

UNITED STATES PATENT OFFICE

2,532,284

COBALT PLATING BY CHEMICAL
REDUCTIONAbner Brenner, Chevy Chase, Md., and
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Serial No. 746,152

5 Claims. (Cl. 117-50)

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amended April 30, 1928; 370 O. G. 757)

1 The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the act of April 30, 1938 (ch. 460, 45 Stat. L. 467).

This invention relates to plating by chemical reduction, and more particularly to a method and bath for plating metallic surfaces with a coating of cobalt by autocatalytic chemical reduction reaction.

Heretofore, it has been common practice to plate metallic surfaces with cobalt by electrodeposition. The electrolytic process, however, requires the use of special and relatively expensive equipment, such as generators, rheostats, and racks. Thus, the electrolytic process is impractical when such special equipment is not at hand or its cost is prohibitive.

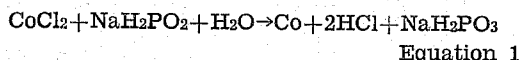
It has also heretofore been proposed to produce metallic cobalt by the reduction of cobalt solutions with hypophosphite. Such prior procedure however encountered disadvantages which discouraged its adoption and practice. The prior proposal was the use of high concentrations of hypophosphite, usually several hundred grams per liter of solution, to effect the reduction. The reaction in the reduction process was usually quite vigorous, much hydrogen was evolved, and the mass bubbled up to 10 or 20 times its original volume. The product of the reduction was mainly a dark powder, but occasionally it also deposited on the walls of the reaction vessel as a coating which gradually became detached and broke up into thin flakes.

The present invention is the discovery of an autocatalytic chemical reduction process and bath for plating metallic surfaces with cobalt. The present process has been found to provide selective deposition of the plating metal, no appreciable metal being precipitated to the bottom of the reaction vessel or being deposited on its walls. The plating metal is deposited in substantially pure, metallic form, has good adhesion to the plated metallic surfaces, and in salt-spray tests has been found to have good protective value.

According to the present invention, the source of the plating material or metallic coating is a cobalt salt. The metallic object is immersed in the plating bath until it has a plating deposit or coating of desired thickness. The bath is an aqueous solution of the cobalt salt and contains a relatively low concentration of hypophosphite.

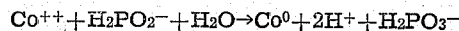
Using sodium hypophosphite as a typical hypo-

2 phosphite, the reaction of the present invention by which cobalt is produced is

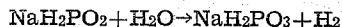


Equation 1

5 or



10 Concurrently, some of the hypophosphite is oxidized by the water, particularly in the presence of certain metals, to phosphite, and hydrogen is liberated:



Equation 2

15 Equations 1 and 2 show that the reaction mixture becomes more acid as either an acid salt or free acid is produced. The reduction of cobalt ion (Eq. 1) is catalyzed by certain metals, including cobalt, and as cobalt is produced by the reaction it is therefore autocatalytic. This explains why the reaction, which is rather slow in starting, proceeds with so much vigor after it once begins.

20 It is therefore an object of this invention to provide a novel and relatively simple chemical reduction process for plating metallic surfaces with cobalt.

25 Another object is to provide an autocatalytic chemical reduction process for the selective deposition of cobalt in the plating of metallic surfaces.

30 A further object is to provide a plating process by which a relatively hard, adherent and protective coating is deposited on metallic surfaces.

35 Another object is to provide an autocatalytic chemical reduction process for plating metallic surfaces, which process requires only materials that are readily available and obtainable.

40 Still another object is to provide a plating process which eliminates the need for special equipment such as is required in electrodeposition.

45 Other objects and advantages of this invention will be apparent from the following description and the appended claims.

In general, this process is applicable to the plating of cobalt on metals, such as steel, iron, nickel, cobalt, palladium, copper or copper base alloys. In advance of the plating treatment, the metallic objects, which are to have their surfaces plated, are preferably cleaned by any of the accepted and conventional procedures and then given a conventional acid dip. Objects of steel, iron, nickel, and cobalt, having been cleaned and acid-dipped are ready for immersion in the plating bath.

50 Objects of copper and copper base alloys, including brass and bronze, should be given addi-

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tional pre-plating treatment in the form of a momentary "bright" acid dip followed by a dip for about one minute in a solution of 0.02 gram of palladium chloride (PdCl₂) and 20.0 grams of hydrochloric acid per liter of solution. The concentration and length of the palladium dip can be varied inversely, and when the solution is heated, can be decreased.

The objects to be plated may be suspended in the plating bath by a string. Small objects may be supported by resting them on cloth stretched over a frame immersed in the plating bath. Small objects while in the bath should be agitated occasionally, although there is no need of constant motion, as in barrel plating, because electric current distribution is not involved.

In proceeding to a description of the bath composition, it should be noted that wherever reference is hereafter made to parts by weight, it is to be understood that the amount is given in parts by weight per 100 parts by weight of the plating bath.

