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PROCESS FOR PLATING BRIGHT BRASS

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The present invention is directed to electroplating compositions for depositing brass and more particularly to improved high efficiency baths capable of producing bright brass platings.

Baths for depositing copper-zinc alloys from aqueous alkaline cyanide solutions have long been known and used. Such baths contained copper and zinc cyanides and free alkali metal cyanide. By varying the ratios of copper to zinc and of the free cyanide to metal, deposits of varying copper to zinc ratios could be obtained, but such baths could operate successfully only at low cathode current densities of about 5 amperes per square foot because of the rapid change in color with changes in current density. These baths generally operated with a copper to zinc ratio of about 3–4 to 1 at temperatures of about 70°–100° F., with a pH generally not exceeding 12.8.

In the prior commercial baths for deposition of brass, cyanide solutions were used because the cyanide complexes of copper and zinc became more electronegative with excess alkali metal cyanide. With increased amounts of cyanide the potential of the copper ion became negative to a greater degree than the zinc so that by increasing the free cyanide a range of alloys low or high in zinc could be deposited. However, such alloys varied in color and composition with relatively small changes in current density and were markedly affected by temperature as well as free cyanide. Varying the free alkali metal cyanide also had a marked adverse effect in reducing the cathode efficiency. Prior baths operated at low cathode efficiency (not exceeding 75%), while the anode efficiencies were generally about 100%, which resulted in a build-up of metal in the plating bath with the destruction of the solution free cyanide metal ratios.

It has been proposed to improve the color characteristics of the brass deposits by adding ammonia to the conventional plating solutions. However, when ammonia was introduced into high concentration baths operated at elevated temperatures, the baths could not operate practically due to the evaporation of the ammonia. It was also proposed to add mono-ethanolamine to such baths while maintaining a copper to zinc ratio of 5 to 1 and operating the bath at 40° C. with about 10 gms./l. of the amine. While the deposit had some lustre, by increasing the temperature to 60° C. the lustre of the deposit was lost and the deposits were high in copper and hence could not produce yellow brasses. It was further found that other amines such as di- and tri-ethanolamines, aniline, and hexamethylene-tetramine were not effective for the purpose.

Another proposed bath of the high efficiency type had high concentrations of copper (42–63 g./l.), high ratios of copper to zinc (up to 10 to 1), and alkali metal hydroxide in an amount equal to 100–150% of the weight of the zinc. While this bath could be operated at elevated temperatures, it was commercially impractical in obtaining uniform yellow brass platings. In order to overcome the practical difficulties encountered in employing high concentrations of alkali metal hydroxide, it was proposed to utilize high concentrations of copper cyanide, low free alkali metal cyanide, with a copper to zinc ratio

of 10–35 to 1 with a preferred range of 10–20 to 1, the bath operating at elevated temperatures. It is quite probable that the zinc in this improved bath is present as the complex zincate and that its deposition potential is so changed from that of the cyanide complex that a uniform yellow brass deposit could be obtained over a wide range of current densities, with low free cyanide, and hence high efficiencies. However, such deposits are not sufficiently bright and for decorative work a subsequent polishing or buffing operation is necessary to secure the necessary lustre. The deposits at current densities below about 25 amps./sq. ft. were not uniformly brass colored.

Also, in low efficiency brass baths, the introduction of addition agents has been described. It was proposed to add soluble arsenic in small amounts (0.001 oz./gal.). Larger amounts were not recommended since they tend to give pasty white deposits. The addition of soluble nickel was also mentioned. These addition agents do not give bright deposits such as are normally obtained from present day bright cyanide copper or nickel baths, and when used alone they are effective only in the low current density baths.

The present invention is intended and adapted to overcome the difficulties and disadvantages encountered in prior art methods of obtaining bright brass deposits, it being among the objects of the invention to provide a bath which is capable of depositing brass coatings over a wide range of current densities.

It is also among the objects of the invention to provide a bath from which uniform yellow brass deposits are obtained at high temperatures and at high efficiencies.

It is further among the objects of the invention to provide a bath which is capable of depositing such coatings in bright or brilliant condition.

