

UNITED STATES PATENT OFFICE

WALTER L. PINNER, OF DETROIT, MICHIGAN, ASSIGNOR TO GENERAL SPRING BUMPER CORPORATION, OF DETROIT, MICHIGAN, A CORPORATION OF MICHIGAN

METHOD OF CHROMIUM PLATING

No Drawing.

Application filed November 13, 1930. Serial No. 495,428.

This invention relates to a method of chromium plating, and more particularly to a method of chromium plating whereby a coating of electrodeposited chromium relatively free from pores or cracks is obtained. The coating secured, therefore, is far more suitable for use in protecting a base metal from atmospheric or other corrosion than is the case of deposits produced by the processes that have been heretofore known, and which have been commonly employed in the art.

My invention, therefore, has as its object the production of more impervious deposits of electrodeposited chromium and the improvement in the art of protecting base metals from corrosion by electrolytically deposited chromium.

For the electrodeposition of chromium I employ a solution consisting principally of chromic acid and an added substance such as sulphuric acid or a sulphate or another salt or acid, these being employed in such proportion as will give a satisfactory deposit of chromium. Any suitable chromic acid chromium plating bath may, therefore, be employed, but I prefer to use one of the chromium plating solutions such as described by G. J. Sargent, and commonly known as the Sargent solution. This solution would contain, for example, 250 grams of chromic acid (CrO_3) per liter of solution and 2.5 grams of sulphuric acid (H_2SO_4) per liter of solution. A suitable anode, for instance lead, is employed. The cathode current density which is suitable depends on the composition of the bath, and may also vary with the temperature, as discussed in the prior art, and may be, for example, a cathode current density of 100 amperes per square foot when the bath is operated at a temperature of 115°F . If the bath temperature is increased, the current density would be increased, and likewise if the bath temperature is decreased, the current density would be decreased.

It has been well established in the prior art that when chromium is electrolytically deposited as a bright or lustrous deposit from any suitable chromium plating solution that

has as its major constituent chromic acid, the porosity or imperviousness changes with increasing thickness of deposit. The first chromium deposited fails to completely cover the base metal, and examination of the deposit by the proper technique will reveal that there are many small openings or pores in the electrodeposited chromium. The subsequently deposited chromium tends to gradually close over and cover up these pores. During this period of the deposition, therefore, the plate becomes progressively less and less porous. Long before the deposit has reached the stage of imperviousness, another action starts in and tends to increase the porosity. Electrodeposited chromium, as is general in the case of all electrodeposited metals, is under stress. Electrodeposited chromium differs from other commonly electrodeposited metals, however, in that when the thickness of metal exceeds the order of 0.00002 inches, this stress results in the formation of fine cracks which extend through the electrodeposited chromium, and results, therefore, in a porous condition. As the thickness of the electrodeposited chromium is still further increased, the number of these fine cracks is decreased, and in their place there is a smaller number of much larger cracks. The net effect, therefore, after this action starts is a progressive increase of porosity and a progressive decrease in the protective value of such deposits, which continues until very great thicknesses of deposits relatively, are obtained, these thicknesses being prohibitive from the standpoint of manufacturing cost in any commercially operable process.

There is, therefore, an optimum thickness of deposits which gives the least porosity, but this porosity is by no means zero, and the electrodeposited chromium, therefore, by any process which has heretofore been known, fails to give to the base metal the protection which it is desired to create by the electrodeposited chromium.

The precise thickness at which minimum porosity, as discussed above, would be obtained varies somewhat with the composition of the bath employed, and the condi-

tions used for electrolytically depositing the chromium. All of this has been well discussed in the prior art, notably in the following publications: "Protective Value of Chromium Plate" by E. M. Baker and W. L. Pinner, S. A. E. Journal, March 1928; "Porosity of Electrodeposited Chromium" by E. M. Baker and A. M. Renta, The Transactions of the American Electrochemical Society, Vol. LIV, 1928; and "Notes on the Hardness and Structure of Deposited Chromium" by Leland E. Grant and Leroy F. Grant, The Transactions of the American Electrochemical Society, Vol. LIII, 1928.

