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3,679,553

## MIRROR BRIGHT SILVER PLATING

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5 Claims

### ABSTRACT OF THE DISCLOSURE

A silver cyanide plating bath for electroplating a mirror bright silver deposit is improved by the addition of highly sulfated castor oil containing at least about 10% combined  $\text{SO}_3$ .

### BACKGROUND OF THE INVENTION

Present commercial electrolytic silver plating processes most commonly use baths composed of silver cyanide, an alkali metal cyanide, and an alkali metal carbonate in a water solution. The source of the silver may be a soluble silver anode which is dissolved in the alkali metal cyanide. The deposits from such solutions are generally required to be bright, ductile, smooth, fine-grained, and relatively hard. Depending on the most desired properties for a given purpose, one or more substances may be added to the bath. The baths must, of course, have long life, operate at suitable current densities, and preferably they should be clear, water-white solutions so that the operator can observe the parts in the bath.

For many purposes the silver deposit must have a bright finish. At one time this could only be achieved by buffing or burnishing the non-lustrous deposits formed from the silver cyanide baths. This procedure is costly, wasteful of metal, and time consuming. Continued efforts were made through many years to develop a bath from which a suitable mirror bright silver deposit could be formed. A particularly effective bath that has been proposed is described in U.S. Pat. No. 2,735,808, which discloses that silver cyanide plating baths can be improved by the addition of a soluble antimony-polyhydroxy complex compound as a brightening agent. Such additives produce uniform mirror bright silver deposits over a wide range of current densities, and they are stable on standing and during the plating process.

Although the silver plating baths of the aforesaid patent are a marked improvement over the baths previously known in the art, efforts have continued to further enhance the brightness of the deposit.

It is known that wetting agents can be used to improve the brightness of a deposit. Among the known detergents are sulfated fatty acids, ricinoleic acid and sulfated esters and salts thereof. For example, Turkey red oil, which is a product of the reaction of cold sulfuric acid on castor oil has been used as an additive in plating baths. Castor oil is mainly a glyceride ester of ricinoleic acid. Often these wetting agents have been used in combination with sulfide additives. The addition of the sulfides has not proved satisfactory with or without the sulfated acids, esters and soaps in that they lacked stability. It has further been found that the addition of the sulfated compounds such as sulfated castor oil, produced a harmful effect. To some extent they enhance the brightness of the finish;

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on the other hand they reduce the limiting current density, and the solutions become cloudy more rapidly than when they are not present.

The limiting current density is the current density at which there is a tendency of dullness or burning to occur at the protruding or high current density areas of objects being plated. The objects then must be buffed or polished to bring them up to the desired brightness in these areas. By reducing the current density the process becomes more costly because it takes a longer time for the plating to be completed.

With respect to the cloudiness this is caused by salting out of the wetting agent when carbonates build up to a certain concentration in the bath. In all cyanide type electroplating solutions carbonates build up and in most baths it has been found that the carbonates at a certain concentration deleteriously affect the electroplating operation. The baths of aforesaid U.S. Pat. 2,735,808, have the advantage that as much as 25 oz./gallon of carbonates can build up without materially affecting the operation. Yet when sulfated castor oil such as Turkey red oil was added, despite the enhanced brightness this additive was not satisfactory in that cloudiness appeared when the carbonate value reached only 12 to 15 oz./gallon. This clouding is not actually harmful to the plate, but it presents a serious disadvantage in that the operator cannot observe the objects in the tank and therefore is not able to make the current adjustments to avoid burning or dulling of the work.

It is accordingly an object of this invention to improve the brightness of the silver deposits from silver plating baths without detrimental consequences of limiting the current density or a more rapid clouding of the solution. It is a further object to produce a silver cyanide plating bath which has long life. It is another object to provide a method of plating articles which have a mirror bright finish through a complete range of flash to heavy deposits. A still further object is to provide a silver plating solution which is stable, produces no deleterious decomposition products and is operable to produce uniform mirror bright silver plate requiring no further burnishing or polishing. Other objects and advantages of the present invention will be apparent from the description and examples following.

