Patented May 9, 1950 2,507,400

# UNITED STATES PATENT OFFICE

2,507,400

## METHOD OF ELECTROPLATING WITH IRON AND COBALT

Frank De Marinis, Cleveland Heights, Ohio, assignor to The S. K. Wellman Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application August 2, 1943, Serial No. 497,038

4 Claims. (Cl. 204—43)

1

This invention relates to the production of corrosion-resistant bodies made of iron, carbon and alloy steels, of alloys composed predominantly of copper and herein for brevity termed bronzes, or of other metal subject to corrosion and especially to oxidation.

It is an object of the invention to provide an improved method of treating the surfaces of such metal bodies which can be carried out rapidly and at relatively low cost to render them corrosion resistant and which is easy to control under commercial operating conditions.

Another object of the invention is to provide at low cost metal bodies, and particularly bodies formed of ferrous metal and bodies formed at least predominantly of copper such as bronze and brass, having corrosion-resistant surfaces capable of being readily welded to the surfaces of other metal bodies and particularly to surfaces formed by compacts of powdered metallic material which are more or less porous and may contain within their pores moisture and oxygen or other corrosive gases which tend to interfere with such welding operations.

The difficulties of carrying out welding operations such as those referred to are explained in the United States patent to Wellman No. 2,178,527 and that patent describes a method of welding powdered metal compacts, usually composed predominantly of copper, to ferrous bodies in which the latter are covered with a thin electroplated coating of copper, nickel or silver which serves to protect the coated ferrous metal from corrosion by gases or water vapor evolved from the compact when the parts are heated to effect welding.

In carrying out the present invention I also protect the ferrous or other metal surfaces to be bonded by electroplating them with a protective coating, but I have discovered an effective method of doing this with a coating of iron, or iron combined with cobalt, which is capable of being carried out more easily and rapidly and at lower cost than the prior methods and which provides the metal body with a surface that bonds well to powdered metal compacts of various compositions.

For the purpose of explaining and illustrating the improved method a description will now be given in detail of the procedure followed in carrying out the invention in one of its preferred forms.

The body to be treated, composed, for example, of steel, may be prepared for coating by cleaning its surface by any of the standard methods. For

2

example, the body may first be cleaned by treating with an organic solvent, such as gasoline, then with an alkali solvent, or preferably one of the commercially available electrocleaners, and finally with an acid dip.

The ferrous chloride electroplating bath is prepared with the following composition:

| | | |
|---|---|---|
| $FeCl_2.4H_2O$ | grams | 360 |
| $CoCl_2.6H_2O$ | do | 21.5 |
| $CaCl_2$ | do | 180 |
| Water (preferably distilled) | liters | 1 |

The amount of cobalt chloride specified is such that the ratio of metallic iron to metallic cobalt in the bath is 95 parts to 5 parts by weight. The calcium chloride, though not essential to the operation of the bath, is preferably included as it increases the conductivity of the bath and facilitates adjustment of its acidity. For the specified composition 180 g. of calcium chloride per liter of water has been found to be a suitable amount for the best results. The chloride salts making up the bath need not be of any greater purity than is usually required for industrial chemical operations, and that is true also of the other plating baths hereinafter described. To the solution described sufficient hydrochloric acid is added to bring the pH of the bath to 1.4. The ferrous body to be plated is suspended in the usual manner as cathode and any iron of the purer forms for industrial use may be used as anode which, by gradually dissolving, replaces the iron plated out, the ratio of iron to cobalt being approximately maintained by addition to the bath of cobalt chloride from time to time as required.

In the operation of the plating bath it is heated to and maintained at a temperature within the range of 70° to 95° C. and preferably between 80° and 90° C. The bath preferably is heated by submerged copper steam coils. With the bath so heated and its pH maintained within the limits of 1.3 and 1.5 a wide range of current densities can be employed. Under operating conditions such as occur in regular commercial production successful use has been made of current densities ranging from 10 amperes per square foot to as high as 240 amperes per square foot, the latter high current density having no deleterious effect whatever on the quality of the plating or upon its welding or bonding properties. Under optimum operating conditions current densities as high as 492 amperes per square foot have been used successfully, within the temperature range of 80° to 90° C.

