This invention relates to the art of electrodeposition and particularly to compositions, baths, and processes for the electro-deposition of indium. In certain of its more specific aspects it relates to the electro-deposition of indium together with another metal, and in certain of its broader aspects it relates to the joint deposition of a plurality of metals.

Although indium can be deposited from various of its salts by electrolytic action, difficulties are experienced in practice which make most of such salts unsuitable for electro-plating of commercial articles. In ordinary practice a bath composed of indium cyanide solution with various addition agents has been used to the exclusion of others. Even this bath, however, is unsatisfactory in several respects, especially in the poisonous character of the salt and the fact that the bath becomes dark and opaque so that one cannot see the work during the plating operation.

It is, therefore, one object of the invention to provide a better bath and plating process which will be free from these objections. It is an object to provide for the plating of indium without the use of highly poisonous chemicals. It is an object of the invention to provide a plating bath and process by which the bath may be kept clear and transparent so that the work can be kept under observation at all times. It is also an object of the invention to provide a plating bath and method which will take indium from metallic anodes and deposit it on the articles being plated without substantial deterioration of the bath.

Another object is to provide a plating bath which, although capable of plating indium through the bath from anode to cathode, will not dissolve the anodes when they are left in the bath without passage of current. Another object is to provide a bath and process for plating indium which has good throwing power, gives a dense electro-plate of high quality and in general meets the requirements of commercial use. Still another object is to provide a bath and method well adapted to co-deposition of indium with other metals. Another object of the invention is to provide a composition which can be prepared under fully controlled conditions of chemical manufacture and furnished to platers for making of baths by simple mixing with water, whereby to eliminate many sources of trouble due to improper composition of plating baths.

In accordance with the invention, these objects are achieved by use of compositions for the plating bath containing the sulfamate radical --SO₃NH₂ which forms an anion in the bath for transfer-ring the indium from anode to the articles being plated at the cathode. The bath should be kept at room temperature to avoid excessive hydrolysis of the sulfamate acid. It should be maintained at a pH below about 3.5 and should not exceed 3.8 at the outside unless certain addition agents are present. Sufficient sulfamate ion should be present to carry the indium, but other anions compatible with the various ingredients of the bath may be present. This permits the supplying of indium to the starting composition in any of a variety of compounds.

The indium may be introduced into the bath or bath-forming composition in the form of the hydroxide or any salt of which the anion would not be incompatible with other ingredients of the bath and would not objectionably attack the anodes or cathodes. It may, for example, be introduced as indium sulfamate, chloride, bromide, sulfate, etc. If the composition is to be stored or packaged dry, the hygroscopic salts should be avoided. In such case indium sulfamate or other salt of an organic acid, e.g. indium carbonate, indium acetate, indium formate, can be used. It is likewise possible to use acids other than sulfamate acid for pH control.

The concentration of the indium sulfamate may be widely varied. For best results the concentration of indium (expressed as equivalent weight of indium metal regardless of the particular salt used) should be about 20 to 60 grams per liter, with the optimum about 30 grams per liter. As much as 130 and as little as 10 grams per liter, however, will give an effective plating. The use of certain organic acids, or their salts, for example, maleic acid, alkali malates, alkali tartrates, or tartaric acid, holds the indium in solution if the conditions in the bath are such as to cause incipient precipitation. With proper concentration of these organic acids or salts in the bath it may be operated at pH values ranging from 0-7 or above the normal precipitating point for indium hydroxide. The concentration of sulfamate ion (expressed as equivalent weight of sulfamate acid whether present as acid, salt, or ion) should for best results be about 226 grams per liter, with the optimum for ordinary commercial conditions about 226 grams per liter. As much as 780 and as little as 98 grams per liter may be present and still give a useful plating of indium. The presence of other anions, e.g. Cl, Br, SO₄, etc., insofar as they are not inconsistent with other ingredients of the bath, do not adversely affect the plating bath.

The indium may also be supplied initially to a
3 strongly acid bath directly from an indium-containing anode by passing a current through the bath from an indium anode. It is better, however, to use a composition which provides indium ions immediately. In any case, the amount of indium deposited from the bath by electrolysis will be effectively replaced from such an anode during a plating operation; and efficiencies at both cathode and anode of approximately 100% are attainable in practice by this invention. The anode may be indium, or a mixture or alloy of indium and one or more of zinc, copper, cadmium, tin, silver, gold; or an indium anode and an anode or anodes of one or more said metals may be employed jointly.

Various sources of —SO$_3$NH$_2$ are satisfactory, among them, sulfamic acid, indium sulfamate, sodium sulfamate, potassium sulfamate, ammonium sulfamate, aluminum sulfamate, and, in general, sulfamates of metals higher in the E. M. F. series than indium.