It has now been found that the objects are achieved by adding to the plating solution highly sulfated castor oil containing at least about 10% combined  $\text{SO}_3$ .

As noted above, sulfated castor oil had been tried and found to be limited in its effectiveness. But it is important to note that the sulfated castor oil and other commercially available substances, such as Turkey red oil, which have as the main active ingredient sulfated castor oil, which have been used heretofore as the additive contained at most 5-7% combined  $\text{SO}_3$ . No reference is made in the previous patents or literature on the plating baths to the degree of sulfation of the additives used. Obviously it was not considered to be a relevant factor. It is also significant that, in fact, the results were poor. Contrastingly, when a highly sulfated castor oil is added in accordance with this invention, the clouding effect due to salting out is completely eliminated, and further such additives extend the limiting current density about 10-20%.

## THE INVENTION

In accordance with this invention a silver cyanide mirror bright plating bath is improved by the addition of highly sulfated castor oil containing at least about 10%  $\text{SO}_3$ .

It will be noted that the theoretical maximum of combined  $\text{SO}_3$  in sulfated ricinoleic acid is about 22%. Castor oil is mainly a glyceride ester of ricinoleic acid. The highly sulfated castor oil, in accordance with this invention, contains at least about 10% combined  $\text{SO}_3$  which is considerably greater than the 5-7% combined  $\text{SO}_3$  in the sulfated castor oil used heretofore.

The highly sulfated castor oil is used as an auxiliary brightening agent in silver cyanide baths for producing bright silver deposits in order to further enhance the brightness of the deposit. It has been found that in addition to enhancing the brightness of the silver deposits, the additive has the further benefits of extending the limiting current density and extending the life of the bath with respect to clarity of the bath as compared with plating solutions containing the sulfated castor oils which are not highly sulfated.

Even small amounts of the highly sulfated castor oil are effective in the plating bath. For example, it may be added to the bath in the amount of about 0.5 to 10 grams per liter of plating solution.

## THE PLATING BATHS

The silver cyanide plating baths to which the highly sulfated castor oil is added to enhance the brightness of the deposit contain alkali metal cyanide and alkali metal carbonate. Preferably the alkali metal is potassium or sodium, but other alkali metals, cesium, rubidium, and lithium, may also be used.

In a preferred embodiment the bath is free of tartrate and contains in addition a soluble complex of antimony and a polyhydroxy aliphatic compound as a brightening agent. This bath is disclosed in the aforementioned U.S. Pat. No. 2,735,808, which gives as suitable examples of the polyhydroxy aliphatic components of the complex glycerine, ethylene glycol, sorbitol, and erythritol. It was found that the straight chain polyhydroxy aliphatic compounds preferably are those wherein the hydroxy groups are attached to consecutive carbon atoms. Also, the preferable compounds are those wherein there are as many hydroxy groups as there are C atoms and also those having from two to six C atoms.

It has been stated above that the antimony is added to the bath in the form of a soluble complex, e.g. potassium-antimony-erythritol complex. However, the exact stoichiometrical relationship of the elements of the complex has not been determined, nor whether mixtures of complexes of these elements are present. Nevertheless, the presence of the several elements in a soluble complex form is all that is required for the electrolyte to perform its desired function. The relative proportions by weight of the complex are: 1 part antimony, 1-6 parts of the straight chain polyhydroxy aliphatic compound and 1-4 parts of an alkali metalhydroxide.

All of the above mentioned complexes are prepared in a similar manner. For example, to prepare a potassium-antimony-glycerol complex there is added 48 g. of glycerol, 24 g. of potassium hydroxide and 50 ml. water to 10 g. of antimony trioxide. The mixture is then heated to boiling until complete solution takes place, after which the volume is brought to 200 ml. Such a solution will contain 0.04 g. antimony per ml. The antimony content may be adjusted to almost any concentration, but it has been found convenient to make it up to the above value since for every ampere hour used in the electroplating process 1 ml. of the antimony concentrate is required.

