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ACID CADMIUM ELECTROPLATING BATH

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14 Claims. (Cl. 204—50)

This invention relates to an acid cadmium electroplating bath, and more particularly to an acid bath that gives a ductile matte plate with a strong bond to steel and aluminum.

A good acid cadmium bath, such as herein disclosed, is very useful, especially in those cases where the cyanide cadmium bath is not suitable. With an acid cadmium bath such as herein disclosed, it is possible to obtain a very much stronger bond to steel than with cyanide cadmium baths. Also in plating on aluminum alloys this acid cadmium bath gives better adherence although the difference is not as great as with steel. The conductivity of the acid cadmium bath is greater than that of the cyanide bath which makes it more advantageous in barrel plating. In still plating the acid cadmium bath permits the use of higher cathode current densities as well as higher anode current densities. The latter fact makes possible the use of smaller anode areas without polarization effects.

There has been comparatively little work published on acid cadmium baths. This is due, in no small measure, to the fact that a simple cadmium salt and acid give very poor plates. The growth of trees occurs to a remarkable extent from such baths. The sulphate and chloride baths are very poor and the fluoride and fluoborate baths, though somewhat better, have other objectionable features: fumes, expense, etc.

From a study of various acid cadmium plating baths, such as the cadmium sulphate bath containing sulphuric acid, it has been found that such baths are practically useless because the plate obtained is coarse grained, the throwing power of such baths is poor and treeing is very extensive. It is the object of this invention to produce an acid cadmium bath which in the electroplating operation will give a cadmium plate with good grain refinement, eliminate treeing and have satisfactory throwing power.

The use of acid cadmium baths has been confined almost totally to electrorefining and in the separation of cadmium from other metals in certain analytical procedures. The electrorefiners have employed various natural organic substances as addition agents, for example, gelatin and various glucosides, saponin, etc. These particular complex organic compounds produce compact plate, and reduce the growth of trees to a minimum or eliminate them completely. It is possible to get bright plates from such baths, but the plates are very brittle and usually pitted. These organic agents hydrolyze in acid solution to simpler molecules having no beneficial effect on the plate. The rather rapid deterioration of such a bath which occurs simply on standing is very objectionable from the electroplaters standpoint. This invention contemplates an acid cadmium plating bath having as an addition agent an organic compound or compounds of uniform composition and which are sufficiently stable so that in the practical operation of the bath no decomposition is noticeable.

It is an object of this invention to produce a properly compounded acid cadmium electroplating bath that will give a ductile matte plate with a strong bond to steel or aluminum and that will eliminate treeing in the electroplating operation. This object has been achieved by adding to the acid cadmium bath an addition agent from the group of water soluble naphthol compounds. These compounds when used as an addition agent in an acid cadmium bath produce grain refinement, reduce or eliminate treeing and promote the throwing power of the acid cadmium bath.

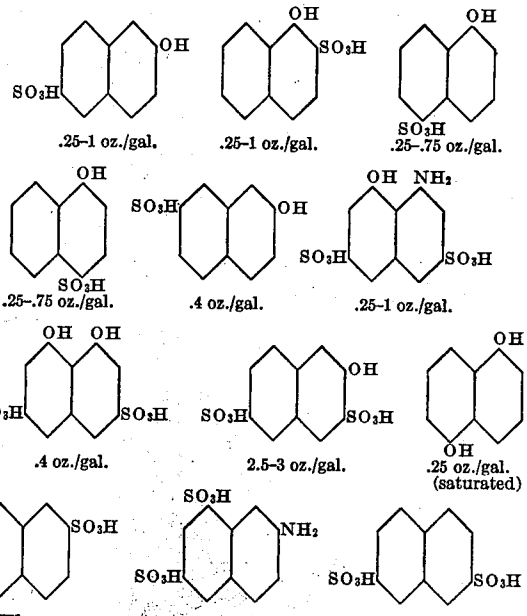
A large number of benzene and naphthalene derivatives were tested in solutions containing about 6 ounces per gallon cadmium and .4 ounce per gallon free sulphuric acid at 15 and 30 amperes per square foot. It was evident from these tests that the benzene derivatives had little commercial promise and that the naphthalene derivatives were much superior. Of the latter the hydroxy derivatives were definitely preferred to the derivatives without an OH group or groups.

Most of these compounds had to be sulphonated in order to obtain sufficient solubility. Thus 1-5 dihydroxy naphthalene is less effective than 1-8 dihydroxy naphthalene 3-6 disulphonic acid because of lower solubility. The degree of sulphonation should preferably be such that too great a solubility is not obtained, excessive solubility decreasing the interfacial activity of the compound. Thus 2-naphthol-3-6-disulphonic acid is less effective than any of the naphthol monosulphonic acids tested.