The invention is based upon the discovery that the alkyl polyamines form complexes with zinc salts which are more stable than the cyanide complexes of the prior art. These complexes are soluble in an excess of the amine and in alkali metal hydroxide. When such complexes are introduced into a basic high efficiency copper cyanide bath, it becomes possible to obtain bright brass colored deposits over a wide range of current densities, with low free alkali metal cyanide and at elevated temperatures. It is not possible to obtain such deposits under the same conditions from the prior art brass plating baths. The present baths can operate over a wide range of temperatures, such as from 70° to 180° F. with or without agitation. The alkyl polyamines adapted for use in said baths have at least 2 amino groups and the alkyl radicals have from 2 to 8 carbon atoms. The molecular weights of the polyamines range up to about 1800. The amounts introduced in the bath may vary considerably, being sufficient to form complexes with at least part of the zinc present. It is preferable to have an excess of free polyamine over that necessary to solubilize said complexes. The copper to zinc ratio by weight may vary between 10 and 40 to 1 when sodium salts are used, the optimum range being about 12–18 to 1.

The following are specific examples of the operation of this phase of the present invention.

EXAMPLE 1

An aqueous solution of the following composition is provided:

CuCN	g./l.	45.0
Total NaCN	g./l.	69.0
Free NaCN	g./l.	19.5
K_2CO_3	g./l.	30.0
Diethylenetriamine	ml./l.	20.0
Zn (in soluble form)	g./l.	1.1

Electrodeposition is conducted at 70°–140° F. with agitation. The zinc may be introduced as the zinc-amine complex made by dissolving a zinc salt, such as chloride or sulphate, and precipitating it with the amine; filtering the complex so formed and dissolving it in an excess of the amine.

The zinc may also be added to the bath as zinc cyanide, zinc oxide or alkali metal zincate, after which the amine is added, resulting in the formation of the complex in situ.

The bath deposits an excellent yellow brass color at room temperature without agitation over a range of current densities of from 5 to 70 amps./sq. ft. Such deposit is semi-bright. At about 120° F. with agitation the bath produces a lustrous brass deposit which is uniform, at current densities from 0 to 70 amps./sq. ft.; the higher the temperature of plating the higher the efficiency thereof.

EXAMPLE 2

Another high efficiency aqueous plating bath in accordance with the invention has the following compositions:

CuCN	g./l.	75.0
Total NaCN	g./l.	97.5
Free NaCN	g./l.	15.0
$Zn(CN)_2$	g./l.	7.5
Triethylenetetramine	ml./l.	20.0

The bath is operated at temperatures from 70° F. to 180° F. with agitation and at current densities up to 70–75 amps./sq. ft. after a breaking-in period. The deposits are uniform, bright and brassy in color. The preferred temperature range is 150°–180° F.

In the same bath there is substituted for the amine the propylene-polyamine having a molecular weight up to about 1800; this results in a brighter deposit than the lower polyamines.

Modified baths

Although the above described baths have good operating characteristics as far as the color of the brass deposit and the current density range are concerned, they have the disadvantage that the anode corrosion is insufficient. They have the advantage of giving good brassy deposits over a wide current density range, whereas prior baths did not do so. Also it is desirable to obtain still brighter and even brilliant deposits. It has been found that the addition of alkali metal hydroxide in amounts of 2–8 oz./gal. to the above baths reduces the anode polarization and increases the anode corrosion. In particular, with a pH over about 13.0, excellent corrosion is obtained.

The following are examples of the so modified baths.

EXAMPLE 3

The composition, dissolved in water, is as follows:

CuCN	oz./gal.	10.0
NaCN	oz./gal.	13.0
Free NaCN	oz./gal.	2.0
NaOH	oz./gal.	2.5
$Zn(CN)_2$	oz./gal.	0.9
Diethylenetriamine	fl. oz./gal.	1.25

The bath is operated at a temperature range of 140°–180° F. with agitation over a current density range from 0 to 70 amps./sq. ft. with good brassy deposits which are bright. The anode corrosion is satisfactory for commercial operation.

