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ELECTRODEPOSITING AND HEAT-TREATING MOLYBDENUM-OXYGEN DEPOSITS

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This invention relates to the treatment of deposits and more particularly to processes in which improved character as protective and ornamental finishes is imparted to colored molybdenum-oxygen electrodeposits by heating such deposits at elevated temperatures, preferably in boiling water, and to products so treated.

In the metal finishing art numerous chemical treatments for imparting surface coloring to metals have been known, but such treatments have found very limited application because the deposits produced are exceedingly thin, are usually only poorly adherent to the metal, provide relatively little resistance to corrosion, and rarely are of pleasing appearance.

In application Serial No. 342,902 filed June 28, 1940 by Raymond A. Hoffman, issued July 10, 1945 as U. S. Patent No. 2,380,044, there is described the electrodeposition of 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 is obtained which is of substantial thickness, adherent to the base metal, highly resistant to corrosion, and of pleasing appearance. In the plating bath from which such deposits are produced, it is preferred to include a soluble compound of nickel, copper, zinc, cadmium, tin, vanadium, titanium, or cobalt, the molybdenum being present in an amount equivalent to about from .25 to 6 times the amount of the other metal. It is preferable also to include in the plating bath a buffer such as boric acid, oxalic acid, tartaric acid, acetic acid, lactic acid, citric acid, a cyanide, or a carbonate.

Now I have found that the character as protective and ornamental finishes of colored molybdenum-oxygen electrodeposits produced from solutions containing a soluble molybdenum compound and a soluble compound of a second metal selected from the group consisting of nickel, copper, zinc, cadmium, tin, vanadium, titanium, and cobalt may be improved by heating such deposits at elevated temperatures, preferably in boiling water.

A colored molybdenum-oxygen electrodeposit which has been heated to an elevated temperature in accordance with a process of my invention is characterized by substantially increased resistance to abrasion. The deposit adheres more firmly to the conducting base upon which it is electrodeposited than a similar deposit not so treated. These improvements in abrasion resistance and adherence combine to make the deposit more suitable as a finish for metal surfaces which

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are subject to wear and handling. They also make the deposit more suitable for use on surfaces subject to deformation, since deformation would tend to cause breaking off of a less adherent coating.

An electroplating bath from which molybdenum-oxygen deposits suitable for treatment by the processes of my invention can be produced 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 a 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 bath should contain a buffer compound in order more easily to maintain a constant pH. 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.

While the pH of the baths may range from acidic to basic, it is preferred to use acid baths which should ordinarily have a pH of about 2.5 to 5, or 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.

In preparing molybdenum-oxygen deposits for treatment by a process of my invention, by far the best results are obtained on deposits made using nickel as the auxiliary metal. As already shown, 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 metal. In acid baths 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 specifi-

cally it is especially desirable to have the molybdenum present in an amount equivalent to 2½ times the amount of the secondary metal. In alkaline baths, some of the more suitable deposits have been obtained when molybdenum was present in an amount equivalent to about 3 times the amount of secondary metal.

In preparing colored molybdenum-oxygen electrodeposits for treatment according to a process of my invention, the current density to use can best be determined for each specific bath by a few simple trials. The current density is an important factor and if substantially too high the deposit will be non-adherent, powdery or brittle. It will generally be found that a current density of from about 1 to 15 amperes per square foot may be used, though above about 5 amperes per square foot the bath must be agitated for best results.

The deposits produced according to the foregoing description vary in color from jet black to brown, red-green, and iridescent, depending upon the exact character of the bath used. It appears that the deposits 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.

According to a process of my invention, a colored molybdenum-oxygen electrodeposit of the character produced according to the above-described processes is heated at elevated temperatures, whereby the character of the deposit as a protective finish is substantially improved. The elevated temperatures to which the deposits are heated may be in the range from about 90 to about 400° C. More specifically, particularly satisfactory results may be obtained by heating the deposits to a temperature in the range from about 90 to 150° C. Still more specifically, it is preferred to employ temperatures which can be attained using boiling water under atmospheric pressure.