Addition agents may be used, as well understood in the art of electro-plating. It is particularly advantageous to use addition salts, especially sodium sulfamate, and various organic compounds, especially nitrogen-containing compounds such as amines, which form very complex series with metals, such, for example, as triethanolamine, ethanalamine, diethanolamine. Dextrose and other saccharides may be used with advantage in the baths of our present invention. Triethanolamine and dextrose in particular are effective to improve the throwing power of the bath and the fineness and density of the deposit. Too much of these latter agents, however, has been found to increase the tendency to gassing. Wetting agents improve throwing power, but many of the common wetting agents so far reduce the rate of deposition as to be regarded as objectionable. The use of addition salts, especially the alkali metal (including ammonium) salts improve the throwing power, giving a more regular deposit, and by increasing the available ions may facilitate co-deposition of metals where one has greater affinity for the sulfamate ions than the other.

A composition such as contemplated by the invention is normally utilized in aqueous solution, but can be used in other ionizing solvents, e.g. the lower acid amides. It is an important feature of this invention, however, that all of the ingredients of the bath except the solvent can be furnished in dry form as a commercial product, which can be mixed with solvent by unskilled help, and the proper specific gravity can be quickly checked with a hydrometer. When the bath is to be thus used as a dry composition, it is advantageous to avoid hygroscopic compounds; and since most of the sodium salts of inorganic acids are hygroscopic, there is an important advantage in the use of indium sulfamate as such in the dry composition.

Indium sulfamate, when used, provides both SO$_3$NH$_2$ ions and the initial In ions in the bath. It is essential that some free acid be present to hold the pH down. The optimum acidity of the bath is between pH 1.0 and 1.5, and excellent results are attained with pH as high as 2.0. A critical point is reached at pH 3.5 to 3.8 beyond which point the bath is no longer satisfactory in the absence of such addition agents as malates, tartrates, etc. It is well in most cases to keep well on the acid side of this critical point. It is advantageous, in many cases, in the absence of such addition agents as malates, etc., to use excess sulfamic acid to give such pH, especially where a dry composition is furnished and where one is co-plating with lead, silver or other metal which would be precipitated or attacked by other acids. For example, as hydrochloric, hydrobromic, sulfuric, etc., is satisfactory in other cases, is within the scope of the invention, and has some distinct advantage.

The composition of our invention may be first assembled in the bath (with the ingredients more or less ionized); or it may be provided as a concentrate solution to be diluted for use, or it may be packaged and distributed as a dry composition to be dissolved in an appropriate amount of water for making up the plating bath.

As an example of this invention, a plating bath embodying our invention may be prepared by dissolving 65 gm. of NaOH in 700 cc. of water, cooling and adding slowly with stirring 207 gms. HSO$_3$NH$_2$ being careful to avoid overheating. To this solution add 57.6 gms. InCl$_3$ (equivalent to about 30 gms. indium metal). This may be added as a slightly acid aqueous solution of InCl$_3$ of the concentration 1.05 grams InCl$_3$ per ml. liter. To this solution is then added 2 cc. triethanolamine and 6 grams dextrose. Water is then added to make a total volume of one liter and the resulting solution stirred thoroughly to effect complete solution and mixing of all constituents. The thus combined solution is filtered and is ready for use as a plating bath. For any required volume of bath the amounts given above are all multiplied by the number of liters of bath required. For example, the amount of free hydrochloric acid in the indium chloride, the baths made up in this way from commercial materials may have slightly different pH values. With the proportions set forth in the above example pH values may range from 1.0 to 1.5, however, pH is not critical in this range, which seems to be an optimum range.

A 2-liter bath of the above composition which tested pH 1.4, was used to immerse an indium anode and a copper cathode, each having an area of 20 sq. in. A current of 1 amp. was passed through the bath 15 hours at room temperature, after which the cathode showed a gain of 21.138 gms. or 23.48 mg./amp. min. The anode showed a loss of 22.0244 gms. or 24.47 mg./amp. min. The difference in cathode gain...
that of indium cyanide baths, and was far superior to other acid type indium baths. Indium anodes used with this bath are not appreciably attacked and a considerable quantity of indium is recoverable as a cathode deposit. Anode solutions of indium cyanide baths are gossipy and to be avoided. Gassing may be desirable by agitation, thorough cleaning (electrolytic) of the cathode, or by leaving for a few seconds at low current density before raising the current density to the final value. Holes in the deposit may be avoided by high current density and cleaning the cathode, they would leave unplated spots. After a flash of indium has been deposited, the bubbles do not cling to the piece, and very little gassing occurs even at relatively high current densities. A coating of lead has a similar deterrent effect on gassing.

Current densities ranging up to 100 amp. per square foot give satisfactory results. 20 amp. per sq. ft. has given optimum results under ordinary plating conditions.

Although in commercial practice addition agents will ordinarily be used, a good plating with indium can be obtained by a simple solution of indium sulfamate with excess sulfamic acid and without other ions remaining from production of the bath. As one example of this indium chloride may be added to strong aqua ammonia in proportion of 1 mol. of the indium chloride to 3 mols. of ammonium hydroxide, and to this is added with stirring 3 mols. of sulfamic acid. The chloride ion seems to aid the solution of the indium hydrogen precipitate and serves as part of the excess acid to maintain the required acidity in the plating bath.

The resulting solution may be packaged as a concentrate which when diluted to a desired concentration, e.g., to 150 or even 10 grams per liter of indium, can be used effectively for plating indium from indium anodes.