EXAMPLE 4

An aqueous solution of the following constituents is used:

CuCN	oz./gal.	10.0
NaCN	oz./gal.	13.0
Free NaCN	oz./gal.	2.0
NaOH	oz./gal.	6.0
$ZN(CN)_2$	oz./gal.	1.0
Triethylenetetramine	fl. oz./gal.	0.25

The bath is operated as set forth in Example 3 with equally acceptable results.

In the baths of Examples 3 and 4 the use of alkali metal hydroxide permits the use of lower concentrations of the polyamines with good results and reduces the cost since the polyamines are relatively expensive. The complexes of the higher polyamines and zinc salts are relatively less soluble in the bath than those of the lower polyamines; and they may even precipitate out of the solution at room temperatures, but they redissolve at the higher temperatures of operation.

Further modified baths

The baths of Examples 1 to 4 when freshly prepared and used show multi-colored deposits as do the deposits of the prior art. After some period of operation this defect disappears. Said baths have the added shortcoming of plating with a skip plate or a double plate in the low current density areas. It has now been found that the incorporation of arsenic or nickel in the form of soluble compounds, with the arsenic in relatively large concentrations (about .03–.75 g./l.) permits immediate operation of the above baths (Examples 1–4) without giving said multi-colored deposits. While the prior art mentioned the use of small amounts of arsenic (.001–.0075 g./l.) it stated that higher amounts gave pasty white deposits.

The following are specific examples of these further modified bright brass plating baths.

EXAMPLE 5

An aqueous solution of the following composition is provided:

	G./l.
CuCN	75.0
NaCN	117.5
Free NaCN	15.0
NaOH	37.5
Zn $(CN)_2$	7.5
Tetraethylenepentamine	2.0
As (in the form of Na_2ASO_3)	0.03

Deposition is obtained at plating temperatures of 140°–170° F. with agitation over a current density range of 0–70 amps./sq. ft.

It is possible to begin plating from this bath without a breaking-in period or purification. The combination of the arsenic and polyamine produces a bath which is practical to operate, giving deposits of better uniformity and higher lustre.

EXAMPLE 6

Nickel also has this beneficial effect and the following aqueous composition is typical:

CuCN	oz./gal.	12.0
NaCN	oz./gal.	15.0
Free NaCN	oz./gal.	1.8
Zn as diethylenetriamine complex	oz./gal.	0.7
Diethylenetriamine	fl. oz./gal.	2.5
Ni (in the form of $Ni(CN)_2$)	oz./gal.	.08

The bath is operated as set forth in Example 5, giving brighter deposits. Highly satisfactory results are obtained when both arsenic and nickel are present in the bath. The baths of Examples 5 and 6 give initially lustrous deposits without multi-colored films, without skip plate or double plate.

Selenium modified baths

There may be added to the arsenic or nickel containing baths, small amounts of soluble selenium compounds, both inorganic and organic, whereby there are obtained brass coatings which have a high degree of brightness equivalent to that obtained from the present day bright cyanide copper baths.

The selenium compounds preferably used are those having a valence of −2, such as alkali metal selenocy-

anates, alkali metal selenides, selenoureas and selenophenols. They are used in concentrations of about .0001 to .01 gl/l., the preferred range being .0001 to .0005 g./l. Alkali metal selenites and selenates (or SeO_2 and SeO_3) may be used in higher concentrations with fair results; concentrations from .001 to 0.10 g./l. are suitable. With such additions the brightness of the baths of Examples 1–4 is enhanced, particularly in the high current density areas, although in the low current density areas control of the color is somewhat critical. While the selenium does not remove the multi-color film deposits from said baths, when added to those baths containing arsenic or nickel such deposits no longer form. The ratio of arsenic (as metal) to selenium should be about 5–50 to 1 when very bright, uniform brassy deposits are obtained. When larger ratios of arsenic are present then full brightness is not obtained and when larger ratios of selenium are present then low current redness occurs.

The following are illustrative of baths of this type.

