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ELECTROPLATING BATH

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My invention relates to the manufacture of electroplating baths, particularly alkaline reacting complex baths, i. e. cyanide baths for the electrodeposition of metals and metal alloys such as, for instance, silver, gold, copper, zinc, cadmium, brass.

With alkaline reacting complex baths I mean baths which contain the metal to be deposited not in the form of a simple kation but essentially as a complex ion whereby in addition to alkali metal compounds, the metal, or metals are present in a dissolved state, for instance, in form of a cyanide. Such baths may, for instance, contain silver as sodium silver cyanide or copper as copper cyanide, and in addition thereto alkali cyanide and alkali carbonate.

Hitherto it was known to add brightening agents to the electroplating baths of the above mentioned type, so for instance, sulphur or sulphur compounds such as carbon disulphide, sodium thiosulfate and the like. These additions, however, are not efficient if stronger deposits, for instance 4 g silver/dm² (that is a 90% silver plating) are desired. The deposited metal is then dull and needs an after treatment in order to obtain a high polished surface. This after treatment may be carried out for example by raking with steel brushes, steel polishing and subsequent burnishing and polishing with a felt disc.

It is further known to add colloidal substances to strongly alkaline silver salt baths containing free caustic alkali, in order to obtain coatings with a bright surface. These baths, however, have the disadvantage as they will more or less readily decompose whereby the decomposition products exert a harmful effect on the electrolysis.

Now I have made the surprising observation that with the above mentioned alkaline complex baths bright metal coatings of an extraordinarily hardness may be obtained if selenium and/or tellurium compounds are present in the electrolyte. The bath solution may contain, for instance, 0.01–20 g/litre selenium or tellurium or both in form of soluble compounds, for instance, as sodium selenite. The presence of selenium or tellurium compounds in the bath solution makes it possible to work with current densities of 0.3–4 amp/dm², for instance, of about 1.5–4 or 2.5–4 amp/dm². On account of the possibility to work with elevated current densities the time of electroplating may, in comparison with the known processes, be shortened considerably. Silver platings which hitherto needed 3–4 hours operation time may now be carried out in the fifth or tenth part of the usual time.

The coatings according to my invention show an excellent hardness. Comparative tests have shown that silver coatings according to my invention have a Brinell coefficient of hardness of about 90–100, whilst silver coatings deposited according to the hitherto known processes show only a Brinell hardness of about 30–40.

The abrasive hardness of the silver coatings was more than twice as great as the abrasive hardness of coatings manufactured according to the former processes.

The extreme hardness of the silver coatings according to my invention involves a lesser abrasion and a better conservation of the brightness.

The objects treated in accordance with my invention emerge from the electroplating baths with an excellent brightness which needs no after treatment such as scratching, polishing with steel or the like. In consequence thereof, losses of material are avoided and working hours saved. Furthermore, the intermediate scratching treatment during the plating process and the losses caused by rinsing may be omitted. It is only necessary to slightly polish with a felt disc in order to produce the final high brightness.

The utilization of selenium or tellurium in silver electroplating, for instance, for knives, forks and spoons, is absolutely without any danger for the human nutrition as the brightening agents cannot be detected in the silver coatings.

One modification of my invention also includes the addition of other brightening substances to the bath besides the soluble selenium or tellurium compounds. These further additions are, for instance, sulphur compounds such as carbon disulfide, thio urea, ammonium thiocyanate, sodium thiosulfate and the like. The bath solutions may contain these sulphur compounds in quantities of, for instance, 0.1–50 grs/litre. The brightness of the metallic coatings may thereby be increased to a certain degree. Moreover, organic brightening substances, preferably aromatic aldehydes and their derivatives, as for instance, piperonal, anisaldehyde, cumarin and the like may be added to the bath solutions. In using such additional substances excellent bright coatings may be deposited over a wider range of current densities than otherwise possible. This exerts a favorable influence on the formation of the metallic coatings as it is possible to produce practically uniform thick and beautiful coatings as even on concave objects like spoons.

In electrodeposition baths which besides seleni-

um and tellurium cyanides contain also other additions such as sulphur compounds or organic brighteners or both of them I may work also with current densities up to 4 amp/dm². The electrolysis is preferably carried out at ordinary temperature with slight agitation of the bath.