In such a bath and with a current density of

240 a./s. f. a continuous, strongly adherent coating 0.0001'' thick is formed in 0.38 minute, and with a current density of 492 a./s. f. a similar coating is formed in 0.183 minute or 11 seconds. The iron-cobalt coating formed in each case is continuous and strongly adherent and provides effective protection of the ferrous metal. The coating has an appearance substantially like that of a nickel plate.

The important saving in time made possible in my method by the use of high current densities is indicated by the fact that with a current density of 10 a./s. f. in the same bath the time required for a 0.0001'' plating is 9 minutes, and by the further fact that with the prior electroplating methods of protecting ferrous bodies the maximum current densities which will avoid "burning," under regular commercial working conditions, for copper and nickel plating are about 30 a./s. f. With such current densities a copper plating bath at a temperature of from 70° to 80° C. requires approximately 2 minutes to form a 0.0001'' plating while for the same current density a nickel bath at the maximum feasible temperature of 60° C. requires approximately 4 minutes to produce a nickel plating of such thickness. And when, under optimum working conditions, the current density of the copper and nickel baths are increased to a maximum of 40 a./s. f approximately 1.5 minutes are required for a 0.0001'' copper plating and approximately 3 minutes for a 0.0001'' nickel plating.

The copper and nickel plating at the current densities specified for the "commercial" and the "optimum" conditions is close to the point of "burning"; but in the improved iron plating process at the much higher current densities there is no evidence of burning.

In the operation of my improved plating method it is important to maintain the pH value of the bath, as by daily check with a pH meter, within the proper limits. Indeed, the success of the method is largely dependent upon this.

While the composition and regulation of the plating bath specified above are such as are preferred, there can be considerable variation in these factors without incurring unsatisfactory results. Thus, the ferrous chloride, per liter of water, may range from 250 to 400 grams and the calcium chloride from 100 to 200 grams, with corresponding adjustment of the amount of cobalt chloride to maintain the ratio of 95:5 between iron and cobalt. However, the ratio may be increased as high as 99.75:0.25 and decreased to much lower ratio values, for it has been found that the use of 0.25% cobalt substantially increases the resistance to oxidation of the plated coating and also its bonding properties and this improvement increases directly with the increase in the percentage of cobalt employed in the bath, at least up to 20%. With respect to the bonding property, a plated coating composed of 80% iron and 20% cobalt bonds approximately as well at 1400° F. as a plated coating of pure iron bonds at 1500° F. Generally speaking, it is considered that the substantial advantages of the iron-cobalt coating can be secured with 10% or less of cobalt and in the majority of cases 5% cobalt is ample and in many cases 3% or even less of cobalt gives satisfactory results.

Also, in the case of the pH of the iron-cobalt chloride plating bath some latitude is permissible, and such bath may be operated with a pH as low as 1.2 and as high as 2.4. A pH lower than 1.2 will cause pitting or pin holes in the plating and a lower deposition of metal for a given current density, while a pH above 2.4 will cause the solution to become cloudy and rough plating will result. This is particularly true when the bath is worked at a high current density to attain a high rate of plating, so that proper regulation of the pH value of the bath is essential to the attainment of minimum cost of operation. Under practical working conditions the preferred pH of 1.4 has been found best to facilitate smooth plating and co-deposition of the iron and cobalt in the approximate ratio of these metals existing in the bath and at the maximum rate of plating.