EXAMPLE 7

An aqueous solution of the following composition is used:

CuCN	g./l.	75.0
NaCN	g./l.	87.5
Free NaCN	g./l.	15.0
$Zn(CN)_2$	g./l.	7.0
NaOH	g./l.	45.0
Tetraethylenepentamine	ml./l.	2.0
Se (in the form of KCNSe)	g./l.	.002
As (in the form of Na_2AsO_3)	g./l.	.03

Electrodeposition is conducted at temperatures of 140°–180° F. with agitation at current densities up to 80 amps./sq. ft.

EXAMPLE 8

Similar excellent results are obtained by replacing the arsenic with nickel in the form of the polyamine complex with a nickel salt, such as the chloride or sulphate, or by introducing it as nickel cyanide.

The composition is as follows:

CuCN	g./l.	75.0
NaCN	g./l.	92.5
Free NaCN	g./l.	10.0
$Zn(CN)_2$	g./l.	7.5
Diethylenetriamine	ml./l.	30.0
$Ni(CN)_2$ (as metal)	g./l.	0.5
Se (in the form of selenourea)	g./l.	.003

The electrolysis takes place at temperatures of 130°–180° F. with agitation at current densities of 0–100 amps./sq. ft.

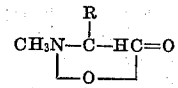
The nickel materially increases the bright current density range and there is a relationship with the amount of selenium present. The lower effective concentration of nickel is about .3 g./l. and it gives effective results up to 1.0 g./l. The ratio of nickel to selenium is 100–300 to 1, and the optimum ratios are 150–200 to 1.

It is common practice to "oxidize" yellow brass deposits by immersion in alkali metal sulphides, such as "liver of sulphur." It is known that when the prior art small amounts of arsenic are added to the conventional brass plating baths, it becomes difficult or even impossible to uniformly oxidize such deposits. On the other hand, in baths of the character of Example 7, the deposits are easily oxidized uniformly and the oxidation takes place more readily.

Surface active agents

While the above baths give good results in actual practice, there is a tendency in extended operations to drag into the bath organic and other contaminants, such as dust or traces of grease or fat not properly removed from the metal being plated, by the alkaline detergents or cleaners. The cyanide itself, being organic, may break down to form products which constitute impurities. These introduce some difficulties for the plater.

It has now been found that the introduction of certain surface active agents, which are in the prior art, may be added to the baths of Examples 1–8, whereby these difficulties are overcome. These agents should be used in small concentrations and large amounts are harmful, tending to reduce the bright plating range. These agents fall into two groups, one of which consists of betaine derivatives having the formula



wherein R is a hydrocarbon radical having 8 to 21 carbon atoms. The other group has the formula

$$R'—O—(C_2H_4O)_x$$

wherein R' is a hydrocarbon radical having 5 to 15 carbon atoms and taken from the class consisting of saturated aliphatic radicals both straight and branched chain in which the ether oxygen is attached to a primary or secondary carbon atom, hydrocarbon substituted cycloaliphatic radicals in which the substituent group is straight or branched chain, hydrocarbon substituted aromatic radicals in which the substituent group is straight or branched chain, and the unsaturated counterparts of said hydrocarbons, and x is a numeral from 10 to 80. The method of preparation of such condensation products is well-known.

The betaines, such as capryl, lauryl or cetyl betaine, when used in concentrations of about .005 to .10 g./l. are very beneficial. Those compounds having from 10 to 18 carbon atoms are most practical, and those having 10 to 16 carbon atoms are preferred. The following are typical examples of such compositions.

EXAMPLE 9

The composition has the following constituents:

CuCN	g./l.	75.0
NaCN	g./l.	87.5
Free NaCN	g./l.	15.0
$Zn(CN)_2$	g./l.	7.0
NaOH	g./l.	45.0
Tetraethylenepentamine	ml./l.	2
Se (in the form of KCNSe)	g./l.	.002
As (in the form of Na_2AsO_3)	g./l.	.03
Trimethyl-laurylbetaine	g./l.	.04

The bath is operated at temperatures of 140°–180° F. with agitation at a bright current density range of 0–70 amps./sq. ft. Higher concentrations of betaines tend to reduce the bright plating range and concentrations over about .10 g./l. have an adverse effect on said range. The betaines have similar advantages when added to the baths of Examples 1–8.

