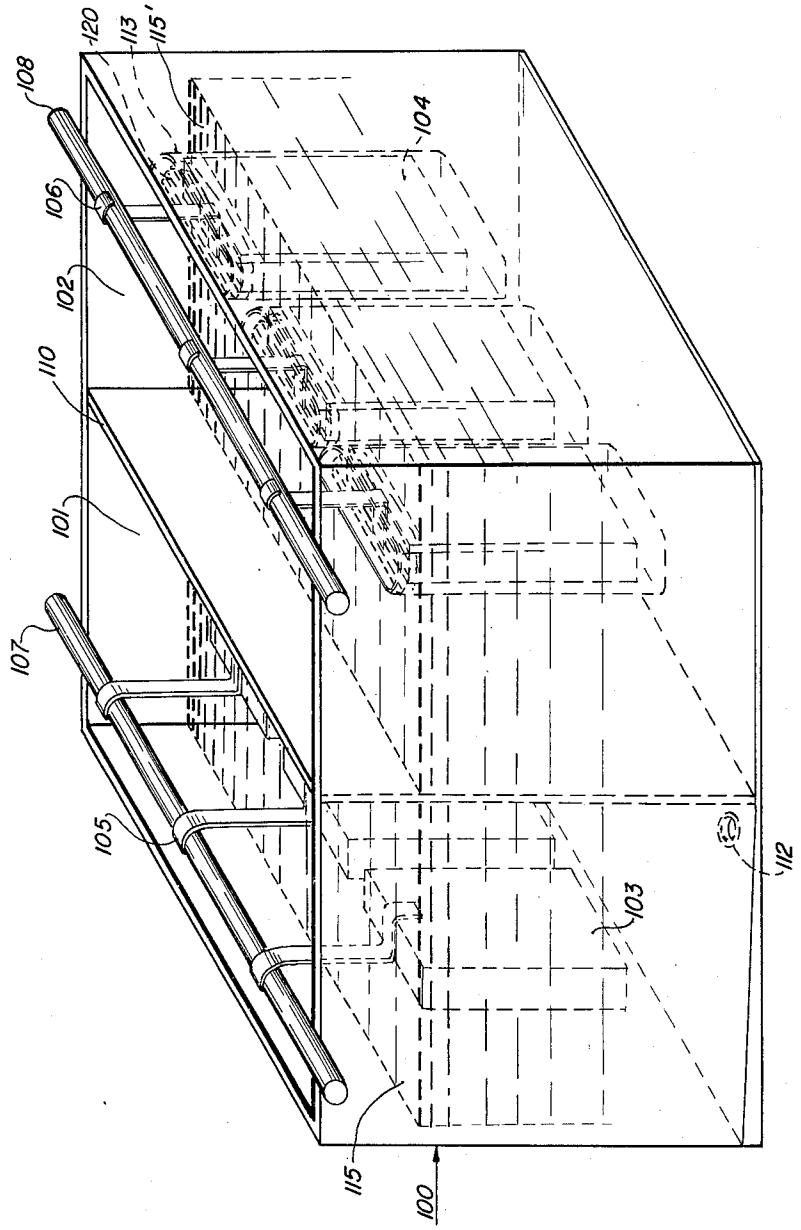
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ARGENTOUS OXIDE, POWDER AND METHOD FOR MAKING SAME

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ARGENTOUS OXIDE, POWDER AND METHOD FOR MAKING SAME

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This invention relates to silver oxide and more particularly to an electrochemical method for the preparation of argentous oxide powder.

Argentous oxide is more commonly prepared by the conventional precipitation of solutions of soluble silver salts with solutions of alkalis. More specifically, the process usually consists in the precipitation of solutions of silver nitrate by solutions of sodium or potassium hydroxide. While such procedures are sufficient on a small scale, they are wholly inadequate from the standpoint of uniformity, purity and price when practiced on a scale large enough to meet the industrial requirements for silver-oxide powder by such large consumers as manufacturers of silver-oxide battery electrodes or the like.

