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ELECTROPLATING

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This invention relates to the electrodeposition of a molybdenum-oxygen compound as a protective and ornamental finish and is more particularly directed to the use of a polyhydric alcohol as an addition agent for molybdenum-containing baths from which an oxygen compound of molybdenum is deposited.

There have recently been developed baths and processes for the deposition of colored deposits from baths containing a soluble molybdenum compound and a soluble compound of a metal selected from the group consisting of nickel, copper, zinc, cadmium, tin, vanadium, titanium, and cobalt, the molybdenum being present in an amount equivalent to from about 0.25 to 6 times the amount of the other metal. While excellent results are obtained with these baths, it is an object of the present invention to improve them by the inclusion of an addition agent. It is a further object to effect a broadening of the allowable current density range within which satisfactory deposits may be obtained from such baths. It is a still further object of this invention to increase the allowable pH variation of the bath. It is a still further object to improve the character of deposit so that it will be more dense, more abrasion-resistant, and more adherent. Further objects will become apparent hereinafter.

The foregoing and other objects of this invention are atttained by the inclusion in baths of the prior art of a polyhydric alcohol. Any polyhydric alcohol may be used and there may be included in the bath, for instance, glycerol or diethylene glycol.

The amount of a polyhydric alcohol to employ can most easily be determined in a particular instance by a few simple trials with the particular system which it is proposed to use. I have found that in general the best results are otbained with from about 0.25 to 1.5 grams per liter of a polyhydric alcohol, glycerol giving particularly good results within this range. Still more specifically, it is preferred to use about 0.75 gram per liter of glycerine in a molybdenum-nickel plating system for the electrodeposition of colored deposits.

The plating baths to which the addition agents of the present invention are added 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.

The plating baths should contain a buffer compound and a suitably selected buffer compound may be used in either the acid or alkaline baths more easily to maintain a constant pH in the way in which buffers have 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 constituent 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 the baths used may range from acidic to basic, it is preferred to use acid baths. Acid baths 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 use the pH of the bath tends to rise and become stable at around 4.8 to 5. In the presence of a polyhydric alcohol this rise in pH does not have any markedly deleterious effect upon the character of deposit. 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 plating baths to which a polyhydric alcohol is added should 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 auxiliary metal to be used with molybdenum will depend upon the particular metal and upon the exact effect desired. In general, the amount of auxiliary metal should be such that there is about 6 to 0.25 times as much molybdenum as of the secondary metal, both metals being computed as the metal. In the pre-

ferred 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 the molybdenum should be 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 metal will apply.

The current density to be used 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 though not so critical as if the polyhydric alcohol were omitted. Without a polyhydric alcohol the optimum current density range for a particular molybdenum-nickel system was about .1 to 5 amperes per square foot and upon the addition of glycerol the current density range broadened so that it extended up to 10 amperes per square foot.

The deposits obtained from baths containing a polyhydric alcohol are more adherent than those which do not use this addition agent. The deposits may satisfactorily be plated upon steel, copper, and brass but the best results are obtained upon a zinc, cadmium, tin, or aluminum base.

The deposits obtained may vary from jet black to brown, red-green, and to iridescent finishes, 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 and they additionally contain small amounts of the auxiliary metal. If a black finish is to be obtained, copper should be carefully excluded from the plating system.

As is common in electroplating solutions, the bath 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.

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

Example

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
Glycerol	do	0.75
pH		4

At current densities from about 0.1 to 10 amperes per square foot and at a pH as high as about 5 which was attained after continued operation excellent black deposits were produced. Sodium thiocyanate was added to the bath at the time that it was made up to remove copper which might have been present in the chemicals as an impurity. The presence of even a trace of copper would tend to make the deposit brown in color.

The boric acid concentration of the bath of this example may be widely varied and excellent results have been obtained using from about 30 grams to 80 grams per liter. It is preferred to use about 45 grams per liter as shown in the example.

The electrodeposits of this invention may be used for a wide variety of ornamental and protective purposes in the same way as deposits obtained from similar baths which do not include a polyhydric alcohol addition agent. The deposits may also be used as an electrical insulator on equipment requiring a thin, non-conducting coating.

The compositions of this invention may be offered to the trade as dry powdered mixtures, as concentrated solutions, or as dilute solutions ready for use. A composition as shown in the example constitutes a product of the invention and it may be offered to the trade mixed and ready for use.

While I have shown certain illustrative compositions and processes, it will be understood that one skilled in the art may readily use numerous solutions and compositions including polyhydric alcohols as addition agents without departing from the spirit of my invention.

I claim:

1. In a process for the production of an electrodeposit, the step comprising electroplating a cathodic deposit of a molybdenum-oxygen compound at a current density of about from 0.1 to 10 amperes per square foot from an aqueous bath including nickel sulfate and a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the bath containing from about 0.25 to 1.5 grams per liter of a polyhydric alcohol selected from the group consisting of glycerol and diethylene glycol, and 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 present, calculated as metal.

2. An aqueous plating composition for the production of a molybdenum-oxygen cathodic deposit at a current density of about from 0.1 to 10 amperes per square foot, the composition including nickel sulfate, a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the bath containing from about 0.25 to 1.5 grams per liter of a polyhydric alcohol selected from the group consisting of glycerol and diethylene glycol, and 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 the nickel present, calculated as metal.

3. In a process for the production of an electrodeposit, the step comprising electroplating a cathodic deposit of a molybdenum-oxygen compound at a current density of about from 0.1 to 10 amperes per square foot from an aqueous bath including nickel sulfate, boric acid, and a soluble molybdenum compound selected from the group consisting of sodium molybdate, potassium molybdate, ammonium molybdate, and molybdic oxide, the bath having a pH of about from 2.5 to 5.0, containing from about 0.25 to 1.5 grams per liter of a polyhydric alcohol selected from the group consisting of glycerol and diethylene glycol, and 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 the nickel present, calculated as metal.

4. An aqueous plating composition for the pro-

duction of a molybdenum-oxygen cathodic deposit at a current density of about from 0.1 to 10 amperes per square foot, the composition 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 bath containing from about 0.25 to 1.5 grams per liter of a polyhydric alcohol selected from the group consisting of glycerol and diethylene glycol, and 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 the nickel present, calculated as metal.

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