Patented July 10, 1945

2,380,044

UNITED STATES PATENT OFFICE

2,380,044

PROCESS FOR PRODUCING ELECTRODEPOSITS

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No Drawing. Application June 28, 1940, Serial No. 342,902

5 Claims. (Cl. 204—56)

This invention relates to the electrodeposition of protective and ornamental finishes and is more particularly directed to the electrodeposition of colored deposits which include an oxygen compound of molybdenum. The present invention is further directed to molybdenum baths from which such deposits may be plated and to the deposits.

The prior art is aware of numerous chemical treatments using molybdenum compounds for the chemical coloring of metals, but these treatments result in the formation of exceedingly thin and even monomolecular layers of colored compound. The compounds, moreover, are usually only poorly adherent to the metal and provide relatively little resistance to corrosion. These chemical coloring processes rarely produce deposits of pleasing appearance and any attempt to improve them by buffing usually removes the coating entirely. Such processes have found very limited application and then are used only because of the absence of anything else which is more satisfactory.

By far the most satisfactory methods of applying ornamental and protective finishes are processes of electrodeposition. By such processes various protective and ornamental metals can be applied under controlled conditions in substantially any desired thickness. These processes have found wide application in the coating of metal surfaces with zinc, cadmium, copper, chromium, and the like. Colored deposits such as those ordinarily applied by chemical treatments can not, however, be applied by electrodeposition.

The provision of protective and ornamental finishes for aluminum has presented a particularly difficult problem because aluminum is not readily amenable to the electrodeposition or chemical coloring treatments used for other metals.

It is an object of the present invention to provide processes for the electrodeposition of a colored deposit. It is a further object to provide processes for the coating of aluminum. It is a still further object to provide an ornamental and protective coating which may be applied by electrodeposition and which may be buffed or subjected to other surface treatments. It is a still further object to provide plating baths of great throwing power and simplicity of operation for the electrodeposition of colored deposits on metals and particularly on aluminum surfaces. Further objects of my invention will become apparent hereinafter.

These and other objects of my invention are accomplished by electrodepositing a molybdenum-oxygen deposit thru the use of a solution containing a soluble molybdenum compound and by the use of a current density such that a non-metallic coating of the desired characteristics is obtained. Preferably a soluble compound of a second metal is included in the plating bath and, according to the preferred embodiment of my invention, boric acid is included. The more specific and preferred aspects of my invention will be set out with more particularity hereinafter.

An electroplating bath according to the present invention may contain molybdenum in the form of any of its soluble compounds such as sodium molybdate, potassium molybdate, and ammonium molybdate. Ammonium molybdate is not preferred, however, because it slowly forms insoluble ammonium complexes with an added metal such as nickel. The amount of molybdenum may be widely varied though in general it will be found desirable to use a relatively large amount approaching or approximating the maximum amount of molybdenum compound which can be dissolved in the particular solution. More particularly it will be found satisfactory to use such an amount of a soluble molybdenum compound as will provide for the bath from about 7 to 150 grams per liter of molybdenum calculated as metal. Still more specifically it will be found desirable in acid baths to use from about 7 to 30 grams per liter of molybdenum and in alkaline baths from about 75 to 150 grams per liter.

In addition to a molybdenum compound the plating baths of my invention should contain a buffer compound. A suitably selected buffer compound may be used in either the acid or alkaline baths of this invention more easily to maintain a constant pH in the way in which buffers have heretofore been used for the maintenance of pH in various systems. There may be used such buffer compounds as oxalic acid, tartaric acid, acetic acid, lactic acid, citric acid,

cyanides, and carbonates. By far the best buffer compound is boric acid which in addition to a buffering action on the pH of the solution appears to exercise a solubilizing action upon the bath constituents and promotes the formation of deposits of good character. Boric acid is unique among buffering compounds in its applicability to the purposes of this invention.

