

2,833,705

CADMIUM PLATING

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Serial No. 628,237

21 Claims. (Cl. 204-50)

This invention relates to the electrodeposition of cadmium and is particularly directed to plating bath compositions from which bright, mirror-like cadmium deposits are plated, consisting of cadmium cyanide baths characterized by containing in solution a N,N,N',N' -tetrakis-(hydroxy alkyl) ethylene diamine; and to compositions of matter containing such compounds for use as cadmium cyanide plating bath addition agents.

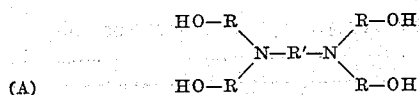
It is an object of this invention to provide cadmium cyanide plating bath compositions containing new and novel addition agents for producing bright, lustrous, mirror-like cadmium electro-deposits, direct from the plating bath.

It is another object of this invention to provide new and novel addition agent compositions for use in cadmium electroplating baths.

Cadmium, electroplated from cyanide baths containing no organic addition agents, or brighteners, is relatively coarsely crystalline in structure and dark or dull and unattractive in appearance. It is, therefore, customary to add organic addition agents or brighteners to the plating bath to refine the crystal structure and improve the appearance of the deposits.

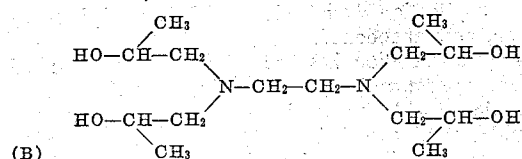
I have now found a class of chemical compounds that are particularly effective in producing bright, lustrous, mirror-like cadmium deposits from cyanide baths containing one or more of these novel brighteners, both alone and in combination with other materials that act in a synergetic manner, as hereinafter explained.

My new and novel cadmium cyanide plating bath addition agents, as this class of compounds will hereinafter be referred to, may be described as consisting of totally hydroxyalkylated alkylene diamines having the general structural formula A as follows:



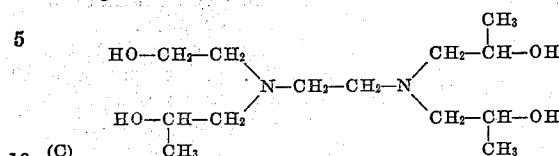
in which R and R' are alkyl radicals containing from 2 to 4 carbon atoms.

As a example of one specific compound of this type that has been found to be particularly effective, I may cite the one in which R is a propyl group and R' is an ethylene group. It is designated as N,N,N',N' -tetrakis(2-hydroxy propyl) ethylene diamine; that is, totally hydroxylated ethylene diamine, and has the following structural formula, B:



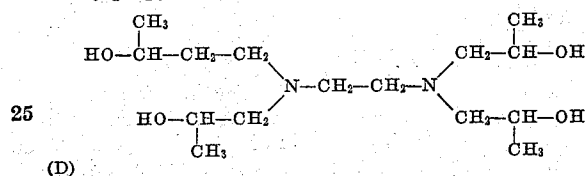
A group of compounds suitable for the present purpose and similar to the compound shown in Formula B is illustrated by the compound in which one of the R radicals is an ethyl group, and the remaining three R radi-

cals are propyl groups; that is, monohydroxyethyl trihydroxy propyl ethylene diamine, as illustrated in the following formula, C:



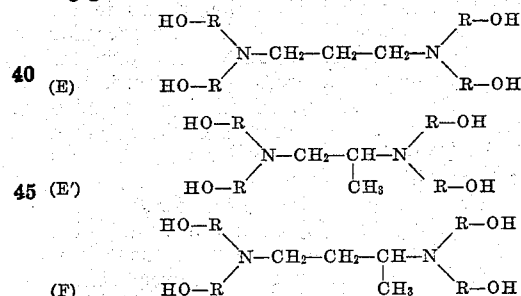
Other members of this group are like Formula C except that one, two or all three of the remaining R groups are hydroxyethyl groups; that is dihydroxyethyl dihydroxy propyl, trihydroxyethyl monohydroxy propyl, and totally hydroxyethylated, ethylene diamine, respectively.

Another group of compounds suitable for the present purpose and having the structure of general Formula A is illustrated in Formula D in which one of the R radicals is hydroxybutyl; that is, monohydroxybutyl trihydroxy propyl, ethylene diamine:



Other members of this group are like Formula D except that one, two or all three of the remaining R radicals are hydroxy butyl groups.

