or adhesion of the composite coating.

In the case of chromium deposits applied directly to a base metal such, for example, as stainless steel or other high chromium or nickel alloys, we have obtained by the heat treatment above described, a resistance to corrosion by acid calcium chloride solutions which, so far as we are aware, had not been hitherto attainable. In applying the chromium to such metals, however, certain precautions are necessary in order to secure sufficient adhesion of the coating to enable it to undergo satisfactorily the heat treatment. If the surface has been cleaned with alkaline compounds all traces of alkali should be removed before plating the chromium deposit. The slight film of oxide which forms on chromium surfaces when exposed to the air should also be removed. Both results may be accomplished by dipping the article, after cleaning and immediately before plating, in a bath of dilute hydrochloric acid for a few minutes. Upon the surface thus treated, placed in the chromium plating bath before the surface becomes dry, the chromium may be deposited under the usual conditions for obtaining the desired decorative surface and may then be subjected to the heat treatment without danger of scaling, blistering or otherwise damaging the appearance of the coating.

Our experiments indicate that the heat treatment has practically no utility when applied to chromium plate deposited directly upon ordinary carbon steels since the chromium, whether treated or not, affords no adequate protection to such steels. We contemplate, therefore, the use of the process only in connection with chromium deposits upon corrosion-resistant sub-coatings, such as those of nickel and copper, or upon alloys, such as the high chromium or nickel alloys or their equivalents, which inherently afford a high degree of resistance to calcium chloride solutions.

We claim:

1. The process of forming upon the surfaces of metal articles a covering resistant to corrosion by acid solutions of calcium chloride comprising electro depositing upon such surface a corrosion resistant multiple metallic sub-coating from acid electrolytic baths only, depositing upon said sub-coating an electrolytic deposit of chromium from a chromic acid bath, and subjecting the coated article to heat at a temperature upwards of approximately 250° F. for a period of at least one

hour at 250° F. and shorter periods for higher temperatures but insufficient to effect alloying of the chromium with the subjacent metal.

2. The process of forming upon articles having ferrous metal surfaces a coating highly resistant to corrosion by acid solutions of calcium chloride comprising applying electrolytically to such surfaces successively nickel, copper, nickel and chromium, all from acid baths, then heating the article to a temperature upwards of approximately 250° F. for a period approximating at least one hour at 250° and correspondingly shorter periods at higher temperatures.

3. The process of forming upon articles having ferrous metal surfaces a coating highly resistant to corrosion in the presence of acid solutions of calcium chloride comprising applying to the surface successively nickel, copper, nickel and chromium, all from acid baths, the conditions being determined to produce a brilliant deposit of chromium, then heating the article at a temperature upwards of approximately 250° F. but below that at which the brilliance of the chromium deposit can be deleteriously affected, the period of heating approximating at least one hour at 250° F. and correspondingly less at higher temperatures.

4. The process of forming upon the surface of metal articles a coating highly resistant to corrosion in the presence of acid solutions of calcium chloride comprising applying to such surface an electrolytic deposit of nickel from an acid nickel bath followed by an electrolytic deposit of chromium from a chromic acid bath, each bath being operated at approximately 125° to 150° F. then heating the coated article by exposure to air at a temperature of approximately 250° to 500° F.

5. The process of preparing a composite metal article adapted to resist attack by acid solutions of calcium chloride comprising applying to an article, the surface portion of which contains sufficient non-corrosive metal such as nickel or chromium to provide a high degree of resistance to attack by such solutions, a brilliant decorative coating of metallic chromium, then subjecting the coated article to heat at a temperature upwards of approximately 250° F., the heat being continued for a period of approximately at least one hour at 250° F. and correspondingly shorter periods for higher temperatures, the time and temperature being below those at which alloying of the chromium with the subjacent metal takes place.

6. The process of treating parts of automobiles to promote their resistance to corrosion by acid solutions of calcium chloride comprising applying to such parts a composite coating a subjacent layer of which is of nickel sufficient to provide a degree of resistance to such corrosion and the outer layer of which is a brilliant deposit of chromium, then subjecting such parts to heat at a temperature between the approximate limits of 250° F. to 500° F. for a period ranging approximately from at least one hour from 250° F. to at least 20 minutes at 500° F.

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