While the pH of baths of this invention may range from acidic to basic, it is preferred to use acid baths. Acid baths according to this invention should ordinarily have a pH of about 2.5 to 5 while more specifically it is preferred to use a pH of about 4. In alkaline baths the pH may vary from about 8 to 13.5 but it will be preferred to use a pH of about 8.

The electroplating baths of my invention contain a metal in addition to molybdenum and this metal should be selected from the group consisting of nickel, copper, zinc, cadmium, tin, vanadium, titanium, and cobalt. By far the best results are obtained using nickel as the auxiliary metal and if vanadium is to be used the amount should be kept small.

The amount of the auxiliary metal to be used with molybdenum will depend upon the particular metal and upon the exact effect desired. I have found that in general the amount of auxiliary metal should be such that there is about 6 to .25 times as much molybdenum as of the secondary metal both metals being computed as the metal. In the preferred acid baths of this invention it will more specifically be found desirable to have from about 1 to 5 times as much molybdenum as of the auxiliary metal while still more specifically some of the best results of the invention have been obtained when the molybdenum is present in an amount equivalent to 2½ times the amount of the secondary metal. In alkaline baths the best results have been obtained when molybdenum was present in an amount equivalent to about 3 times the amount of secondary metal. If a number of auxiliary metals are used with molybdenum the same general considerations as to total amounts of secondary metals will apply.

The plating baths according to this invention may be modified as are plating baths for metals by the use of various addition compounds and they are in general amenable to similar handling as to technique. The organic addition agents sometimes found useful in other plating baths may frequently be used to advantage, and I have found, for instance, that glucose or glycollic acid effect an improvement in the character of the deposits. Other addition agents which have been tried include naphthol disulfonic acid, naphthalene sulfonic acid, and phenyl sulfonic acid.

The current density to be used for the electrodeposition of colored electrodeposits according to my invention can best be determined for each specific bath by a few simple trials. It will usually be found that the current density is a very important factor in the operation of these baths. If the current densities are substantially too high the deposits will be non-adherent, powdery or brittle. Generally it will be found that deposits of fairly satisfactory character will be produced with current densities up to about fifteen amperes per square foot.

Since the character of deposit is affected by the current density more than ordinary attention will want to be given to the selection of the current density for any particular plating system of this invention. At low current densities the deposits are not permanent but are thin, soft, and nonadherent. Moreover, the color of the deposit is not permanent. It will generally be found that a current density from about 1 to 15 amperes per square foot may be used tho above about 5 amperes per square foot the bath must be agitated for best results. In order to obtain adherent, dense deposits a current density of about 2 to 5 amperes per square foot should be used while still more specifically the best results are obtained with a current density of from about 2 to 3 amperes per square foot.

The baths of this invention have been found quite stable upon continued electrolysis and it has been found that they may readily be maintained in operating condition by replenishing materials plated out. It has also been found that the baths have great throwing power and in fact some of them are unique in having a throwing power greater than the theoretical. As a result of the great throwing power deeply recessed articles may readily be plated without the use of specially shaped anodes.

The deposits obtained from the baths of my invention are adherent upon various metal surfaces such as steel, copper and brass, but the best results are obtained upon a zinc, cadmium, tin, or aluminum base. Prior to applying a deposit of this invention the surface to which it is to be applied is preferably etched slightly with an acid such as hydrochloric, nitric, or sulfuric.

The deposits very markedly increase the corrosion resistance of metals to which they are applied and they are quite resistant to abrasion. The colors of the deposits vary from jet black to brown, red-green, and to iridescent finishes depending upon the exact character of the bath used, and it appears that they are composed largely of compounds of molybdenum combined in some manner with oxygen. The deposits also contain small amounts of the additional metals used with the molybdenum.

Like other plating solutions the baths of this invention are affected by the temperature of operation. The temperature used has a definite effect upon the quality of deposit produced and although the temperature of the bath can be varied from room temperature to the boiling point best results are obtained at a temperature of about 70° C. the deposits produced at this preferred temperature being more uniform, ductile, adherent, and glossy than at other substantially different temperatures.