Still other groups of compounds which are suitable for the present purpose and similar to those of the above-stated general Formula A are the groups in which the R' may be either propylene or butylene. Examples of these types of compounds are illustrated by the following general structural formulae:



The foregoing propylene and butylene compounds may be prepared as follows:

(1) Chlorinate propylene or propane to



1-dichloro propylene

treat 1-3 dichloro propylene with an excess of NH_3 under pressures of from about 1-10 atmospheres at 50°C .- 100°C . until substantially all organically bound Cl has been replaced with NH_2 . Treat the resulting propylene diamine with alkylene oxide, i. e. ethylene oxide, propylene oxide or butylene oxide as set forth in U. S. Patent No. 2,697,118.

(2) Chlorinate butylene or butane as per 1 above to 1-4 dichloro butane and then proceed as stated above.

One or more of the R groups of compounds of these propylene amine and butylene amine types may be hydroxyethyl, hydroxypropyl or hydroxy butyl, and any combination of two or more of these hydroxy groups.

The bath solubility of any of the foregoing compounds is important since enough of the material must dissolve in the bath to be effective. In the case of the

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above-mentioned compound in which all four R radicals are hydroxypropyl radicals and the radical R' is ethylene, the preferred amount to use in the cadmium cyanide plating bath is about 0.5 gram per liter, although some effect is produced with as little as 0.1 gram per liter, while 1 gram per liter can be used without ill effects.

Similar amounts of each of the other above-mentioned compounds may likewise be used in cadmium cyanide plating baths with some noticeable effect in each instance.

While my novel cadmium cyanide plating bath addition agents are effective in any operable cadmium cyanide plating solution, I prefer to use a bath having the general formula,

	Grams per liter
Sodium cyanide, NaCN-----	120
Cadmium oxide, CdO-----	26

My novel cadmium cyanide plating bath addition agents have numerous advantages over other such materials now being used commercially. They are not only brighteners, but also anti-pit agents, so that no secondary materials are needed to prevent pitting of deposits. Another advantage is that my novel brighteners are definite chemical compounds whose composition can be controlled and duplicated, in distinction to those brighteners which contain organic matter of unknown composition. Still another advantage is that my novel brighteners act as sequestering agents for the deleterious metallic impurities, such as copper for example, that commonly contaminate cadmium cyanide plating baths in commercial operation, thus preventing the harmful effects of such impurities. Still another advantage is that my novel addition agents act effectively as brighteners on the anodes as well as on the cathodes, so as to keep the anode surfaces bright and clean. They act to promote uniform anode corrosion and prevent selective attack at the crystal boundaries, which results in fine metallic particles being dispersed in the bath, which migrate to the cathode, thereby producing rough deposits.

Still another advantage is the high degree of stability of my novel cadmium plating addition agents in the alkaline cadmium cyanide plating bath under operating conditions, which makes for economy, since only the brightener lost by bath dragout needs to be replaced.

While my novel cadmium cyanide plating bath addition agents are effective when used alone in cadmium cyanide plating baths, it is expedient for some purposes to combine them with other materials that act synergistically to produce certain desirable results under some conditions. For example, they may be used in combination with certain colloidal materials to improve the brightness of deposit and coverage in the low current density areas on irregularly shaped objects, particularly in barrel plating solutions. As examples of colloidal materials suitable for use with my novel cadmium cyanide plating bath addition agents, I may cite gelatin, peptone, and hydroxy ethyl cellulose, the last named being preferred. These materials are added to the plating bath to produce concentrations of from about 0.1 to 1 gram per liter, but in general not greater than the concentration of my novel addition agent in the bath at the time.

In order to broaden the bright plating current density range, particularly in the higher ranges, I have found it expedient to add a soluble nickel or cobalt salt as taught in U. S. Patent, 1,681,509. Any bath soluble compound of nickel may be used to produce a bath concentration of approximately 0.02 to 0.2 gram of nickel per liter, but in general the nickel concentration should not be greater than about one-fifth the concentration of my novel addition agent in the bath at the time.

It is apparent from the foregoing that under certain conditions it will be advantageous to use mixtures of one or more of my novel brighteners with a colloidal material. As an example of such a mixture that I have found to be effective is a mixture of N,N,N',N' tetrakis

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(2-hydroxy ethyl) ethylene diamine one part and hydroxy ethyl cellulose one part, the mixture being added to the bath to produce a concentration of about one gram of the mixture per liter of plating bath. Under other conditions, it will be advantageous to use mixtures of one or more of my novel brighteners with a bath soluble nickel compound. A convenient compound for this purpose is crystalline nickel sulfate, NiSO₄·7H₂O. One such mixture that I have found to be effective is N,N,N',N' tetrakis (2-hydroxy butyl) ethylene diamine, one part, and NiSO₄·7H₂O, one part, the mixture being added to the bath to produce a concentration of about one gram of the mixture per liter of plating bath.