It is to be noted that this porous character of electrodeposited chromium has been well recognized as has also been the desirability of producing a deposit which is more nearly impervious. Except for my invention, all processes which have been at all successful along this line have involved heating of the deposit to remove the hydrogen which is adsorbed or occluded within the electrodeposited chromium. Such a process is described by R. J. Wirshing in "Heat Treatment of Chromium Deposits to Increase Their Resistance to Corrosion," The Transactions of the American Electrochemical Society, Vol. LVIII, 1930. This process, however, of heating the deposit and, of course, with it the metal on which the deposit is made, is expensive.

I have now discovered a method by which I can achieve progressively decreasing porosity of a chromium deposit with increasing thickness, and at substantially no greater cost than is required to produce the chromium deposits heretofore known in the art. My process consists simply in dividing the total plating time into two or more increments. For example, if by the old process, the plating were to be done at a current density of 100 amperes per square foot and for a time of four minutes, by my process I would plate, for example, at this current density for 2 minutes then stop the plating. The exact duration of time for which the plating is stopped is not critical, and may, for example, be from 1 second to a much longer period of time, as will appear in the further description of my process. The plating would then be resumed for a second period of 2 minutes. Expressed differently, my process contemplates, in a specific case, chromium plating until 200 ampere minutes of electricity per square foot of cathode surface have passed through the plating circuit, breaking the circuit and again plating until a like quantity of electricity has passed through the circuit.

While this process is simple, it produces a tremendous and wholly unexpected result with respect to the porosity of the deposit obtained. For example, if steel, which has

been previously plated with certain deposits of copper and nickel, and the nickel then buffed, is subsequently plated for 4 minutes with chromium, all being deposited as a single deposit as known in the old art, the protective value in the standard salt spray test might be 35 hours before the appearance of rust. When the chromium deposit, however, is applied in two increments by my process, as described above, a protective value of from 150 to 200 hours in the salt spray can be obtained.

I have achieved even superior results by dividing the total deposit into 3 increments, as in the above case for example, of $11\frac{1}{3}$ minutes each. When thicker deposits are to be made, as for instance, if the total plating time, as described above were 10 minutes, then better results would be obtained by using more than 3 increments for the deposition of the chromium. In fact whereas it is well established in the prior art that steel cannot be adequately protected from atmospheric corrosion by the electrodeposition of chromium alone, I find that I can produce on low carbon steel a protective value, as measured in the salt spray, of 40 hours before the appearance of rust by plating with chromium for a total time of $7\frac{1}{2}$ minutes when this is divided into 5 increments of 1.5 minutes each.

I have stated that in my process the deposition of chromium is interrupted one or more times in the course of forming the total deposit. Such interruption of deposition is obtained, for instance, by merely lowering the current density to a point at which chromium ceases to be deposited. It is not necessary that the current be totally stopped from flowing, but merely that the current be reduced to a value where chromium is no longer deposited and where the actions at the cathode consist of such things as the deposition of hydrogen and the reduction of 6 valent chromium to lower states of oxidation.

I prefer, however, when this may be conveniently done, to discontinue entirely the flow of current in the intervals between the several increments of the plating. In fact I achieve better results from the standpoint of porosity and protective value if I remove the articles from the bath and rinse them in water and then return them to the bath for the next increment of chromium plating. Even better results are obtained if after rinsing with water, the articles are rinsed in dilute acid, for instance, a 5% solution of hydrochloric acid or sulphuric acid and are then again rinsed in water before they are returned to the chromium plating bath for the next increment of chromium plating. It will be obvious, however, that these procedures, while increasing the protective value, nevertheless involve increased expense both

for the labor of operation and also for the chromic acid which is lost or washed away when the articles are removed from the chromium plating bath and rinsed. Likewise where this procedure is employed, there would be the expense of acid for the acid dip referred to.