Metal bodies, such for example as a steel clutch disk, protectively coated in the manner described may have friction facings of compacted metallic powder welded thereto in the manner described in the Wellman Patent No. 2,178,527 with the production of excellent bonds, coatings 0.0001'' thick being suitable for the purpose. As examples of powdered metal compositions which have been welded to ferrous bodies protected by my improved method, the following compositions (by weight) may be noted:

*Powdered metal composition A*

| | Per cent |
|---|---|
| Copper | 70.49 |
| Tin | 6.33 |
| Lead | 11.43 |
| Graphite | 7.23 |
| Silica | 4.52 |

*Powdered metal composition B*

| | Per cent |
|---|---|
| Copper | 67.20 |
| Iron | 7.20 |
| Tin | 5.31 |
| Lead | 8.70 |
| Graphite | 7.17 |
| Silica | 4.42 |

Some of the benefits of the improved method can be secured with coatings of compositions other than the iron-cobalt compositions which have been described. Thus, insofar as rapidity of plating, ease of control and protective quality of the coating are concerned, very good results can be secured with platings of pure iron and with platings in which the cobalt of the above described composition is replaced with nickel. For the pure iron plating bath the composition should be the same as that given for the iron-cobalt bath with the cobalt chloride omitted.

For the production of an iron-nickel coating the bath composition given for the iron-cobalt coating may be employed with the substitution for the cobalt chloride of 21.6 grams of nickel chloride ($NiCl_2 \cdot 6H_2O$), this amount of nickel chloride giving a proportion of iron and nickel of 95 parts iron to 5 parts nickel. Other compositions corresponding to those specified for the iron-cobalt bath can be employed.

The plating baths for pure iron and for iron-nickel should be adjusted to the same pH as the bath for iron-cobalt and they may be operated at the same temperatures and current densities as the latter bath with substantially equal speed of plating and good quality of plated coatings.

However, the protective coatings of pure iron or of iron-nickel alloy are not as widely applicable for welding or bonding purposes as is the iron-cobalt plating. Thus in the case of the "Powdered metal composition A" compact a metal body

which has been given either a pure iron coating or an iron-nickel coating by the improved method has been found to give an excellent bond under regular bonding or welding conditions, but it is not so satisfactory for bonding in the case of a "Powdered metal composition B" compact as the latter requires a somewhat higher welding temperature than the iron-cobalt coating with resultant tendency to cause sweating out of lead from the compact. In other words, from the standpoint of both plating and bonding or welding properties, the iron-cobalt coating has been found most satisfactory in the practice of the invention.

While, as above stated, the protective coating of pure iron formed as above described is not as widely applicable as the iron-cobalt coating, it has been found that the pure iron coating is especially effective for the protection of metal bodies composed at least predominantly of copper and particularly bodies of bronze and brass. Thus it has been found that bodies of bronze and brass protectively coated with plating of copper or nickel which cannot be satisfactorily welded to powdered metal compacts such as have been described above, can be so welded if they are protectively coated with pure iron by the improved plating process.

While the improved method is preferably carried out by the use of the chloride type of plating bath, it is also possible to carry out the coating of the metal bodies with a bath of the sulphate type. Thus iron-cobalt coating can be carried out by the use of a bath of the following composition:

| | |
|---|---|
| Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ | 300 g. ($Fe^{++}$ 89.5) |
| Cobalt sulphate, $CosSO_4 \cdot 7H_2O$ | 24 g. ($Co^{++}$ 10.5) |
| Water (distilled) | 1 liter |

In this bath the concentration of the ferrous ammonium sulphate can be varied within the range of 250 to 350 grams, with corresponding adjustment of the concentration of the cobalt sulphate if the ratio between the two metals is to be maintained.

This bath should have its pH adjusted and maintained within the range of 3.3 to 3.5 The bath can be operated satisfactorily at a temperature of from 60° to 70° C. and at current densities of from 20 to 60 a./s. f., though with a lowered efficiency for the higher current densities.

For pure iron plating a sulphate plating bath of the following composition may be employed:

| | | |
|---|---|---|
| Ferrous sulphate, $FeSO_4 \cdot 7H_2O$ | grams | 490 |
| Sodium sulphate, $Na_2SO_4$ | do | 230 |
| Water (distilled) | liter | 1 |

This sulphate bath, in which the sodium sulphate corresponds more or less in function to the calcium chloride of the first described bath, will operate well with lower concentrations of the salts, namely, down to 300 grams per liter of water of the ferrous sulphate and down to 150 grams of the sodium sulphate.