I have found that mixture addition agents can be compounded so as to produce superior results over the wide range of operating conditions encountered with commercial cadmium cyanide plating baths. Such mixtures are made by mixing one or more of my novel addition agents with a colloidal material and a bath soluble nickel compound. For convenience, such addition agents are best compounded in the form of a solution portions of which can be added to a cadmium cyanide plating bath. As an example of one such solution that I found to produce particularly good results, I cite the following formulation:

	Grams per liter
N,N,N',N' tetrakis (2-hydroxy propyl) ethylene diamine-----	20
Hydroxy ethyl cellulose-----	10
NiSO ₄ ·7H ₂ O-----	10

This mixed addition agent solution is then added to a cadmium cyanide plating bath in the proportion of about 18 cc. of addition agent solution per liter of plating bath, or about 250 fluid ounces of mixed addition agent solution per 100 gallons of plating bath.

Example 1

A general formula for such mixed addition agent formulations coming within the scope of my invention would be:

	Parts
N,N,N',N' - tetrakis (hydroxy alkyl) ethylene diamine-----	20
Hydroxy ethyl cellulose-----	10
NiSO ₄ ·7H ₂ O-----	20
Water-----	950

Other compounds which come within the scope of my invention and have been found to give satisfactory results are illustrated in Examples Nos. 2 and 3:

Example 2

	Parts
Monohydroxyethyl trihydroxypropyl ethylene diamine-----	18
Peptone-----	12
NiSO ₄ ·7H ₂ O-----	16
Water-----	954

Example 3

	Parts
Dihydroxyethyl dihydroxypropyl ethylene diamine--	16
Gelatin-----	13
NiSO ₄ ·7H ₂ O-----	14
Water-----	957

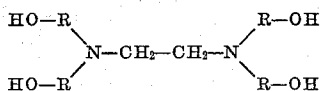
This application is a continuation-in-part of my co-pending application Serial No. 481,969, filed January 14, 1955, now abandoned.

While the invention has been described as embodied in concrete form and as operating in a specific manner in accordance with the provisions of the patent statutes, it should be understood that the invention is not limited thereto, since various modifications will suggest themselves to those skilled in the art without departing from the spirit of the invention, the scope of which is set forth in the annexed claims.

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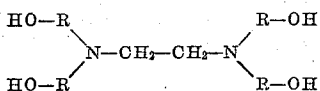
I claim:

1. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated ethylene diamine having the formula



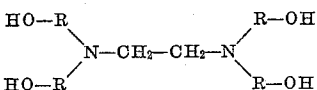
in which each R is an alkyl radical containing from 2 to 4 carbon atoms, in a concentration of about 0.1 to about 1 gram per liter.

2. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated ethylene diamine having the formula



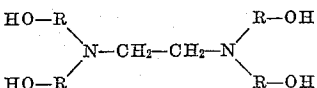
where each R is an alkyl radical containing from 2 to 4 carbon atoms, in a concentration from about 0.1 to about 1 gram per liter and a colloid selected from the group consisting of gelatin, peptone, and hydroxy ethyl cellulose in a concentration of about 0.1 to about 1 gram per liter.

3. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated ethylene diamine having the formula



where each R is an alkyl radical containing from 2 to 4 carbon atoms, in a concentration of about 0.1 to 1 gram per liter and nickel in bath soluble form in a concentration of about 0.02 to 0.2 gram per liter.

4. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated ethylene diamine having the formula



where each R is an alkyl radical containing from 2 to 4 carbon atoms, and a colloid selected from the group consisting of gelatin, peptone, and hydroxyethyl cellulose, each being in concentration of about 0.1 to 1 gram per liter, and nickel in bath soluble form in a concentration of about 0.02 to 0.2 gram per liter.

5. A cadmium cyanide plating bath composition containing N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine in a concentration of about 0.1 to 1 gram per liter.

6. A cadmium cyanide plating bath composition containing N,N,N',N'-tetrakis (2-hydroxy ethyl) ethylene diamine and a colloid selected from the group consisting of gelatin, peptone, and hydroxy ethyl cellulose, each in concentration of about 0.1 to 1 gram per liter.

7. A cadmium cyanide plating bath composition containing N,N,N',N'-tetrakis (2-hydroxy butyl) ethylene diamine in a concentration of about 0.1 to 1 gram per liter and nickel in bath soluble form in concentration of about 0.02 to 0.2 gram per liter.

8. A cadmium cyanide plating bath composition containing N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine and hydroxy ethyl cellulose, each in a concentration of about 0.1 to 1 gram per liter and nickel in bath soluble form in a concentration of about 0.02 to 0.2 gram per liter.

