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3,004,903

ANODIZING METHOD

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No Drawing. Filed Aug. 29, 1946, Ser. No. 693,805

7 Claims. (Cl. 204-38)

This invention relates to methods of forming silver chloride layers on a base of metallic silver particularly for use as electrodes for electric cells.

Silver chloride electrodes have been proposed as cathodes in electric cells using various electrolytes and anodes. It has been proposed to form such cathodes by anodizing a body of silver in an aqueous solution containing chloride ions for a sufficient time to produce a layer of silver chloride of the desired thickness on the silver body. Since silver chloride itself is a substantially non-conductive substance, the effective conductivity of such a layer of silver chloride is dependent upon the looseness or porosity of the layer or, in other words, upon the degree to which the conductive electrolyte is able to penetrate through the nonconductive silver chloride layer and maintain contact with the conductive silver base beneath. It is obvious that, as the thickness of the silver chloride layer increases, the effective conductivity of the layer decreases so that a higher and higher voltage must be applied during the course of the anodizing procedure in order to maintain the initial current density and the initial anodizing rate.

When a reasonably heavy layer of silver chloride is to be deposited from a single chloride solution, it is often impossible to complete the anodizing operation within a desirably short time using a reasonable voltage since at the available voltage the current density falls off to a small value during the latter part of the operation. It had been found prior to the present invention that the effective conductivity of the silver chloride layer could be increased by maintaining the anodizing bath at an elevated temperature, such as about 75° C. or 80° C., and by maintaining a small proportion of nitrate ions in the bath. It was also found that the conductivity of the deposited layer increased with increasing acidity of the bath.

According to the present invention, the effective conductivity of the deposited silver chloride film, and therefore the rate at which anodizing may be accomplished, is increased by carrying out the anodizing operation in an aqueous chloride bath containing a relatively small proportion of iodide or bromide ions, that is, halide ions having a molecular weight greater than chlorine. When nitrate as well as iodide or bromide ions are present in the anodizing bath, it is possible to carry out the anodizing operation at a substantially lower temperature than was commonly employed previously with baths containing nitrate ions, but no iodide or bromide ions, and still obtain a silver chloride film having a greater effective conductivity. The ability to carry out the process at a lower temperature, for instance, a temperature of about 60° C. to 65° C. as compared to a temperature of about 75° C. to 80° C. is of considerable value since the corrosive effect of the anodizing bath upon the metal equipment which it is used is very much greater at the more elevated temperatures.

Since iodide ions are much more effective than bromide ions in increasing the effective conductivity of the deposited silver chloride layer, the invention will be described below, by way of illustration, in terms of the process employing iodide ions.

The effect of the addition of iodide ions to an anodizing bath containing nitrate ions is shown in Table 1 below. The values shown in this table were obtained by suspend-

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ing a silver screen as an anode in an aqueous solution having a chloride ion concentration of .6 mol per liter (obtained by adding 5 percent by volume of a 36.4 percent solution of hydrochloric acid), a nitrate ion concentration of about .008 mol per liter (obtained by adding .052 percent by volume of 69.5 percent nitric acid) and an iodide ion concentration as shown in the table (obtained by adding potassium iodide in the amounts shown in the table). The anodizing bath was maintained at 70° C. and the applied voltage was adjusted periodically so as to maintain the current density at .1 ampere per square inch of screen area. The anodizing operation was discontinued after an amount of silver chloride corresponding to 7.5 ampere minutes per square inch had been deposited. The effective conductivity of the silver chloride layer is indicated by the final voltage which it was necessary to apply to maintain the current density at .1 ampere at the end of the run. It will be noted that when no iodide ions were present it was impossible to maintain the desired current density throughout the entire run with the available voltage since the conductivity of the layer was increased so greatly that it was necessary to apply the full voltage of the generator before the end of the run had been reached.

Table 1

Percent by weight of Potassium Iodide	Mols of Iodide per Liter of Solution	Final Voltage
0	0	19.6 (reached before end of run).
.0003	1.8×10^{-5}	16.5.
.0005	3.0×10^{-5}	6.3.
.0010	6.0×10^{-5}	5.8.
.0020	1.2×10^{-4}	4.4.
.0040	2.4×10^{-4}	4.1.
.0420	2.6×10^{-3}	4.1.

It can be seen from this table that a substantial improvement in the effective conductivity of the deposited silver chloride layer is brought about by the addition of as little as about 2×10^{-5} mols of iodide per liter of solution. The most significant effect is achieved when the concentration of iodide ions is at least about 3×10^{-5} mols per liter of solution. It will be seen that, when a substantial proportion of nitrate ions is present, little is to be obtained by the addition of more than about 2.5×10^{-4} mols per liter of iodide. Obviously, however, larger amounts of iodide may be added if desired, for instance, up to about 6×10^{-3} mols per liter or more.