The molybdenum-oxygen electrodeposits may be heated to the desired temperature by any suitable means. They may, for instance, be heated directly in a flame, although this is ordinarily the least desirable method. They may be heated by passing a high amperage electric current thru the conducting base upon which they are deposited or by introducing the conducting base into the field of a high frequency induction furnace. They may be heated by means of a fluid, such as a liquid or a gas, preferably an inert gas such as nitrogen or water vapor. As liquid media there may be used such liquids as glycerine, ethylene glycol, petroleum derivatives such as paraffin and other high boiling hydrocarbons, and other liquids which have heretofore been used by the art for transferring heat from an external source to various objects. I have further found it particularly preferable to accomplish the desired heating by means of a liquid which is a solvent for the salts of the plating bath from which the deposit was produced. I have found that boiling water is especially suitable for this purpose. It will be apparent that whatever liquid is used should not attack the base metal upon which the molybdenum oxygen compound is electrodeposited.

The time and specific character of the heating will depend on a variety of factors such as the thickness of the deposit, the character of the underlying base, and the desired lustre and adherence of the deposit, and as a result the best period

of heating to be used can most easily be determined by a few simple tests. More specifically, it will usually be found that the higher the temperature, the shorter is the time required for treatment. In boiling water, for instance, a period of 5 to 15 minutes may be found suitable, while at a temperature of 300° C. attained by direct heating, only a momentary period of heating is required. In any event, the period of heating to the elevated temperature should be sufficient to impart increased abrasion resistance to the deposit.

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

Example I

A bath for the production of colored molybdenum-oxygen electrodeposits was prepared having the following composition:

	Grams per liter
Boric acid, H_2BO_3	48
Sodium molybdate, Na_2MoO_4	22.5
Molybdic oxide, MoO_3	15
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	30
Sodium thiocyanate	3.8

The pH of the bath was 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.

In this bath a strip of cadmium plated steel was used as a cathode at a current density of about 4 amperes per square foot. The deposit so obtained was washed and dried and then treated according to a process of this invention by heating it to 200° C. and maintaining it at this temperature for 5 minutes, after which it was allowed to cool. The deposit which had thus been treated was found to be remarkably resistant to abrasion and to chipping off by deformation of the base metal as by bending. When compared with a deposit which had been prepared in a similar manner but which had not been heated at elevated temperatures, the sample which had been treated according to the process of my invention was found to be superior with respect to abrasion characteristics.

As a medium for applying heat to colored molybdenum-oxygen electrodeposits in a process of this invention, outstandingly successful results may be obtained by using boiling water at atmospheric pressure as shown in Example II.

Example II

A molybdenum-oxygen electrodeposit which was black in color was prepared as described above in Example I, the base metal employed as cathode being a strip of zinc-plated steel. The deposit so obtained was subjected to heating at elevated temperatures by immersing it for 10 minutes in boiling water. After this treatment the deposit was found to have substantially better resistance to removal by abrasion and by deformation of the base metal than a deposit which had been prepared in the same manner but had not been subjected to the heating step.

While I have shown certain illustrative processes and products, it will be understood that one skilled in the art may readily devise numerous processes and prepare numerous products without departing from the spirit of my invention.

I claim:

1. In a process for the production of an adherent, abrasion-resistant electrodeposit, the steps comprising electrodepositing a cathode de-

posit 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, and heating the deposit to a temperature of about from 90 to about 400° C.

2. In a process for the production of an adherent, abrasion-resistant electrodeposit, the steps comprising electrodepositing a 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, and heating the deposit in boiling water under normal atmospheric pressure for about from five to fifteen minutes.

3. In a process for the production of an adherent, abrasion-resistant electrodeposit, the steps comprising electrodepositing a 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 being from 7 to 150 grams

per liter and from 1 to 5 times the amount of nickel, and heating the deposit to a temperature of about from 90 to about 400° C.

4. In a process for the production of an adherent, abrasion-resistant electrodeposit, the steps comprising electrodepositing a 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 being from 7 to 150 grams per liter and from 1 to 5 times the amount of nickel, and heating the deposit in boiling water under normal atmospheric pressure for about from five to fifteen minutes.

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