Also, for example, a sodium-antimony-glycerol complex for use with baths containing sodium salts may be prepared as follows: To 10 grams of antimony trioxide, there are added 48 g. of glycerol, 17 g. of sodium hy-

droxide and 50 ml. of water. The mixture is boiled until complete solution takes place and is then diluted to 200 ml. with water.

It was noted above that this preferred bath is free of tartrates. It has found that when no tartrates are present the antimony content can be decreased to as low as 0.01 gram per liter (0.0015 ounce per gallon) while still obtaining mirror bright results. The use of high Sb content tends to embrittle the plate, especially if thicker plates are made. However, with higher silver content the Sb content can be increased and as much as 5 grams per liter of Sb has been used with success. Also, it was found that theoretically there is no upper limit to the antimony content if one is willing to increase the silver content beyond commercially practical values. Preferably, however, it is here recommended that the Sb content be kept within the range of about 0.2 g./liter to about 5.0 g./liter.

Typically the preferred baths contain about 17.8 to 48 grams per liter of silver as potassium silver cyanide, about 75 to 115 grams per liter of free or uncombined alkali metal cyanide, and about 15 to 150 grams per liter of an alkali metal carbonate (based on potassium as the alkali metal ion), 7.5 to 150 grams per liter of glycerine, 0.3 to 5.0 grams per liter of antimony.

In general the process of this invention involves operating a bath at conventional silver plating temperatures ranging from about 20° to 35° C., but most conveniently at about 25° to 28° C. The pH values for the bath range from about 11.5 to 12.5, the optimum value being about 12.0 to 12.3. The cathodic current densities to be used are generally about 5 to 40 amperes per square foot. Selection of the most suitable current densities depend, for example, on the temperature, the degree of solution agitation, and the composition of the bath. Higher temperatures and more rapid agitation permit the use of higher current densities. In the course of operation the antimony may be replenished in the form of a complex or by anodic dissolution from a soluble silver antimony or antimony anode. The highly sulfated castor oil is lost by simple drag-out and additions are made from time to time.

Using a solution according to this invention, the bath has almost water white clarity so that one can watch the work in process of being plated. It is possible when electroplating with the above described solutions to purify by filtration through activated carbon while maintaining operation with no appreciable loss of brightener. Also, the solution should be agitated or the work to be plated should be moved.

The term "mirror brightness" is used herein and the following considerations are set forth in order to define this term as clearly as possible. It is well known that if a surface is perfectly plane, mirror-like reflection is obtained. According to the wave theory of light, a surface reflects like a plane surface as long as there are no elevations or depressions in it which have dimensions exceeding a small fraction of the wavelength of light. For a given degree of roughness, it also follows that the regularity of the reflection depends not only on the wavelength of the light but also on the angle of incidence. The smoothness of the surface is therefore best tested with light falling on it at nearly grazing incidence. This may be seen by examining a plate which is just on the border line of being fully bright. When looked at in the usual way, it seems bright, but if it is held so that it can be viewed by light falling on it at nearly grazing incidence, it shows a faint haziness or cloud. Perfectly bright plates, though, do not show this cloud. "Mirror brightness" is generally measured by the percent of diffuse reflection. Results obtained with the above described solutions showed mirror brightness without cloudiness at every angle, with no measurable diffuse reflectivity.

As has been pointed out, the solution of this invention enables the electroplating of silver on an object with a mirror bright finish, which is acceptable to the trade as silver plate. If it is desired to obtain a silver alloy plate,

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silver anodes containing various percentages of metals such as antimony, bismuth or tin may be used.

Even when the underlying metal has a surface which is dull but has a smooth finish to begin with, by the use of solutions as described above, the surface becomes more and more bright as the plating proceeds and the final appearance is greatly improved if sufficient thickness of deposit is applied, whereas the usual result gives a rougher and more matte finish.

#### Example 1

Two liters of a silver plating solution are prepared containing:

	G./l.
Silver cyanide .....	55
Potassium cyanide .....	115
Potassium carbonate .....	15
Potassium-antimony-glycerol complex .....	1.5
Glycerol .....	15

The solution is divided into two equal portions of 1000 ml. each, one labeled Solution A, the other Solution B.