In anodizing solutions which have been used in previous anodizing operations, a certain amount of silver has passed into solution. The iodide or bromide has its greatest effectiveness in such solutions when present in sufficient concentration that insoluble particles of the resulting silver iodide or silver bromide are colloiddally suspended in the bath, indicating that the solution is saturated with the particular silver halide.

As the concentration of nitrate ions is decreased, the effectiveness of the iodide ions in increasing conductivity of the silver chloride layer is also decreased. Thus, under conditions which were the same as those used in determining the values given in Table 1 except that no nitrate ions were present it was necessary to use a concentration of .1 percent by weight of potassium iodide (corresponding to an iodide ion concentration of 6.0×10^{-3} mols per liter) to achieve a conductivity such that the final voltage was 12 volts. Therefore, although it can be seen that iodide ions may be used in the absence of nitrate ions in order to reduce effectively the final voltage required for anodizing, it is ordinarily desirable that both nitrate and iodide ions be present. The effect of varying nitrate ion concentration is shown in Table 2

below in which the values were obtained under the same conditions as in Table 1 except that the nitrate ion concentration was varied as shown in the table.

TABLE 2

Percent by Volume of 69.5 Percent Nitric Acid	Mols of Nitrate Per Liter of Solution	Percent by Weight of Potassium Iodide	Mols of Iodide Per Liter of Solution	Final Voltage
0-----	0	.013	7.8×10^{-4}	19.2 (reached before end of run).
.002-----	3.0×10^{-4}	.004	2.4×10^{-4}	8.5.
.052-----	8.0×10^{-3}	.004	2.4×10^{-4}	4.1.

In general it is desirable that the nitrate ion concentration exceed about .001 mol per liter. The best results are obtained if the nitrate ion concentration exceeds about .002 mol per liter or preferably .003 mol per liter. Very suitable nitrate ion concentrations are between about .005 mol per liter and about .008 mol per liter. However, concentrations up to about .1 mol per liter or even considerably higher may be employed if desired.

As indicated above, the effective conductivity of the silver chloride layer is dependent upon the temperature of the anodizing bath. It is ordinarily desirable to maintain the temperature as high as is practicable in order to maintain the effective conductivity of the film layer as high as possible. On the other hand, the lowest temperature consistent with a good anodizing rate at a reasonable voltage is desirable in order to avoid excessive corrosion. When both nitrate and iodide ions are present it is possible to achieve the desired anodizing rate at a reasonable final voltage at temperatures in the vicinity of 60° C. at 65° C. At these temperatures, corrosion is not ordinarily a serious problem. Obviously, however, where the corrosive tendencies of the bath and where the loss of water from the bath by evaporation are not serious problems, higher temperatures up to about 75° C. or 80° C. or even higher may be employed. Where a slower anodizing rate or a higher voltage is permissible, it is obvious that a lower temperature down to 50° C. or less may be employed.

The conductivity of the deposited silver chloride layer is also dependent upon the rate at which the deposition of the layer takes place as indicated in Table 3 below. The values in this table were obtained using an anodizing bath which was maintained at 70° C. and which contained initially 5 percent by volume of 36.4 percent hydrochloric acid, .052 percent by volume of 69.5 percent nitric acid and .004 percent by weight of potassium iodide. The current density was maintained in each run at the value indicated throughout the entire run by periodically increasing the voltage.

TABLE 3

Rate of deposition, ampere-seconds per second per square inch:	Final voltage
.075 -----	3.2
.100 -----	4.1
.150 -----	6.0
.200 -----	12.0
.250 -----	18.5

It can be seen from this table that, as the rate of deposition is increased, the ratio of final voltage to current density increases. Therefore, where a limited voltage is available the most rapid anodizing rate is not necessarily obtained by utilizing the highest possible initial rate of deposition since the time advantage gained by the initial high current density may be more than lost because of the resulting low current density when the full available voltage is applied during the latter portion of the run. It is ordinarily more desirable to maintain the current density at a substantially uniform value throughout the anodizing procedure. A current density of about .1 ampere per square inch has been found to

be very satisfactory although obviously the current density is not critical and any reasonable value may be employed.

In order to avoid formation of the silver oxides at the anode the acidity of the bath should be maintained at a pH lower than about 6.5. Best results are obtained if the initial pH of the bath has a value of 2.5 or less.