Instead of aqua ammonia, other alkali metal hydroxides may be used especially sodium hydroxide or potassium hydroxide.

A similar bath may be made without the addition of chlorine, merely adding three mols. of sulfamic acid for each mol. of indium chloride either in concentrated solution for distribution or in a dilute solution for the actual plating bath. All products of the reaction may be left in solution.

Such a bath of 30 gm. per liter strength gives approximately 100% anode and cathode efficiencies, no sludging at the anode and no substantial dissolution of the anode when standing in the idle bath. The pH of the bath as first made is, for example, in a particular case using commercial chemicals, 2.48 and after plating for 10 hours at 10 amperes per square foot was pH 2.5. Throwing power in this bath was excellent.

Where indium sulfamate is to be supplied to the plating composition or otherwise used as such, it can be readily made by precipitation from an amorphous hydroxide of a solution of indium salt with a strong base, the corresponding salt of which is soluble. Thus three mols. of sodium hydroxide may be added to a water solution of one mol. of indium trichloride. Indium hydroxide precipitates and can be separated from the solution of sulfamic acid in equivalent amount (i.e., three mols.). The indium sulfamate thus formed can be used directly in solution or the solution can be evaporated under vacuum, e.g., at a temperature below about 60°C. to recover the solid salt.
with the complex plating of other metals in other baths, apply here also. The sulfamate ion has been found especially well adapted for such co-deposition.

All parts and proportions herein are by weight unless otherwise specified.

Although certain specific examples of this invention and its application in practical use and also certain modifications and alternatives are given herein, it should be understood that these are not intended to be exhaustive or to be limiting of the invention. On the contrary, these illustrations and the explanations herein are given in order to acquaint others skilled in the art with this invention and the principles thereof and a suitable manner of its application in practical use, so that others skilled in the art may be enabled to modify the invention and to adapt it and apply it in numerous forms, each as may be best suited to the requirement of a particular use.

What is claimed is:

1. An electroplating bath containing as essential electroplating ingredients the anion \( \text{SO}_3\text{NH}_2 \) and the cation \( \text{In} \) in an ionizing solvent, the pH of said bath being below about 3.5, and the concentration of indium being at least 20 grams per liter and the concentration of sulfamate radical being at least 167 grams per liter.

2. An electroplating bath containing as essential electroplating ingredients the anion \( \text{SO}_3\text{NH}_2 \) and the cation \( \text{In} \) in an ionizing solvent, the pH of said bath being below about 3.5, the concentration of indium in said bath being approximately between 10 and 130 grams per liter.

3. An electroplating bath containing as essential electroplating ingredients the anion \( \text{SO}_3\text{NH}_2 \) and the cation \( \text{In} \) in an ionizing solvent, the pH of said bath being below about 3.5, the concentration of indium in said bath being approximately between 20 and 60 grams per liter.

4. An electroplating bath containing as essential electroplating ingredients the anion \( \text{SO}_3\text{NH}_2 \) and the cation \( \text{In} \) in an ionizing solvent, the pH of said bath being below about 3.5, the concentration of indium in said bath being approximately 30 grams per liter, and the concentration of the \( \text{SO}_3\text{NH}_2 \) being greater than 167 grams per liter expressed as the equivalent of sulfamic acid whether present as acid, salt or ion.

5. An electroplating bath containing as essential electroplating ingredients the anion \( \text{SO}_3\text{NH}_2 \) and the cation \( \text{In} \) in an ionizing solvent, the pH of said bath being not greater than 2.0, and the concentration of indium being at least 20 grams per liter and the concentration of sulfamate radical being at least 167 grams per liter.

6. The process of electrodepositing indium which comprises passing a plating current from an indium-containing anode through a bath in which indium is the essential active cation, alkali metal is present as a secondary cation, and sulfamate is the essential active acid ion, and in which are also substantial but smaller amounts of an amine which forms heavy complexes with metals and maintaining the pH of said bath approximately between 0.75 and 2.0, the concentration of indium at approximately 30 grams per liter, and the temperature at approximately room temperature.

7. The process of electrodepositing indium by passing a plating current through a cathode and an electrolytic bath in which indium is the essential active cation and the essential active amion is \( \text{SO}_3\text{NH}_2 \), while maintaining said bath at pH below 3.5 and temperature below 80°C.

8. The process of electrodepositing indium as defined in claim 7 in which the concentration of indium in the bath is maintained between approximately 20 and 50 grams per liter calculated as metallic indium.

9. The process of electrodepositing indium as defined in claim 7 in which the bath contains lead and indium as the essential active cations and sulfamate as the essential active anion.

J. ROBERT DYER, Jr.
TIMOTHY J. ROWAN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>197,433</td>
<td>Walter</td>
<td>Nov. 20, 1877</td>
</tr>
<tr>
<td>1,955,251</td>
<td>Murray et al.</td>
<td>July 3, 1934</td>
</tr>
<tr>
<td>2,310,503</td>
<td>Cupery</td>
<td>May 11, 1943</td>
</tr>
<tr>
<td>2,358,029</td>
<td>Phillips et al</td>
<td>Sept. 12, 1944</td>
</tr>
</tbody>
</table>