The plating bath or solution of this invention comprises

	Parts by weight
Cobalt ion of a cobalt salt	0.125 to 2.5
Hypophosphite radical	0.7 to 10.7
Water	50 to 98.5

The cobalt ion is provided by the use of such water soluble cobalt salts as cobalt chloride and/or cobalt sulfate.

The hypophosphite radical in the plating bath may be secured by the use of sodium hypophosphite, ammonium hypophosphite, or potassium hypophosphite.

Throughout the plating process, the bath according to a preferred embodiment of this invention is heated to maintain it at a temperature in the range of about 90° C. to about 100° C. The boiling temperature of the bath, however, is to be avoided. The indicated range of temperature has been found to promote the chemical reduction reaction. At lower temperatures the reaction proceeds slowly and so does the deposition of the plating metal. At higher temperatures than indicated, the bath evaporates, and in the case of the ammoniacal bath, the ammonia escapes to an undesirable degree. The temperature of the bath during the plating operation may be any temperature in the range of about 80° C. to about 100° C., but it is found that the rate of deposition is greatest and the soundness of the deposits is better if the temperature is maintained in the 90° C. to 100° C. range.

The thickness of the plating deposit in a given length of time depends in part on the relation of the area of the surface of the metal object being plated to the total volume of the plating bath composition. In general, the rate of plating is somewhat less than that usually employed in electroplating with the same metals in a tank, but is about the same as in barrel plating. Because of the gradual exhaustion of the hypophosphite, less deposit is secured during each successive unit interval of time. Usually the rate of deposition is greatest during the first hour, and the reaction is virtually complete in two hours, unless additional hypophosphite is introduced into the bath. Some of the typical rates of deposition are stated hereinafter.

As the hypophosphite is gradually exhausted, more hypophosphite must be added if thick deposits are required, especially if the area to be plated is relatively large compared to the volume

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of the plating solution being used. Additions of five grams of hypophosphite per liter of bath solution may be made at half-hour to one-hour intervals. Thereby, deposits 0.002 inch (0.05 mm.) thick have been obtained in about six hours. As pointed out in Equations 1 and 2, the hypophosphite becomes converted into phosphite, which however does not interfere with the operation of the bath. When the bath becomes too concentrated with the phosphite, it is more economical to discard the bath than to try to remove the phosphite.

Under the conditions provided by this invention, the plating is selective; that is, the plating occurs only on the surface of the metal object—not on the walls of the bath vessel.

After a bath has operated in a glass vessel for about five hours, a small amount of a precipitate containing the plating metal may deposit on the bottom of the bath vessel where the source of heat has been applied. If this metallic precipitate is not removed, it may decompose some of the hypophosphite, just as another metal surface does. The removal can be secured by filtering.

The optimum yields in the practice of this invention are decreased by the presence in the bath of such ions as cadmium, copper, zinc, magnesium, aluminum and thiocyanate. These contaminants can be removed by conventional procedures, and the rate of deposition brought back to normal.

Tests of products resulting from the present process show that the plating deposit has good adhesion to the base metal and that the adhesion may be improved by acid-dip treatment of the cleaned base metal prior to the plating operation.

pH VALUE OF BATH OR PLATING SOLUTION

It has been discovered that the plating process is successfully performed by maintaining the pH value of the bath in the alkaline range of about eight (8) to about eleven (11).

In practicing this invention, the cobalt and hypophosphite salts are used for the described purposes and other compounds are used to control the pH value and to hold the cobalt ion in solution. If the solution consists only of the cobalt and hypophosphite salts, water, and material for holding the cobalt salt in solution, it initially has a slightly alkaline pH value, but proceeds rapidly to an acid pH value. The alkalinity of the bath is secured by the use of such basic compounds as ammonium hydroxide, and the cobalt salt is held in solution by the use of a salt or salts of citric, tartaric or other hydroxy-organic acids and/or ammonium salts. The addition of ammonia water (NH₄OH), or other hydroxides, during the plating operation, is recommended to maintain the pH value within the basic range of about 8 to about 11.

The preferred alkaline range is a pH value of 9 to 10 which may be conveniently maintained by the constant addition drop-wise of a dilute hydroxide solution.

Plating in the practice of this invention is successfully secured when an organic salt is used without the ammonium salt or when the ammonium salt is used without an organic salt. The organic salt may be used in an amount up to substantially 40 parts by weight, and the ammonium salt may be used in an amount up to substantially 20 parts by weight, these amounts being variable according to the particular composition of the desired plating bath.