EXAMPLE 10

They may be added, for instance, to the composition of Example 7. Trimethyl-laurylbetaine in the amount of .08 g./l. is added thereto and plating is conducted under the stated conditions.

The deposits are uniformly lustrous and of a higher degree than those obtained in the absence of the betaine, and more markedly when the bath has been contaminated with organic material. Also, the bath is rendered more tolerant to such impurities.

EXAMPLE 11

Surface active agents which are condensation products of ethylene oxide and which are known in the prior art are equally as effective as the betaines, the following being typical of such uses:

CuCN	g./l.	45.0
Total NaCN	g./l.	69.0
Free NaCN	g./l.	19.5
K_2CO_3	g./l.	30.0
Diethylenetriamine	ml./l.	20.0
Zn (as the polyamine complex)	g./l.	1.1
1-methyl heptyl ether of polyethyleneglycol 1200	g./l.	.04

The plating is conducted as described in the above Example 10.

Condensation products of this type are used in concentrations of .005 to .10 g./l. in the preferred embodiments. They are described in co-pending application Serial No. 478,908, filed December 30, 1954.

EXAMPLE 12

Although the invention has been described setting forth several specific embodiments thereof, the invention is not to be limited thereto as many variations are possible within the scope thereof. For instance, the lower ratios of copper to zinc may be used in barrel plating with a high free cyanide content as in the following bath:

CuCN	oz./gal.	10.0
NaCN	oz./gal.	16.0
Free NaCN	oz./gal.	5.0
Zn (as polyamine salt)	oz./gal.	0.7
As (as Na_2AsO_3)	oz./gal.	.05
2-ethylbutyl ether of polyethylene glycol 800	oz./gal.	.01

EXAMPLE 13

Other alkali metals than sodium may be used, for example KCN may be substituted for NaCN, whereby the bright current density range is increased. In such cases the copper to zinc ratio in the bath should be altered in order to obtain bright brass deposits over a wide current density range. In the prior art no such difference has been noted between sodium and potassium. For instance, with an all sodium bath as described in Example 7, a brass colored deposit is obtained at current densities from 5 to 100 amps./sq. ft. But when equivalent amounts of potassium salts are substituted for the sodium salts, the brass colored range is decreased to about 40 to 100 amps./sq. ft. By decreasing the copper to zinc ratio, as in the following composition, the brass colored range is widened. It is desirable to increase the zinc concentration to 2–3 times over that in those formulations having sodium as the alkali metal.

The following composition is typical:

CuCN	oz./gal.	10.0
KCN	oz./gal.	16.5
Free KCN	oz./gal.	2.5
$Zn(CN)_2$	oz./gal.	1.8
KOH	oz./gal.	7.5
Tetraethylenepentamine	oz./gal.	.16
KCNSe	oz./gal.	.00014
As (in the form of K_2AsO_3)	oz./gal.	.001

The plating is conducted at temperatures of 140°–180° F. and preferably at 150°–160° F. with substantial agitation. The range of current densities is 15–100 amps./sq. ft and uniform, bright brass deposits are obtained. In the above formula the copper to zinc ratio is about 7 to 1, but the ratio may vary from 4–10 to 1 with excellent results.

From the above examples, it is apparent that many variations in the details are contemplated and the invention is to be broadly construed. In copper plating baths, contamination with zinc often occurs which may co-deposit with the copper. The addition to such baths of the polyamines described above in the stated amounts complexes the zinc in solution and retards such deposition.

In the claims the term "soluble complex" is intended to include such compounds which may be only slightly soluble at room temperatures but which, under the conditions of plating will dissolve to give the desired concentrations thereof. The zinc-polyamine complex need not be added to the bath as such, but the zinc salt and the polyamine may be added separately. Also, it is not necessary that there be present an excess of polyamine over the total zinc present as only part of the zinc need be in the form of the complex at any time. There should be present enough polyamine or alkali metal hydroxide to solubilize the zinc-polyamine complex.