In order that my invention may be better understood reference should be had to the following illustrative examples:

Example 1

A preferred bath for the production of colored deposits according to my invention was prepared as follows:

Boric acid (H_3BO_3)	grams per liter	48
Sodium molybdate (Na_2MoO_4)	do	22.5
Molybdic oxide (MoO_3)	do	15
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	do	30
Sodium thiocyanate	do	3.8
pH		4.0

In use the bath was maintained at a temperature of about 70° C. Nickel anodes and carbon anodes were used to supply current to the bath. Black deposits were produced on zinc die castings, zinc plated articles, tin plated articles, and cadmium plated articles all of which were given a slight preliminary etch in hydrochloric acid.

At current densities of about 2 to 5 amperes per square foot the black deposit had a density of about 3.3. At higher current densities the density of deposit diminished to about 1 at 10 amperes per square foot. A typical analysis showing per cent by weight of some of the constituents of a deposit made at 3 amperes per square foot is as follows:

Molybdenum as Mo	56.10
Oxygen as O	37.46
Nickel as Ni	4.71
Boron as B	1.49

Sodium thiocyanate is used in the bath of this example to remove copper which may be present as an impurity. The effect of copper in causing deposits to be brown in color is so marked that the copper must be removed in some manner if jet-black deposits are to be obtained. The use of sodium thiocyanate has been found a very satisfactory way of removing this copper.

The relative amounts of molybdenum and auxiliary metals have been mentioned above and it is now noted that for the best results the ratio of secondary metal to molybdenum should be held within even closer limits at a given molybdenum concentration. As has been indicated the molybdenum content of the bath should vary between about 7 and 30 grams per liter and the nickel content for baths such as that of this example would vary from about 1.25 to 30 grams per liter when the molybdenum is at 7 grams per liter and the nickel content should vary from 5 to 120 grams per liter when the molybdenum is at 30 grams per liter. With the preferred molybdenum content of about 19 grams per liter the nickel content may vary from about 3 to 75 grams per liter but preferably will be about 7 grams per liter. Considerations as to the relative amounts of other metals will be similar.

Example 2

A preferred bath for the production of colored deposits according to my invention was prepared using the following ingredients in the indicated amounts:

Boric acid (H_3BO_3) grams per liter	75
Ammonium molybdate ($(NH_4)_2MoO_4$) do	35
Nickel sulfate ($NiSO_4 \cdot 6H_2O$) do	30
pH	4.2

An aluminum article was plated in this bath after a thorough cleaning preparatory to electrodeposition. The electrodeposition was effected at a current density of about five amperes per square foot and at a temperature between about fifty-five and sixty-five degrees centigrade. Nickel and carbon anodes were used, about ten per cent of the anodes being nickel, and about ninety per cent of them being carbon.

A lustrous, jet black deposit was obtained.

Similar deposits were produced on zinc and on other base surfaces with great success. It was found desirable when treating ferrous articles to plate them with bright zinc preparatory to the application of the black molybdenum finish, though this was not essential.

The deposits obtained with this bath at the current density used were much lighter in weight than metal deposits and they were so light in fact that when pieces of the deposit were stripped from the base surface some of them would float in water. Upon determination it was found that the average density of the deposit was about 1.006 compared to water. By reason of the low density of these deposits and the high rate of deposition by weight, the rate of deposition by thickness is very great. The deposit of this example is plated at a rate approximately twenty-one times as fast as nickel. It is to be observed, however, that the rate of deposition falls off after about ten minutes of plating and the maximum thickness of deposit obtained under the conditions of this example was about 0.001 inch.

