United States Patent Office

3,227,638

Patented Jan. 4, 1966

3,227,638

ALKALI CYANIDE BATH AND PROCESS FOR ELECTROPLATING THEREWITH

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No Drawing. Original application June 16, 1961, Ser. No. 117,502. Divided and this application June 19, 1964, Ser. No. 376,547

4 Claims. (Cl. 204—50)

This application is a division of copending application Serial No 117,502 filed June 16, 1961, now abandoned.

This invention relates to the electrodeposition of metals and is directed particularly to the use of novel organic addition agents employed in plating baths for improving the luster and brightness of the metallic deposits obtained.

The invention is particularly useful in producing bright deposits of zinc or cadmium from alkaline baths such as conventional alkali-cyanide electroplating baths heretofore used. However, the invention may also be employed in the plating of tin, copper, silver and other metals and may be used in various types of electroplating baths.

The usual electroplating baths generally contain various addition agents as well as the salts or compounds of the metal to be deposited. These addition agents may be designed to improve the throwing power, the brightness of the deposit or to vary or control other properties of the bath. For this purpose, protective colloids, wetting agents, other brightening agents and the like may be used, among which may be included gelatine, heliotropine, anisic aldehyde, polyvinyl alcohol, sodium bisulfite, other metals and various other materials.

In accordance with the present invention, such electrolytic baths further contain a brightening agent consisting of a product of reaction between hexamethylenetetramine and epichlorhydrin or alpha-chlorglycerol. These agents, when present in amount varying from about 0.01% to 0.5% based on the weight of the electrolytic bath, have been found to improve materially the luster or brightness of the metallic deposit obtained.

The products of the present invention are particularly useful in producing bright deposits of zinc and cadmium from alkali-cyanide baths.

Accordingly, the principal object of the present invention is to provide new reaction products of hexamethylenetetramine and epichlorhydrin or alpha-chlorglycerol which are adapted for use in increasing the brightness and luster of metals deposited from electrolytic baths.

Another object of the invention is to provide methods for producing the new reaction products.

A particular object of the invention is to provide alkali-cyanide, zinc and cadmium containing electrolytic baths wherein there is a brightening agent consisting of the product of reaction of hexamethylenetetramine and epichlorhydrin or alpha-chlorglycerol.

A further object of the invention is to provide new methods for the electrolytic deposition of metals wherein the baths employed contain controlled amounts of the new reaction products as brightening agents.

These and other objects and features of the present invention will appear from the following description thereof in which reference is made to typical compositions and methods of procedure adapted for use in producing and using the brightening agents of the present invention.

The brightening agents of the present invention may be conveniently produced by reacting hexamethylenetetramine with epichlorhydrin or alpha-chlorglycerol in

the presence of water and at temperatures varying from about 25° C. to refluxing temperatures for a period of about 15 minutes to 3 or 4 hours. In general, from about 5 to 50 parts by weight of hexamethylenetetramine may be reacted with about 10 parts of epichlorhydrin or alpha-chlorglycerol. In the preferred reactions, the hexamethylenetetramine and the epichlorhydrin or alpha-chlorglycerol are employed in approximately equimolar amounts while the amount of water used may vary from about equal to about twice the amount of the hexamethylenetetramine. Larger amounts of water may be used but are not necessary.

The new reaction products are in the form of brown or dark colored liquids which may be concentrated to a viscous or gummy state and are completely soluble in water. They are stable in alkaline solutions but tend to decompose in the presence of oxidizing acids such as nitric acid or chromic acid.

While the exact nature of the reaction products is not known, it is believed from the character of the process by which it is produced that the epoxide ring of epichlorhydrin is opened up by reaction with water to give two hydroxyl groups and that the chlorine of the epichlorhydrin reacts with the hexamethylenetetramine to form a quaternary ammonium salt. This is confirmed by the fact that similar reaction products are obtained when using alpha-chlorglycerol instead of epichlorhydrin in carrying out the reaction. In any event, analysis of the reaction products shows that all of the chlorine has reacted and is present as anionic chlorine in the product. Moreover, the complete solubility of the reaction products in water suggests that the products are either quaternary salts or amine hydrochlorides.