We claim:

1. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide.

2. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, substantially all the copper being present in the form of cuprocyanide, the ratio of copper to zinc being about 10–40 to 1.

3. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, substantially all the copper being present in the form of cuprocyanide, the ratio of copper to zinc being about 12–18 to 1.

4. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing alkali metal hydroxide in amount of about 2–8 oz./gal.

5. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath having a pH over about 13.

6. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of arsenic in the amount of at least .03 g./l.

7. A bath for plating bright brass which comprises cop-

per cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of about .03–.75 g./l.

8. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates.

9. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, said —2 compounds having a metal content of about .0001–.01 g./l. and said selenites and selenates in amounts of about .001–.10 g./l.

10. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, said —2 compounds having a metal content of .0001 to .0005 g./l. and said selenites and selenates in amounts of about .001–.10 g./l.

11. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, said —2 compounds having a metal content of about .0001–.01 g./l. and said selenite and selenates in amounts of about .001–.10 g./l.

12. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of arsenic in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, the ratio of said arsenic to selenium being about 5–50 to 1.

13. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a surface active agent which is an alkyl betaine in which the alkyl radical has 8–21 carbon atoms.

14. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing a surface active agent which is an alkyl betaine in which the alkyl radical has 8–21 carbon atoms.

15. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting or organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, said bath containing a surface active agent which is an alkyl betaine in which the alkyl radical has 8–21 carbon atoms.

16. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide and a soluble zinc-alkylpolyamine complex, and an alkyl polyamine present in an amount sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said polyamine having a molecular weight up to 1800, and a substance which solubilizes said complex.

17. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide and a soluble zinc-

alkylpolyamine complex, and an alkyl polyamine present in an amount sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said polyamine having a molecular weight up to 1800, and a substance which solubilizes said complex, the alkyl groups of said polyamine having 2 to 8 carbon atoms.

18. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide and a soluble zinc-alkylpolyamine complex, and an alkyl polyamine present in an amount sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said polyamine having a molecular weight up to 1800, said excess polyamine solubilizing said complex.

19. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide and a soluble zinc-alkylpolyamine complex, and an alkyl polyamine present in an amount sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said polyamine having a molecular weight up to 1800, and alkali metal hydroxide which solubilizes said complex.

20. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, the ratio of copper to zinc being about 4–40 to 1.

21. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of nickel, said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, the ratio of said nickel to selenium being about 100–300 to 1.

22. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of nickel in the amount of at least .3 g./l.

23. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide and a soluble zinc-alkylpolyamine complex, and an alkyl polyamine present in an amount sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said polyamine having a molecular weight up to 1800, and a substance which solubilizes said complex, said alkali metal being potassium, at least in part.

24. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a surface active agent which is an alkyl ether of polyethylene oxide wherein the alkyl radical has 5–15 carbon atoms and the polyethylene radical contains 10–80 ethylene groups.

25. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing a surface active agent which is an alkyl ether of polyethylene oxide wherein the alkyl radical has 5–15 carbon atoms and the polyethylene radical contains 10–80 ethylene groups.

26. A bath for plating bright brass which comprises copper cyanide, alkali metal cyanide, soluble complex zinc-polyamine and an alkylpolyamine having at least two amino groups, the alkyl groups thereof having 2 to 8 carbon atoms, said polyamine having a molecular weight up to 1800, the amount of said polyamine being sufficient to form said complex and provide an excess of uncomplexed polyamine, the ratio of copper to zinc being about 4–40 to 1, substantially all the copper being present in the form of cuprocyanide, said bath containing a soluble compound of a metal taken from the class consisting of arsenic and nickel in the amount of at least .03 g./l., said bath containing also a soluble compound taken from the class consisting of organic and inorganic selenium compounds with the selenium having a valence of —2, selenites and selenates, said bath containing a surface active agent which is an alkyl ether of polyethylene oxide wherein the alkyl radical has 5–15 carbon atoms and the polyethylene radical contains 10–80 ethylene groups.

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