9. A composition of matter for use in cadmium cyanide electroplating baths containing totally hydroxyalkylated ethylene diamine in which all the alkyl substituents contain from 2 to 4 carbon atoms, a colloid selected from the group consisting of gelatin, peptone, and hydroxyethyl cellulose, and nickel in bath soluble form in proportions

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to each other effective when added to a cadmium cyanide plating bath to produce the bath composition of claim 4.

10. A liquid addition agent for use in cadmium cyanide electroplating baths containing in aqueous solution, N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine one part, hydroxy ethyl cellulose in amount equal to from about one-fifth part to one part, and nickel in the form of water soluble salt equivalent to nickel from about one-twenty-fifth part to one-fifth part.

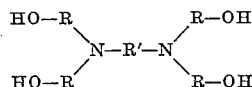
11. A liquid addition agent for use in cadmium cyanide electroplating baths containing in aqueous solution, N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine one part and hydroxy ethyl cellulose one part, and nickel in the form of a water soluble compound in proportion of approximately one-fifth part of nickel.

12. A cadmium cyanide plating bath addition composition containing substantially equal parts of N,N,N',N'-tetrakis (hydroxy propyl) ethylene diamine, a colloid selected from the group consisting of gelatin, peptone, and hydroxy ethyl cellulose, and nickel in bath soluble form.

13. A cadmium cyanide plating bath addition composition containing about one part of N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine and between about one-fifth part and about one part of hydroxy ethyl cellulose.

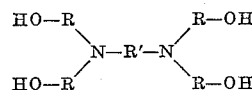
14. A cadmium cyanide plating bath addition composition containing about one part of N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine and between about one twenty-fifth part and about one part of nickel in the form of a water soluble salt.

15. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated alkylene diamine having the formula



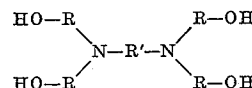
in which each R and R' is an alkyl radical containing from 2 to 4 carbon atoms, in a concentration of about 0.1 to about 1 gram per liter.

16. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated alkylene diamine having the formula



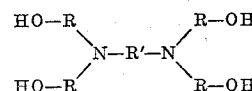
in which each R is an alkyl radical containing from 2 to 4 carbon atoms and R' is a propyl radical, in a concentration of about 0.1 to about 1 gram per liter.

17. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated alkylene diamine having the formula



in which each R is an alkyl radical containing from 2 to 4 carbon atoms and R' is a butyl radical, in a concentration of about 0.1 to about 1 gram per liter.

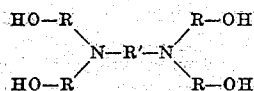
18. A cadmium cyanide plating bath composition containing a totally hydroxyalkylated alkylene diamine having the formula



where each R and R' is an alkyl radical containing from 2 to 4 carbon atoms, and a colloid selected from the group consisting of gelatin, peptone, and hydroxyethyl cellulose, each being in concentration of about 0.1 to 1 gram per liter, and nickel in bath soluble form in a concentration of about 0.02 to 0.2 gram per liter.

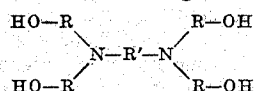
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19. A composition of matter for use in cadmium cyanide electroplating baths containing a totally hydroxy-alkylated alkylene diamine having the formula



in which each R and R' is an alkyl radical containing from 2 to 4 carbon atoms, a colloid selected from the group consisting of gelatin, peptone, and hydroxyethyl cellulose, and nickel in bath soluble form in proportions to each other effective when added to a cadmium cyanide plating bath to produce the bath composition of claim 18.

20. A composition of matter for use in cadmium cyanide electroplating baths containing a totally hydroxy-alkylated alkylene diamine having the formula

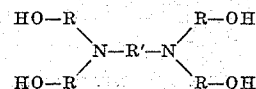


in which each R is an alkyl radical containing from 2 to 4 carbon atoms and R' is a propyl radical, a colloid selected from the group consisting of gelatin, peptone and hydroxyethyl cellulose, each being in concentration of about 0.1 to 1 gram per liter, and nickel in bath soluble

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form in a concentration of about 0.02 to 0.2 gram per liter.

21. A composition of matter for use in cadmium cyanide electroplating baths containing a totally hydroxy-alkylated alkylene diamine having the formula



in which each R is an alkyl radical containing from 2 to 4 carbon atoms and R' is a butyl radical, a colloid selected from the group consisting of gelatin, peptone and hydroxyethyl cellulose, each being in concentration of about 0.1 gram to 1 gram per liter, and nickel in bath soluble form in a concentration of about 0.02 to 0.2 gram per liter.

References Cited in the file of this patent

FOREIGN PATENTS

731,102 Germany Feb. 3, 1943

OTHER REFERENCES

"Sequestrene," Alrose Chemical Co., Providence, R. I., July 25, 1952, page 28.