The deposits include molybdenum in the form of some oxygen compound, but I do not understand the exact nature of the substance. The deposit, on the basis of a partial analysis, included the following:

	Per cent by weight
Molybdenum calculated as Mo	43.28
Oxygen calculated as O	39.48
Nickel calculated as Ni	9.73
Boron calculated as B	4.54

From the analysis of this particular deposit it will be observed that nickel is also present in minor amount. This may be combined with the oxygen or with the other materials present in some unknown manner. Boron is present in an amount greatly in excess of what would be expected from a mere occlusion, and it is quite possible that the boron is in some manner electrolytically deposited or else is in some manner co-deposited with the other materials present. These novel deposits containing molybdenum, oxygen, nickel, and boron constitute an important and preferred embodiment of my invention.

The amount of nickel sulfate present in the bath of this example may be widely varied, but I have found that it is in general most satisfactory to use between about twenty-five and sixty grams per liter of the nickel sulfate crystals. With much larger amounts of nickel sulfate the deposits are less black, verging on a gray color and with amounts much below about twenty-five grams they are likewise less black and are less adherent and less ductile.

The amount of ammonium molybdate employed is about an optimum under the conditions of this example, but this may be widely varied. In use the bath composition will naturally fluctuate considerably and over a period of four weeks of intermittent operation the ammonium molybdate fell to about seventeen grams per liter. At this concentration the bath was still operating satisfactorily. It is to be observed that under these conditions the nickel sulfate had dropped to twenty-two grams per liter. In general it will be found desirable in a bath such as the one of this example to use from about fifteen to fifty grams per liter of ammonium molybdate. It is particularly to be observed that the amount of ammonium molybdate must be adjusted depending upon the specific additional metals employed together with molybdenum.

The boric acid concentration of the bath of this example may be widely varied and excellent results have been obtained using from about thirty-five to eighty grams per liter. It is preferred to use about 45 grams per liter.

Various additional materials may be added to the bath to adjust its pH or its properties as desired. I have found that by adding a small amount of copper sulfate crystals to the bath of this example brown to mahogany colored deposits are produced. Various copper compounds give similar results and it is noted that four milligrams per liter of copper sulfate ($CuSO_4 \cdot 5H_2O$)

was found to give a pleasing color. Other metals may similarly be added to the baths of this invention if desired. As a caution it is noted that if jet black deposits are desired copper must carefully be excluded from baths such as those of Examples 1 and 2. Copper if present in the bath as an impurity may readily be removed in any suitable way and it may be removed, for instance as in Example 1, by the use of sodium thiocyanate.

Example 3

Another bath suitable for use according to my invention was prepared with the following:

	Grams per liter
Ammonium molybdate ($(NH_4)_2MoO_4$)	100
Stannous chloride ($SnCl_2$)	30
Sodium hydroxide (NaOH)	75
Glucose	60

Black deposits were obtained from this bath on aluminum and on various other base metals. The deposits contained about fifty-two per cent of molybdenum and five per cent of tin in addition to oxygen. The bath was operated at a temperature of forty degrees centigrade and it was observed that with higher temperatures the deposits were somewhat more brittle.

The ammonium molybdate was varied in this bath from about one hundred to one hundred and fifty grams per liter and satisfactory deposits were obtained.

The tin chloride may be used in widely varying amounts though it is in general desirable that the amount be considerably smaller than the amount of molybdenum. In general from about ten to thirty grams per liter could be used with satisfactory results. The bath of this example had an amount of molybdenum about three times as great as the amount of tin.

The glucose serves as an addition agent and when it is omitted the deposit is less ductile and less adherent. The amount of glucose may be widely varied as is customary in the use of addition agents in plating baths for metals, and the specific amount to use in a particular bath can easily be determined by a few simple trials.

Example 4

Another bath according to my invention was made up as follows:

	Grams per liter
Ammonium molybdate ($(NH_4)_2MoO_4$)	200
Zinc cyanide ($Zn(CN)_2$)	60
Sodium cyanide (NaCN)	42
Sodium hydroxide (NaOH)	78

With this bath black deposits of good character were produced on aluminum, zinc, copper, and other metal articles. The bath was operated at a temperature of about thirty degrees centigrade. It is noted that the amount of molybdenum present is about three times as great as the amount of zinc.