Since the solubility of silver chloride increases with the chloride ion concentration of the bath it is desirable to maintain the chloride ion concentration at a value at which the loss of silver chloride from the deposited layer into the solution is not excessive. It is, therefore, ordinarily desirable that the chloride ion concentration be not greater than about 1 mol per liter of solution. At a chloride ion concentration of 1 mol per liter the silver chloride remaining deposited on the silver base is about 93 percent of the amount theoretically deposited for the number of ampere minutes passed. Where greater loss of silver chloride into the solution is not objectionable, it is obvious that larger concentrations of chloride ion may be employed. The lower limit of chloride ion concentration is set only by the amount necessary to give the desired conductivity to the anodizing bath. In general, it is desirable that at least .1 mol per liter of chloride ions be present.

The following specific examples are illustrative of particularly suitable conditions for carrying out the process of the present invention.

Example 1

A piece of fine silver screen, which was to be formed into a silver-silver chloride electrode, was lacquered over those portions of its surface to which electrical contact was to be made in the final electrical cell. The screen was then immersed in an anodizing bath maintained at 60° C. and made up of an aqueous solution containing 2 percent by volume of 36.4 percent hydrochloric acid, .02 percent by volume of 69.5 percent nitric acid and .003 percent by weight of potassium iodide. A suitable cathode was immersed in the bath in such position as to afford a substantially uniform current distribution over the screen and the screen was connected as the anode. A voltage was applied across the anode and cathode sufficient to maintain the current density at .1 ampere per square inch over the surface of the screen. As the anodizing proceeded, the voltage was increased periodically by the amount required to maintain the initial current density. After an amount of silver chloride equivalent to 7.5 ampere minutes per square inch had been deposited, about 15 volts were required to maintain the initial current density. At this point the screen was removed from the bath and a new batch of screen was introduced and subjected to the same procedure. Since both nitrate and iodide ions are consumed in the anodizing process, it is necessary to replenish these ions to maintain the solution at its original concentration. For this purpose, .0004 gram of potassium iodide and .007 milliliter of 69.5 percent nitric acid were added after each anodizing operation for each square inch of screen surface anodized. The lacquered portions of the screen, which had been protected from silver chloride formation, were then cleaned mechanically to remove the lacquer, thus exposing the original silver screen over these areas.

Example 2

A silver screen was anodized as described in Example 1 except that the bath was maintained at 65° C. and was made up of an aqueous solution containing 3.5 percent by weight of sodium chloride, .02 percent by volume of 69.5 percent nitric acid, and .003 percent by weight of potassium iodide. The final impressed voltage required to maintain the initial current density of .1 ampere per square inch was between about 12 volts and about 16 volts, depending upon the acidity of the solution.

The silver bases, coated with silver chloride as described

above, are well fitted for the production of cathodes capable of carrying very high current densities, as described and claimed more particularly in the copending applications of H. E. Haring, Serial Nos. 585,417, now abandoned, and 585,418, filed March 29, 1945. These electrodes are prepared by maintaining the anodized body, produced as above, as a cathode in a suitable electrolyte for a time sufficient to cause reduction of a portion of the silver chloride layer to form a large number of narrow, conductive bridges of reduced silver extending from the silver base outward through the silver chloride layer. The anodized and partially reduced electrode is then immersed in a solution of a reducing agent so as to form a thin layer of porous reduced silver over the entire outer surface of the silver chloride layer.

This surface layer of silver connected by the conductive bridges to the silver base forms an exceedingly effective current collecting framework which is responsible for the outstanding current carrying capacity of the electrode. Electrodes of this type have been found useful in the manufacture of batteries designed to develop an extremely high power output for a relatively short period of time particularly when used with weak electrolytes such as sea water and with anodes such as magnesium or zinc.

In carrying out this subsequent treatment of the anodized silver base the cathodizing operation in which the conductive silver bridges are formed may conveniently be carried out in a solution containing about 5 percent of sodium chloride. Obviously, any other electrolyte which does not have a detrimental effect on the silver chloride layer may be employed. The cathodizing operation is usually carried out at or above the current density at which the cathode is intended to be discharged in the cell in which it is employed. This operation is made very brief, usually lasting about four or five seconds, so that only a minimum of the capacity of the electrode is destroyed by reduction of the silver chloride to metallic silver.

In the subsequent surface reducing operation, one of the most effective reducing agents is an aqueous solution of hydroxylamine. Other suitable reducing agents are aqueous solutions of any of the common photographic developers, such as p-aminophenol, o-aminophenol, amidol (2,4-diaminophenol hydrochloride), metol (p-methylaminophenol sulphate), catechol or hydroquinone. The concentrations which are common for photographic developing are suitable and the pH of the solutions should be adjusted as in photographic developing solutions. Immersion for one to three minutes is ordinarily satisfactory.