In addition, the preparation of the silver nitrate and the recovery of the nitrogen oxides and/or alkali nitrates requires major investment in capital equipment—towers, scrubbers, nitration pots etc. for the recovery and re-use of nitric acid from the reaction products. Without such recovery equipment, the cost of silver-oxide powder would be too high for advantageous use, even for special-purpose batteries.

It is an object of this invention to provide an electrochemical method for the manufacture of silver-oxide powders.

It is another object of this invention to provide high-purity silver-oxide powders that are electrochemically prepared.

It is another object of this invention to provide silver-oxide powder of extremely small particle size.

It is a further and accessory object of this invention to provide a method for the manufacture of silver-oxide powder of extreme purity and within a very narrow particle-size range at minimal cost.

In its broader aspects this invention embodies the general principle of the electrochemical deposition and precipitation of silver oxide at the anode from conductive solutions in which silver oxide is insoluble and with which it does not react chemically.

According to more specific aspects, this invention embraces the method of preparing a silver-oxide powder by electro-precipitation from silver anodes in alkaline solutions containing anions which do not form insoluble silver compounds.

According to other aspects, it embraces the electro-precipitated silver-oxide powder resulting from electro-precipitation in alkaline solutions, which powder, due to its mode of precipitation, is of uniform particle size.

In addition, certain aspects of this invention include modifications of the electrochemical cell to provide for the isolation of the cathode in a special electrolyte, different from the electrolyte effecting the precipitation. The isolation of the cathode assures a low concentration of reduceable anions, thereby maintaining the purity of the precipitated silver oxides.

A further aspect of this invention is the provision for a porous cathode cup surrounding the cathode, at which hydrogen is liberated, in order that there be a minimum of reduction of nitrogenous salts to ammoniacal compounds (these later tend to react with silver oxide to form azides of an extremely explosive nature).

The invention will be more particularly described with respect to an apparatus shown in the drawing.

The sole figure shows a plating apparatus designed for the electro-precipitation of silver-oxide powder.

The plating tank **100** illustrated may be any suitable vessel divided into two compartments, one of which is an anode compartment **101** and the other a cathode compartment **102**, separated from each other by a porous electrolyte-permeable compartment separator **110**.

The anode compartment **101** contains the silver anode **103** suspended in the electrolyte **115**. The anode **103** is connected to a current-carrying bus bar **107** via anodic bus leads **105**. The anode **103** should be spaced with clearance from the bottom of the compartment sufficient to permit collection of silver oxide.

Within the cathode compartment **102** is suspended a stainless-steel or other inert cathode **104** which is connected to bus bar **108** via cathodic bus leads **106**. Each of the cathodes is surrounded by a porous electrolyte-permeable cathode cup **113**, the top of which protrudes above the level **115'** of the electrolyte **115** in the cathode compartment. Within each of the cathode cups **113** a second electrolyte **120** is contained. This electrolyte is maintained at a level **116** above the electrolyte level **115'** existing in the main cathode compartment.

The anode compartment may preferably be constructed with a sloping bottom to permit the accumulation and collection of the precipitated silver oxide; at the lowest point of the sloping bottom of this compartment a valve arrangement **112** is provided to permit the removal of the collected silver oxide. The silver oxide is then separated from the electrolyte which flushes it through the valve by means of filters, centrifuges or the like (not shown).

Referring now specifically to the cathode portion of the tank, it is preferred that the second electrolyte in the cathode-enveloping cup should be maintained at a level at least 1 centimeter above the electrolyte level in the main tanks. As a result of this positive hydrostatic head, the flow of liquid through the electrolyte-permeable membrane inhibits the migration of the anions through the porous cathode cup **113** from the main tank. They are, therefore, kept away from close proximity to the reducing conditions in effect at and near the surface of the cathode. This prevents reduction of nitrates to ammonia and possible reduction of acetates.