In order to illustrate typical procedures which may be employed in producing the reaction products of the present invention, the following examples are cited.

Example I

A solution of 140 gms. hexamethylenetetramine in 279 gms. water was heated to about 90° C. and 93 gms. epichlorhydrin added with stirring during about 15 min. Reaction took place with evolution of heat and after the addition was complete the mixture was refluxed for about one-half hour. A brown fluid, homogeneous liquid was obtained which was completely soluble on further dilutions with water.

Example II

The process of Example I was repeated except that the hexamethylenetetramine solution was added to the epichlorhydrin.

Example III

A solution of 140 gms. hexamethylenetetramine in 279 gms. water was admixed with 93 gms. epichlorhydrin. An exothermic reaction ensued and the temperatures rose to about 65° C. Heat was then applied and the temperature increased to about 90° C. at which point a further exothermic reaction took place. The reaction was finally completed by refluxing for about one-half hour.

Example IV

140 gms. hexamethylenetetramine dissolved in 279 gms. water was admixed with 111 gms. alpha-chlorglycerol and the mixture refluxed for about 2½ hours.

In using the reaction products thus obtained from about 0.01 to 0.5%, and preferably about 0.25%, of the reac-

tion product is employed in the bath. The bath may also contain the usual agents employed for improving the throwing power and other properties of the bath. Thus for example, gelatine, polyvinyl alcohol, anisic aldehyde, heliotropine and the like may be used. A typical electrolytic bath of this character may contain 0.25 part by weight of the new reaction product together with 1.5 parts of heliotropine or anisic aldehyde, 1.5 parts of sodium bisulfite, 0.75 part of gelatine and 0.50 part of polyvinyl alcohol.

The formation of the reaction product can, in fact, be carried out in the presence of those bath modifying agents which do not react or otherwise impair the formation of the reaction product.

Example V

135 gms. of hexamethylenetetramine were mixed with 90 gms. of epichlorhydrin and 270 gms. of water and 20 gms. of polyvinyl alcohol were added to the mixture. The mixture was then heated to refluxing temperatures for a period of about one-half hour.

The brightening agents of the present invention are of particular advantage when used in plating zinc or cadmium from conventional alkali-cyanide containing baths. The current densities employed in such processes may be varied considerably so as to permit the use of a wide range of operating conditions. Typical procedures of this nature are as follows:

For use in tests on the plating of zinc, a bath was prepared which contained 4.2 oz. per gallon of zinc (as metal), 13.1 oz. per gallon of cyanide (as sodium cyanide) and 14.4 oz. per gallon of sodium hydroxide. The tests were carried out in a Hull cell at temperatures from 70 to 120° F. and both with and without agitation.

Tests were conducted when using the reaction product of Example I in amounts varying from 0.01% to 0.5% based upon the weight of the bath and at current densities ranging from 5 to 100 amperes per square foot. Similar tests were also conducted using the products of each of Examples I to V.

In each case unusually bright deposits of zinc were obtained in 5 minutes of plating time. No burning occurred at the high current density areas. The throwing power of the bath was diminished at low current areas and the deposit then was not quite so bright under such conditions. There was an increase in the cathode efficiency at high current densities. Thus, for example, when plating zinc at a current density of 60 amperes per square foot, the addition of 0.25% of the reaction product results in approximately 20% increase in the thickness of the deposit. Excellent plating results were also obtained when other agents were added to the bath such as anisic aldehyde, heliotropine, polyvinyl alcohol, gelatine and nickel.

While it is generally accepted practice to operate zinc plating baths at temperatures of about 70° F. to 90° F. in order to prevent chemical breakdown of the brightening agent used, it was found that when the products of the present invention are employed the temperature may rise to 120° F. without loss in brightness of the deposit.