EXAMPLES

The following table shows examples of plating baths or solutions embodying this invention:

Table

	I	II	III	IV	V	VI	VII
Cobalt Chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$5	10	3	3	3.5	3	3
Cobalt Sulfate $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$					2	10	2
Sodium Hypophosphite $\text{NaH}_2\text{PO}_3 \cdot \text{H}_2\text{O}$	2	2	1	2	2	10	2
Sodium Citrate $\text{NaC}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$			10				
Rochelle Salts.....	20	10			20	10	35
Ammonium Chloride NH_4Cl		5		20		5	5
Water H_2O	77.5	73	86	75	74.5	72	55
Total.....	100	100	100	100	100	100	100
Thickness, in./half hour.....	.00006	.00009	.00014	.0002	.00048	.00031	.00029
Appearance.....	Dull	Dull	Dull	Dull	Dull	Dull	Dull
Alkali for neutralizing.....	NH_4OH	NH_4OH	NH_4OH	NH_4OH	NH_4OH	NH_4OH	NH_4OH
pH.....	8-10	8-10	8-10	8-10	8-10	8-10	8-10

In the examples of the foregoing table the compositions are expressed in parts by weight; the rates of deposition are shown in inches per half hour; the appearance of the deposits is set out; and the pH values are stated.

The bath compositions of the foregoing examples are useful in plating objects of any of the metals heretofore described.

The soluble cobalt salts serve as the source of the cobalt ions and the cobalt plating, and the hypophosphite serves as the reducing agent. The organic salts and the ammonium salt serve to hold the cobalt salts in solution. The preferred organic salt is sodium potassium tartrate (Rochelle salt). The ammonium hydroxide serves to maintain the bath alkalinity and also to hold the cobalt salts in solution.

In each of the baths of the foregoing examples, the temperature of the bath is maintained in the range of about 90° C. to about 100° C. throughout the plating process which is continued for such length of time as is required to secure the desired thickness of deposited cobalt on the base metal.

When both an organic salt and an ammonium salt are used in the plating bath, it is found that the concentration of the organic salt may be varied inversely to the concentration of the ammonium salt.

It is also found that the ammonium salt may be replaced by sodium hydroxide to furnish the required pH value, but the pH value of the bath is the more difficult to control.

The foregoing is to be understood as illustrative as this invention includes all modifications and embodiments coming within the scope of the appended claims.

I claim:

1. An autocatalytic chemical reduction process for continuously plating cobalt on metallic objects consisting essentially of a metal selected from the group consisting of iron, nickel, cobalt, palladium, and copper, said process comprising the steps of: providing an aqueous solution of a cobalt salt and an alkaline hypophosphite, the cobalt ion being present in an amount not substantially in excess of about 2.5 parts by weight to about 100 parts by weight of said solution, the hypophosphite radical being present in an amount not substantially in excess of about 10.7 parts by weight to about 100 parts by weight of said solution, immersing an object of one of said metals in said solution, cobalt plating said immersed object by autocatalytic reaction of said salt and said hypophosphite, removing said plated object from said solution, maintaining said solu-

tion throughout the period of said immersion at a temperature in the range of about 90 degrees centigrade to about 100 degrees centigrade and at a substantially uniform pH value in the range

of about 8 to about 11 by the presence in the solution of at least one of the salts selected from the group consisting of sodium citrate, Rochelle salts and ammonium chloride, and introducing throughout said immersion period and at substantially regular intervals additional hypophosphite into said solution in amounts of about 5 grams per liter of said solution.

2. A process as defined in claim 1 wherein the metallic object consists essentially of copper and prior to immersion in the cobalt plating solution is dipped in a solution of palladium chloride and hydrochloric acid.

3. An autocatalytic chemical reduction process for continuously plating cobalt on metallic objects consisting essentially of a metal selected from the group consisting of iron, nickel, cobalt, palladium, and copper, said process comprising the steps of: providing an aqueous solution of 3.5 parts by weight of cobalt sulfate, 2 parts by weight of sodium hypophosphite, 20 parts by weight of sodium potassium tartrate per 100 parts by weight of solution, immersing an object of one of said metals in said solution, plating said immersed object by autocatalytic reaction of said cobalt salt and said hypophosphite, removing said plated object from said solution, maintaining said solution throughout the period of said immersion at a temperature in the range of about 90° C. to about 100° C. and at a pH value in the range of about 8 to about 10 by the addition of ammonium hydroxide, and introducing additional hypophosphite into said solution and at substantially regular intervals in amounts of about 5 grams per liter of said solution.

4. A process as defined in claim 3 wherein the metallic object consists essentially of copper and prior to immersion in the cobalt solution is dipped in a solution of palladium chloride and hydrochloric acid.

5. An autocatalytic chemical reduction process for continuously plating cobalt on metallic objects consisting essentially of a metal selected from the group consisting of iron, nickel, cobalt, palladium, and copper, said process comprising the steps of: providing an aqueous solution of not substantially more than 3 parts by weight of cobalt chloride, not substantially more than 2 parts by weight of sodium hypophosphite, and not substantially more than 20 parts by weight of ammonium chloride per 100 parts by weight of said solution, immersing an object of one of said metals in said solution, plating said immersed object by autocatalytic reaction of said cobalt chloride and said hypophosphite, removing

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said plated object from said solution, maintaining said solution throughout the period of said immersion at a temperature in the range of about 90° C. to about 100° C. and at a pH value in the range of about 8 to about 10 by the addition of ammonium hydroxide, and introducing additional hypophosphite into said solution and at substantially regular intervals in amounts of about 5 grams per liter of said solution.

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Number
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Name
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Date

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