In addition, the cathode cup **113** confines hydrogen which is liberated at the cathode to this small area and prevents the reduction and/or decomposition of nitrogenous anions present in the first electrolyte, which might be reduced if the hydrogen were not so confined.

The first or prime electrolyte **115** consists of an aqueous solution of salts of alkalis. The salts are those whose anions form soluble silver compounds. Preferred salts of this type include sodium nitrate and sodium acetate. In general, it is preferred to maintain the salt content of the solution at that concentration which affords the highest conductivity. However, it has been found that the silver oxide may be prepared from electrolytes containing sodium nitrate from concentrations of 2% up to the limit of solubility.

The second electrolyte **120** may be any alkali, but sodium and potassium hydroxide are preferred due to their solubility and cheapness.

The invention will now be more particularly described in connection with the following examples:

Example I

In an apparatus as shown in the drawing, with the compartments separated by a porous cloth resistant to concentrated salt solutions (Dynel), and filled with an electrolyte compound of 10% $NaNO_3$ adjusted at a pH in the

range 9–11 by the addition of NaOH, the silver was electrochemically precipitated from the surface of a cast-silver-ingot anode. The current density ranged up to 0.15 amp./cm.^{2}. The solution was not externally heated but reached an equilibrium temperature of 60° C. after ½ hour of operation. The solution was mildly stirred, but agitation was not necessary due to internal agitation promoted by the current flow.

The porous cups of ceramics or cellulosic fibers were filled with NaOH solution which was slowly added at a rate sufficient to maintain a slight hydrostatic head in the cathode cup. At low and high current densities, at temperatures ranging from that of the room up to 60° C. and at pH ranges from nearly neutral to strongly alkaline, no ammonia or ammoniacial compounds could be detected by any of the common tests. It was found that the efficiency approached 100% at an anode current density of approximately 0.15 amp./cm.^{2}.

The silver oxide powder resulting from this process, after removal from the tank, washing and drying, was found to have an average particle size of 0.7–1.2 microns as determined on Fisher Sub Sieve Sizer and yielded a powder of apparent densities in the range 0.6 to 1.0 gms./cc. using standard methods.

Example II

The apparatus illustrated was charged with a 10% solution of sodium acetate adjusted to a pH range of 9–11. The other conditions described in Example I were duplicated with the exception that KOH was used for adjusting the pH and for filling the cathode cup. The silver oxide from this process was comparable in physical properties to that obtained by the process of Example I.

The argentous oxide of this invention, because of its extremely small and uniform particle size, finds an important use in the storage battery field for the preparation of special silver electrodes. Such electrodes, consisting of extremely finely powdered argentous oxide and silver, are capable of charging and discharging to only the argentous level. The voltage from such batteries is therefore extremely constant. Such electrodes have been disclosed in U.S. application Ser. No. 696,174, filed 13 November 1957 by Frank Solomon. Applicant's electrolytic argentous oxide powder may be used directly as the positive element of silver/zinc or silver/cadmium batteries with silver powder admixed to provide conductive pathways, or it may be treated as set forth in the Solomon application.

I claim:

1. The process for electrochemically preparing substantially pure argentous oxide which comprises electrolyzing a silver anode against an inert cathode through an interposed electrolyte permeable separator in a liquid electrolyte comprising an alkaline solution of a salt having an anion which forms soluble salts with silver compounds, maintaining at said cathode a hydrostatic pressure greater than that at said anode, and collecting the silver oxides which precipitate near the anode.

2. The process according to claim 6, wherein the hydrostatic head between said first and said second electrolyte is at least 1 cm.

3. The process according to claim 1, wherein the said salt is chosen from the group consisting of alkali nitrates and acetates.

4. The process according to claim 1, wherein the electrolyte is maintained at a pH in the range 9 to 11.

5. The process according to claim 1, wherein the electrolyzing current is approximately 0.15 amp./cm.^{2}.

6. The process according to claim 1, wherein the difference in hydrostatic pressure is maintained by surrounding the inert cathode with a second electrolyte confined by another separator and comprising an alkali-metal hydroxide.

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