A particularly effective reducing solution of the photographic developer type contains, in each liter of aqueous solution, approximately 1.5 grams of hydroquinone, .5 gram of elon (p-methylaminophenol sulphate), 6 grams of anhydrous sodium sulphite and 9 grams of anhydrous sodium carbonate.

In order to consolidate and impart mechanical strength to the silver chloride coating, the electrode should be subjected to a high mechanical pressure, such as 3 to 4 tons per square inch, applied perpendicular to the plane of the coating. A silver chloride coated silver screen electrode subjected to such compression is ordinarily reduced to about two-thirds its original thickness. This pressing operation may be performed at any time after the anodizing operation. Thus the electrode may be subjected to mechanical pressure immediately after anodizing and before the subsequent reducing operations, or it can be pressed after cathodic reduction and before the chemical surface reduction, or it can be pressed after all three operations have been completed.

The manufacture of electrodes has been described above as applied to silver screen. The process of the present invention is applicable to other silver bases such as silver

sheets, either perforate or imperforate, and grids of silver or silver plated metal.

The most satisfactory results upon anodizing according to the present invention are obtained if the silver base, and particularly silver screen, is annealed prior to anodizing. Annealing at a temperature of about 600° C. for about 30 minutes has been found suitable. In the absence of annealing, non-uniformity of the metal due to mechanical stress in manufacture has a tendency to cause non-uniform anodizing.

The invention has been described in terms of its specific embodiments which are to be considered to be illustrative only and not to be a limitation upon the scope of the invention which is to be limited only by the scope of the appended claims.

What is claimed is:

1. The process of forming a layer of silver chloride on a body of silver which comprises maintaining said body of silver as an anode in an aqueous bath which has a pH below about 6.5, which contains chloride ions in a concentration between about .1 mol per liter and about 1 mol per liter, ions of a halogen of atomic weight greater than chlorine in a concentration of between about .00002 mol per liter and about .006 mol per liter, and nitrate ions in a concentration of between about .001 mol per liter and about .1 mol per liter.

2. The process of forming a layer of silver chloride on a body of silver which comprises maintaining said silver body as an anode in an aqueous bath which has a pH below about 6.5, which contains chloride ions in a concentration of between about .1 mol per liter and about 1 mol per liter, nitrate ions in a concentration of between about .001 mol per liter and about .1 mol per liter and is saturated with silver iodide.

3. The process of forming a layer of silver chloride on a silver body which comprises maintaining said silver body as an anode in an aqueous bath having a chloride ion concentration between about .1 mol per liter and about 1 mol per liter, a pH below about 6.5, a nitrate ion concentration between about .002 mol per liter and about .1 mol per liter and an iodide ion concentration between about .00002 mol per liter and about .006 mol per liter, said bath being maintained at a temperature between about 50° C. and about 75° C.

4. The process of forming a silver chloride coating on a silver base which comprises maintaining said silver base as an anode in a bath consisting of an aqueous solution containing sufficient hydrochloric acid to form a solution having a normality between about .1 and about 1, sufficient potassium iodide to impart an iodide ion concentration between about .00003 and about .006 mol per liter and sufficient nitric acid to impart a nitrate ion concentration between about .003 and about .008 mol per liter.

5. The process of forming a silver chloride coating on a silver base which comprises maintaining said silver base as an anode in a bath consisting of aqueous solution containing sufficient hydrochloric acid to form a .24 normal solution, about .003 percent by weight of potassium iodide and about .02 percent by volume of nitric acid of a 69.5 percent concentration, maintaining said base at such an electric potential that the current density over the surface of said base is maintained at about .1 ampere per square inch and maintaining said bath at a temperature between about 60° C. and 65° C.

6. The process of forming an electrode for an electric cell comprising maintaining a body of silver as an anode in an aqueous bath which has a pH less than about 6.5, which contains between about .1 mol per liter and about 1 mol per liter of chloride ions and between about .00002 mol per liter and about .006 mol per liter of halide ions of an atomic weight greater than chlorine until a layer of silver chloride has been formed on the surface of said silver body, maintaining said body as a cathode in an electrolyte until a plurality of filamentary bridges of

metallic silver extending between the silver base and the external surface of the deposited silver chloride have been formed by the electrolytic reduction of a portion of the silver chloride, and subsequently immersing said body in a solution of a reducing agent capable of reducing the silver chloride to metallic silver for a time sufficient to form a thin layer of porous metallic silver on the surface of the silver chloride.

7. The process of forming a layer of silver chloride on a silver body which comprises maintaining said silver body as an anode in an aqueous bath having a chloride ion concentration between about .1 mol per liter and about 1 mol per liter, a pH below about 6.5, a nitrate ion concentration between about .001 mol per liter and

about .1 mol per liter and an iodide ion concentration between about .00002 mol per liter and about .006 mol per liter.

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