The ammonium molybdate was varied in this bath from twenty-five to two hundred grams per liter. The zinc cyanide was varied from ten to ninety grams per liter, sodium cyanide from twenty-five to one hundred and fifty grams per liter, and the sodium hydroxide from two to one hundred grams per liter. It will be understood that the various constitutents may be considerably varied in accordance with the practice known to the art in conjunction with the electrodeposition of metals.

The compositions of this invention may be offered to the trade as dry, powdered mixtures and such composition as that shown in Example 1 constitutes a preferred feature and embodiment of my invention. The plating compositions may if desired be offered as concentrated solutions or even as solutions ready for use.

The electrodeposits of this invention will be found suitable for a wide variety of ornamental and protective applications. Deposits of this invention have been used on hardware such as grass shear handles, stove parts, and builders hardware; on instrument parts such as telescope, camera, and calculating machine elements; on toys such as skates, velocipedes, and model trains; on automobile parts such as tire rims, interior trim, and motor elements; on appliances such as fire extinguishers, razors, and washing machines; on fishing equipment such as rods, reels, and accessories; on novelty articles such as lipstick cases, key rings, and pins; and on electrical equipment such as radio parts, motors, and any element requiring insulating covering.

While I have shown certain illustrative compositions and processes, it will be understood that one skilled in the art may readily devise numerous solutions and compositions containing molybdenum for the electroplating of molybdenum-oxygen deposits without departing from the spirit of my invention.

This application is a continuation-in-part of application Serial Number 235,799, filed October 19, 1938.

I claim:

1. In a process for the production of an electro-deposit, the step comprising electrodepositing an adherent, abrasion-resistant cathode deposit of an oxygen compound of molybdenum at a current density of about from 1 to 15 amperes per square foot from an aqueous acid bath including boric acid, a soluble nickel compound, and a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the amount of molybdenum present, calculated as metal, being from 7 to 150 grams per liter.

2. In a process for the production of an electrodeposit, the step comprising electrodepositing an adherent, abrasion-resistant cathode deposit of an oxygen compound of molybdenum at a current density of about from 1 to 15 amperes per square foot from an aqueous acid bath of pH 2.5 to 5, the bath including boric acid, nickel sulfate, and a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the amount of molybdenum present, calculated as metal, being from 7 to 150 grams per liter and from 1 to 5 times the amount of nickel.

3. In a process for the production of an electrodeposit, the step comprising electrodepositing an adherent, abrasion-resistant cathode deposit of an oxygen compound of molybdenum at a current density of about from 1 to 15 amperes per square foot from an aqueous acid bath of pH 2.5 to 5, the bath including about 35 to 80 grams per liter of boric acid, about 7 grams per liter of nickel in the form of a soluble nickel compound, and about 19 grams per liter of molybdenum in the form of a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium moybdate, and molybdic oxide, the

amount of molybdenum present, calculated as metal, being from 1 to 3 times the amount of nickel.

4. An aqueous solution for the electrodeposition of an adherent, abrasion-resistant, molybdenum-oxygen cathode deposit, the solution including from about 35 to 80 grams per liter of boric acid, about 20 to 50 grams per liter of sodium molybdate, and from about 10 to 30 grams per liter of nickel sulfate, the amount of molybdenum present, calculated as metal, being from 1 to 5 times the amount of nickel.

5. A composition for the electrodeposition of an adherent, abrasion-resistant, molybdenum-oxygen cathode deposit, the composition consisting essentially of 35 to 80 parts by weight of boric acid, 7 parts by weight of nickel in the form of nickel sulfate, and 19 parts by weight of molybdenum in the form of a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the amount of molybdenum present, calculated as metal, being from 1 to 5 times the amount of nickel.

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