Further investigations have shown that proteolytic products condensed with organic acids, especially fatty acids, known under the trade marks "Lamepon" A, B, D and C or Lamephan, are excellent brightening agents for alkalicyanide electrodeposition baths, particularly baths for the electrodeposition of silver, gold, copper, zinc, cadmium and brass coatings. Perfect effects may be obtained if condensation products of the above mentioned type kind are added as brightening substances to the plating baths containing selenium and tellurium. The coatings resulting from these baths show a special brightness. It is particularly advantageous to use these brightening additions in the treatment of concave or shaped articles, such as, for instance, spoons and also in the treatment of highly polished articles. Through the simultaneous presence of selenium and/or tellurium compounds and of proteolytic products condensed with organic acids the brightening effect is improved over a wider range of the current density in such a degree that also in the deepest points of concave objects a uniform brightness is attained and dull places in these hollows avoided. Baths according to my invention are also suitable for the manufacture of stronger coatings. It is possible to produce bright layers of a thickness of 4 grs/dm² and even more, if polished bases are used.

The amount of the brightening condensation products in the baths may vary in a definite range: 1 litre of a baths solution may contain, for instance, about 1–10 grs, preferably 0.5–1 g of the above mentioned additions.

Instead of alkali cyanide baths the well known thiocyanate baths may also be used, for instance, such which contain potassium silver thiocyanate or sodium silver thiocyanate in addition to free alkali thiocyanate.

Examples

1. The objects to be electroplated, for instance, knives, forks and spoons are degreased and immersed in a bath of the following composition:

Silver as sodium silver cyanide	grs	30
Free potassium cyanide	grs	30
Potassium carbonate	grs	30
Selenium as sodium selenite	grs	2
Sodium thiosulfate	grs	0.5
Water	liters	1

The cathodes are slightly agitated and the electrodeposition is carried out at 2.5 amp/dm², 1.6–1.8 volt during 24 minutes at room temperature. Current efficiency anodically and cathodically 100%. A silver coating of 4 grs. silver per dm² which is equal to a 90% silverplating was obtained. After rinsing the surface of the treated object is smooth and bright. Brinell coefficient of hardness 95. If desired, the objects to be electroplated are degreased and may then be dipped in a known way into a solution of mercury salts and mercurized whereupon they are electroplated according to my invention.

2. Instead of the plating bath in Example 1, the bath solution may have the following composition:

Silver as sodium silver cyanide	grs	30
Free potassium cyanide	grs	30
Potassium carbonate	grs	30
Selenium as sodium selenite	grs	2
Sodium thiocyanate	grs	5
Anisaldehyde as a bisulfite compound	grs	1
Water	liters	1

The article to be treated in this bath according to the prescription in Example 1 obtained a high polished silver coating after a time of 30 minutes. Brinell hardness 90.

3. After degreasing the object is brought into the following plating bath:

Sodium cyanide	grs	48
Copper cyanide	grs	30
Sodium carbonate	grs	30
Sodium tellurite	grs	2
Water	liters	1

The electroplating is carried out in 30 minutes with a current density of 1.7 amp/dm² and an agitated cathode. The copper coating is bright, Brinell and scratch hardness far better than with coatings from a usual copper plating bath. The object is rinsed and treated with the felt disc until an excellent brightness is attained.

4. The objects are cleaned and degreased and then dipped into a bath of the following composition:

Silver as potassium silver cyanide	grs	40
Free potassium cyanide	grs	30
Potassium carbonate	grs	30
Selenium as sodium selenite	grs	5
Sodium thiosulfate	grs	0.5
Lamepon A	grs	1
Water	litres	1

The plating is carried out at room temperature with slightly agitated cathodes, current densities of 3 amp/dm² with 1.6–1.8 volt during a period of 20 minutes. The current efficiency is anodically and cathodically 100%. The silver deposit obtained is bright and has a thickness of 4 grs/dm². Brinell hardness 95. The polished obtained articles show also in the hollows of the article a uniform smooth and bright coating.

5. A bath of the following composition:

Silver as potassium silver cyanide	grs	30
Free potassium cyanide	grs	30
Potassium carbonate	grs	30
Selenium as sodium selenite	grs	5
Sodium thiocyanate	grs	5
Lamephan	grs	1
Water	litres	1

is used. Here the object is treated nearly 30 minutes. The silver coatings are everywhere uniform and perfectly bright Brinell hardness 90.

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