The introduction of a group which decreases solubility improves compounds which are too soluble for maximum effect. Thus 1-naphthyl

amine-8-hydroxy 3-6-disulphonic acid is more effective than 2 naphthol-3-6-disulphonic acid.

The position of the hydroxy and sulphonic groups makes some difference in effectiveness as shown below, where the naphthalene derivatives have been arranged in order of decreasing efficiency.



The amounts required for maximum effect are given beneath the formula of the compounds.

The 2-naphthol-6-sulphonic acid was studied in detail. Best results were obtained under the following conditions:

Oz./gal. Cd	3	6	12
Oz./gal. free H_2SO_4	.4–2	.4–3.5	.4–13
Oz./gal. addition agent	.25–.7	.25–.7	.25–.7
Amp./sq. ft.:			
Range	10–20	15–40	20–60
Optimum	15	25	40

The upper limit of the current density range within which ductile plate is obtained is where visible gassing begins over the surface of the plate. The plate then tends to become powdery crystalline. Below the lower limit of the current density range for ductile plate blackish velvety areas tend to form. In the current density range for ductile plate the plate is always a soft matte-white. The optimum current density is the best value for long plating, that is, over one-half hour plating time. With longer plating burning occurs on edges. If the cathode is moved or the solution agitated, the tendency for burning is greatly reduced. Also the agitation makes possible the use of higher current densities, for example, in the 12 oz./gal. Cd bath, the still plate range of 20–60 amp./sq. ft. can be raised to 25–70 amp./sq. ft. by even moderate agitation.

The concentration of acid is not critical except in the low metal baths (6 and 12 oz./gal. Cd) where increasing acid concentration lowers the visible gassing range appreciably. For example, in the 6 oz./gal. Cd bath 7 oz./gal. free H_2SO_4 lowers the current density range of ductile plate to 5–15 amp./sq. ft.

It has been found that the adherence of cadmium coatings from cyanide baths, both plain and with such addition agents as described in United States Patent No. 1,692,240 or in United States patent application Serial No. 83,347, is much improved by the interposition between it and the basic metal of a thin coating of cadmium applied in the baths described above.

I claim:

1. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from an acid cadmium solution in the presence of an addition agent from the group consisting of naphthol sulphonic acids.

2. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from an acid cadmium solution in the presence of an addition agent from the group consisting of mono-hydroxy naphthalene mono-sulphonic acids.

3. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from an acid cadmium solution in the presence of an addition agent consisting of 2-naphthol-6-sulphonic acid.

4. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing cadmium from a cadmium sulphate solution containing free sulphuric acid in the presence of an addition agent from the group consisting of naphthol sulphonic acids.

5. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing cadmium from a cadmium sulphate solution containing free sulphuric acid in the presence of an addition agent from the group consisting of mono-hydroxy naphthol mono-sulphonic acids.

6. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing cadmium from a cadmium sulphate solution containing free sulphuric acid in the presence of an addition agent consisting of 2-naphthol-6-sulphonic acid.

7. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from a cadmium sulphate solution containing free sulphuric acid in the presence of an addition agent from the group consisting of 2-naphthol-6-sulphonic acid ranging in concentration from .25–.7 oz./gal. of solution.

8. The method of obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from a solution containing from 3–12 ounces cadmium per gallon of solution, from .4–13 ounces free sulphuric acid per gallon of solution, and .25–.7 ounce 2-naphthol-6-sulphonic acid per gallon of solution, and a current density ranging from 10 amp./sq. ft. upward to where visible gassing begins over the surface of the plate.

9. A bath for electrodepositing ductile matte adherent cadmium plate comprising a solution of a cadmium salt containing free acid and an addition agent from the group consisting of naphthol sulphonic acids.

10. A bath for electrodepositing ductile matte adherent cadmium plate comprising a solution of a cadmium salt containing free acid and an addition agent from the group consisting of mono-hydroxy naphthalene mono-sulphonic acids.

11. A bath for electrodepositing ductile matte adherent cadmium plate comprising a solution of a cadmium salt containing free acid and an addition agent consisting of 2-naphthal-6-sulphonic acid.

12. A bath for obtaining ductile matte adherent cadmium plate upon a metal base which comprises electrodepositing said cadmium from a solution of cadmium sulphate and free sulphuric acid and an addition agent from the group consisting of naphthol sulphonic acids.

13. A bath for obtaining ductile matte cadmium plate upon a metal base which comprises electrodepositing said cadmium from a solution of cadmium sulphate and free sulphuric acid and an addition agent from the group consisting of mono-hydroxy naphthalene mono-sulphonic acids.

14. A bath for obtaining ductile matte cadmium plate upon a metal base which comprises electrodepositing said cadmium from a solution of cadmium sulphate and free sulphuric acid and an addition agent consisting of 2-naphthol-6-sulphonic acid.

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