If it is necessary that the articles be coated with a bright or lustrous deposit of chromium at the completion of the process, it is best to observe certain precautions in the operation of this process. When a subsequent increment of chromium is to be deposited, the current should not be increased to the full value immediately, but rather the voltage between the anode and cathode should be increased from a low value at a gradual rate. This minimizes the likelihood of a grey or cloudy second or subsequent deposit of chromium being obtained. Also if the articles being chromium plated are removed from the chromium plating bath between the several increments of plating, it is best to leave them in the chromium plating bath for a few seconds so that the articles may assume the temperature of the bath, and so that the water in which they were last rinsed may be replaced, by the process of diffusion, by the chromium plating solution before the current is again turned on for the next increment of plating. I also find that it aids in maintaining the brightness of the deposit to use a current density for the subsequent increments somewhat lower than the current density used for the first increment. The current density used with the subsequent increments may be 85% of the current density used for the first increment. I do not wish to imply, however, that either the slow reestablishment of current density or the reduction or change of the current density between increments is essential to my process. While the same current density may be rapidly reestablished and applied for all increments, I find slightly improved results as regards luster with the modified procedure just described.

When the chromium plating operation is completed, as usual in the art, I rinse the plated articles first with cold water, then with hot water. The articles may be used in this condition. However, I find that the luster of the articles is improved and that some further improvement in quality from the standpoint of resistance to corrosion is obtained if the chromium plated articles are buffed. This operation of buffing chromium plated articles is not in itself new, as buffing has been employed throughout the art when a grey or milky deposit inadvertently resulted from the chromium plating operation. Buffing of the chromium deposit for the express purpose of improving the rust resistance or protective quality as contrasted to buffing to remove dull or milky plating is to

the best of my knowledge new. This buffing, while desirable, is not an end in itself nor of the essence of my invention.

I am quite aware that when an article has been defectively plated with chromium so that only part of the surface has been so coated, it is old to return such article to the chromium plating bath and to again plate them with chromium, the effort being directed to coating those parts of the article which were not plated with chromium in the first operation. My process should be clearly distinguished from that old operation. The old operation was directed purely for the purpose of getting some chromium on all surfaces of the article. Some parts of the article plated according to the old operation would have, therefore, only a single deposit. My process is directed to the securing of two or more deposits on all of the those surfaces of the article which it is desired to protect by the electrodeposit of chromium. Furthermore, it should be noted that in my process each plating increment, including the first constitutes an electrodeposit of chromium that is a commercially satisfactory one, except that it is not sufficiently impervious according to my standards and possibly not sufficiently thick for some purposes. In my process, the first plating increment deposits chromium on all those surfaces which it is desired to protect, and is a deposit such as heretofore would not, under good commercial practice, be given a second plating. My process is, therefore, to be distinguished from any case of double plating due to a defective first deposit. As used in the claims, the term "commercially satisfactory", as applied to the chromium deposit, means a deposit free from such defects as would, in common commercial practice heretofore, have required a second plating.

Although I have described for the purpose of illustration, certain specific ways in which my invention may be carried out, it is to be understood that within the scope of my invention, wide deviations may be made therefrom without departing from the spirit of my invention.

I claim as my invention:

1. The process of chromium plating as a continuous treatment, which comprises electro-depositing a layer of chromium of a bright character on an article to be plated, reducing the current to a point at which electro-deposition of chromium ceases without removal of the article from the bath, and again passing a current of plating strength through the bath to deposit a second coating of chromium also of a bright character on the first coating.

2. The process of chromium plating as a continuous treatment which comprises passing a current through a bath until a bright

but relatively thin and porous layer of chromium has been deposited upon an article to be plated, reducing the current below plating strength and subsequently passing a current of plating strength through the same bath to deposit a second layer of chromium of a bright character on said first layer, the combined layers having considerably reduced porosity as compared with that of said first layer or with that of a layer of the same thickness obtained in a single continuous plating step under otherwise identical conditions of plating.

In testimony whereof I have hereunto subscribed my name at Detroit, Wayne County, Michigan.

WALTER L. PINNER.

20

25

30

35

40

45

50

55

60

65