The pH of the bath should be maintained in the range of 2.5 to 3.0

This ferrous sulphate bath has been operated successfully at a temperature as high as 90° C. and at current densities ranging widely up to 374 a./s. f., at which density a 0.0001" coating of pure iron is produced in 0.29 minute.

Whether the improved method be carried out with a chloride or with a sulphate plating bath or with the production of iron-cobalt, iron-nickel



or pure iron coatings the specified regulation of the pH of the plating bath is necessary to insure successful operation of the method at maximum efficiency and minimum cost.

The marked economy attained by the method is, of course, due in part to the rapid rate of plating, in part to the low cost of the coating metals employed and in part to the ease with which the plating operation, particularly with the preferred chloride solution, can be regulated and carried out with the use of simple apparatus.

It will be understood that the specific procedures which have been described are given by way of example and for purposes of explanation and that other equivalent procedures may be employed without departing from the invention as hereinafter claimed.

What I claim is:

1. A method of protectively coating ferrous and bronze bodies which comprises the steps of providing a water solution of ferrous chloride in a concentration within the range of 250 to 400 grams per liter of water, cobalt chloride in a concentration such that the ratio by weight of the iron to the cobalt in the solution is from 80 to 99.75 parts of iron to 20 to 0.25 parts of cobalt, and calcium chloride in a concentration of 100 to 200 grams per liter; suspending in the said solution as cathode said bodies to be coated, passing an electric current through the solution with a density of from 10 to 490 amperes per square foot to form on the bodies continuous coatings composed of iron and cobalt; meanwhile maintaining the pH of the solution within the range of 1.2 to 2.4 and the temperature of the solution between about 70° C. and 95° C.; and replacing in the solution metals plated out therefrom to maintain the concentration of the solution.

2. A method as claimed in claim 1 in which the pH of the chloride solution is maintained within the range of 1.3 to 1.5, the temperature of the said solution is maintained between about 80° C. and about 90° C. and the electric current passed through the said solution has a density of from about 10 to about 240 amperes per square foot.

3. A method of protectively coating ferrous and bronze bodies which comprises the steps of providing a water solution of ferrous chloride in a concentration within the range of 250 to 400 grams per liter of water, cobalt chloride in a concentration such that the ratio by weight of the iron to the cobalt in the solution is from 80 to 99.75 parts of iron to 20 to 0.25 parts of cobalt, and calcium chloride in a concentration of 100 to 200 grams per liter; providing the said solution with an iron anode soluble in the solution as iron is plated out therefrom; suspending in the solution as cathode said bodies to be coated; passing an electric current through the solution with a density of from 10 to 490 amperes per square foot to form on the bodies continuous coatings composed of iron and cobalt; meanwhile maintaining the pH of the chloride solution within the range of 1.2 to 2.4 and the temperature of the said solution between about 70° C. and about 95° C.; and supplying to the solution additional amounts of the cobalt chloride to replace the cobalt plated out on the cathode bodies.

4. A method as claimed in claim 3 in which the pH of the chloride solution is maintained within the range of 1.3 to 1.5, the temperature of the said solution is maintained between about 80° C. and 90° C. and the electric current passed through

the solution has a density of from 10 to 240 amperes per square foot.

FRANK DE MARINIS.


REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 992,951 | Fischer | May 23, 1911 |
| 1,544,579 | Herr | July 7, 1925 |
| 1,920,964 | Burns | Aug. 8, 1933 |
| 1,970,548 | Batten | Aug. 21, 1934 |
| 2,036,667 | Williams | Apr. 7, 1936 |
| 2,131,427 | Crowder | Sept. 27, 1938 |

OTHER REFERENCES

Transactions of Faraday Society, vol. 28 (1932), pp. 733–740.

Principles of Electroplating and Electroforming, by Blum et al., 1930, pp. 94, 95, 138.

Transactions of the Electrochemical Society, vol. 78 (1940), p. 403.