In general, the optimum amount of the brightening agent employed is 0.25%. The deposits obtained when using the reaction products of Examples II and III were somewhat brighter than those obtained with the products of Examples I and IV. The throwing power of the bath when using the product of Example III was best while the brightness of the deposit and the throwing power of the bath when using the reaction product of Example IV was inferior to that of Examples I, II and III but still represented a marked improvement over that of baths which do not contain the reaction product.

In carrying out tests on the plating of cadmium, the Hull cell was again used and the bath employed contained 3.0 oz. per gallon of cadmium oxide and 16.5 oz. per gallon of sodium cyanide. Bright cadmium deposits were obtained and the results in general corresponded to those obtained when plating zinc as described above.

Bright deposits are also obtained when using the reaction product of Example V and in some instances, this product resulted in the formation of even brighter deposits than are obtained when using the reaction products of Examples I to IV.

Further tests have resulted in an increase in brightness of the deposits obtained when plating tin, copper and silver.

Although the reaction products of the present invention are primarily useful as addition agents for use in electrolytic baths, they may also be employed as acid inhibitors. For this purpose a 15% solution of the reaction product may be mixed with a suitable wetting agent as for example, 1% of sodium lauryl sulfate. 1% by volume of this mixture inhibits reaction of concentrated hydrochloric acid on steel, whereas 2% of the mixture prevents reaction of 30% sulfuric acid on steel. Moreover, in contrast with most acid inhibitors, the products of the present invention do not leave any film on the surface of the metal treated.

It is thus apparent that the reaction products of the present invention are adapted for use in various types of electrolytic baths and for other purposes. In view thereof, it should be understood that the procedures described above and the methods employed in producing and using the reaction products are intended to be illustrative only and are not intended to limit the scope of the invention.

We claim as our invention:

1. An aqueous alkali-cyanide bath for use in electroplating, said bath containing metal ions and a brightening agent which is the product resulting from the heating of a mixture containing approximately equimolar amounts of hexamethylenetetramine and a compound selected from the group consisting of epichlorhydrin and alpha-chlorglycerol, in the presence of about 1 to 2 parts by weight of water based on the weight of the hexamethylenetetramine to a temperature of from about 25° C. to refluxing temperature for a period of about 15 minutes to 4 hours.

2. An aqueous alkali-cyanide bath for use in electroplating, said bath containing metal ions selected from the group consisting of zinc and cadmium together with a brightening agent which is the product resulting from the heating of a mixture containing approximately equimolar amounts of hexamethylenetetramine and a compound selected from the group consisting of epichlorhydrin and alpha-chlorglycerol, in the presence of about 1 to 2 parts by weight of water based on the weight of the hexamethylenetetramine to a temperature of from about 25° C. to refluxing temperature for a period of about 15 minutes to 4 hours.

3. A process for producing a bright metallic deposit of a metal which comprises the step of electrolyzing an aqueous alkali-cyanide bath containing the metal to be deposited and from about 0.01 to 0.5 part by weight of a brightening agent which is the product resulting from the heating of a mixture containing approximately equimolar amounts of hexamethylenetetramine and a compound selected from the group consisting of epichlorhydrin and alpha-chlorglycerol, in the presence of about 1 to 2 parts by weight of water based on the weight of the hexamethylenetetramine to a temperature of from about 25° C. to refluxing temperature for a period of about 15 minutes to 4 hours.

4. A process for producing a bright deposit of a metal selected from the group consisting of zinc and cadmium which comprises the step of electrolyzing an alkali-cyanide bath containing the metal to be deposited and from 0.01 to 0.5 part by weight of a brightening agent which is the product resulting from the heating of a mixture containing approximately equimolar amounts of

hexamethylenetetramine and a compound selected from the group consisting of epichlorhydrin and alpha-chlorglycerol, in the presence of about 1 to 2 parts by weight of water based on the weight of the hexamethylenetetramine to a temperature of from about 25° C. to refluxing temperature for a period of about 15 minutes to 4 hours.

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