To Solution A is added 2 ml. of Parapon SA, an anionic surfactant (product of the Arkansas Co. Inc. of Newark, N.J.), which is essentially an aqueous solution containing 36 to 37% sulfated castor oil having about 14 to 16% combined  $\text{SO}_3$ .

To Solution B is added 2 ml. of Turkey red oil, an aqueous solution containing 50% sulfated castor oil having about 3 to 5% combined  $\text{SO}_3$ .

#### Example 2

This example illustrates the performance of Solution A and B under comparable plating conditions. The operating conditions were as follows:

pH .....	12.3
Temperature .....	27° C.
Agitation .....	Moderate

Using identical conditions with respect to relative positions of the silver anode and the cathode, temperature, and degree of agitation, polished cathodes of brass 1" by 3" were first given a strike in a conventional silver strike bath and then plated, one in Solution A and the other in Solution B. The current density in each case was increased at intervals from 7.5 amperes per sq. ft. to 37.5 amperes per sq. ft. In both cases the deposit obtained was mirror bright up to a current density of 30 amperes per sq. ft. In the case of Solution B on further increasing the current density to 37.5 amperes per sq. ft. the edges of the cathode showed burning and dullness. In the case of Solution A (containing the highly sulfated castor oil) the edges remained mirror bright at 37.5 amperes per sq. ft.; an improvement of more than 20% over the Solution B (containing castor oil of lower sulfation).

Additions of potassium carbonate to Solutions A and B produced the following results: When a concentration of 13 oz./gal. (97.5 g./l.) of potassium carbonate was reached Solution B (containing the sulfated castor oil with 3-5%  $\text{SO}_3$ ) became cloudy and Solution A (containing the highly sulfated castor oil in accordance with

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this invention) remained crystal clear. Further additions of potassium carbonate up to 25 oz./gal. (187 g./l.) were made to Solution A and the solution remained perfectly clear.

What is claimed is:

1. An electroplating bath for depositing bright silver deposits comprising a tartrate-free alkaline aqueous solution containing about 17.8 to 48.0 grams per liter of silver as potassium silver cyanide, from about 75 to 115 grams per liter of an alkali metal cyanide, from about 15 to 150 grams per liter of an alkali metal carbonate, from 0.3 to 5.0 grams per liter of antimony as a soluble complex of an alkali metal, antimony and a straight chain polyhydroxy aliphatic compound, from 7.5 to 150 grams per liter of a straight chain polyhydroxy aliphatic compound, and 0.5 to 10.0 grams per liter of a highly sulfated castor oil, said sulfated castor oil containing at least about 10% to 16% of combined  $\text{SO}_3$ .

2. An electroplating bath of claim 1 wherein the sulfated castor oil contains at least about 14% combined  $\text{SO}_3$ .

3. An electroplating bath according to claim 1, wherein the polyhydroxy aliphatic compound is glycerine.

4. In a process for electrodepositing bright silver, which comprises electrolyzing a tartrate-free alkaline solution containing about 17.8 to 48.0 grams per liter of silver as potassium silver cyanide, from about 75 to 115 grams per liter of an alkali metal cyanide, from about 15 to 150 grams per liter of an alkali metal carbonate, from 0.3 to 5.0 grams per liter of antimony as a soluble complex of an alkali metal, antimony and a straight chain polyhydroxy aliphatic compound to impart brightness to the silver electrodeposit, from 7.5 to 150 grams per liter of a straight chain polyhydroxy aliphatic compound, said complex being formed by heating to boiling an aqueous mixture of 1 part antimony compound, 1-6 parts polyhydroxy aliphatic compound, and 1-4 parts alkali metal hydroxide until complete solution is obtained, the improvement of adding to the bath as an auxiliary brightening agent from 0.5 to 10.0 grams per liter of a highly sulfated castor oil, said sulfated castor oil containing at least about 10% to 16% combined  $\text{SO}_3$ .

5. The process of claim 4 wherein the bath is operated between about 20° to 40° C. with a cathode current density of 1 to 40 amperes per square foot.

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