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ELECTROLYTIC METHOD FOR THE PREPARATION OF GEM-DINITROCOMPOUNDS

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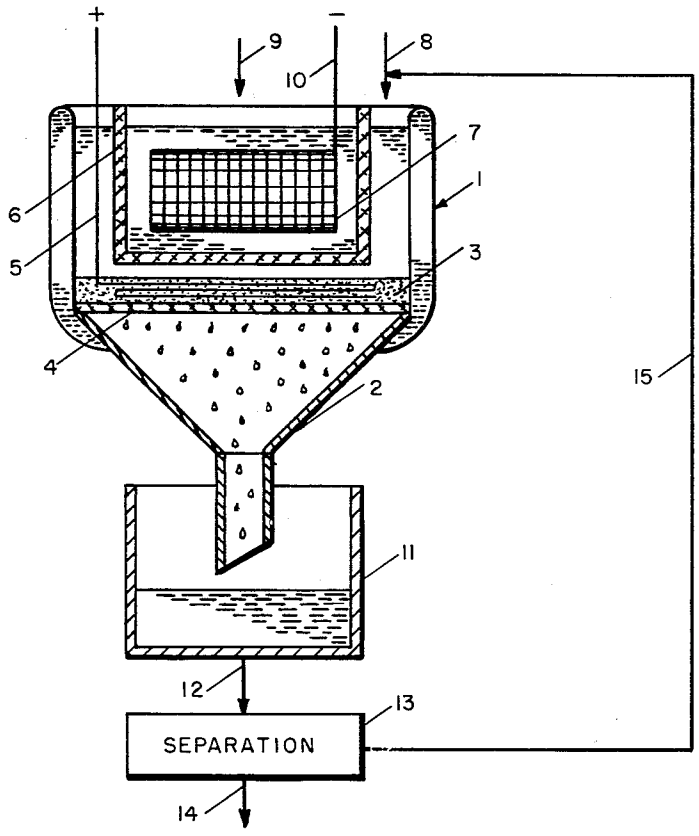


FIG. 1

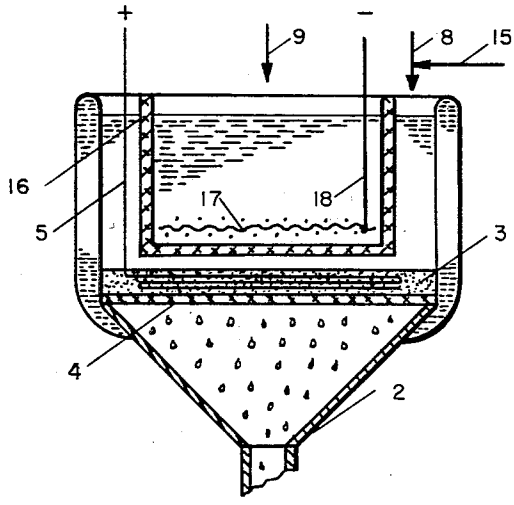


FIG. 2

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ELECTROLYTIC METHOD FOR THE PREPARATION OF GEM-DINITROCOMPOUNDS

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This invention relates to an electrolytic method for the preparation of gem-dinitrocompounds and more particularly to a method whereby nitrocompounds are converted to corresponding gem-dinitrocompounds by a reaction involving oxidative electrolysis.

Electrolytic methods involving oxidative electrolysis of nitrocompounds have not been generally utilized. This to an extent has been due to the complex reaction mechanism which takes place at the oxidative pole or anode and the uncertainty of behavior involved for obtaining end products. Perhaps, to a greater extent, this has been due to the fact that known methods for the preparation of gem-dinitroparaffins, for example, by the electrolysis of aqueous alkaline solutions of primary nitroparaffins using a platinum or other inert anode, have heretofore been found to be limited in respect to the variety of end products obtainable and have been found to be deficient in respect to yields and current efficiencies and not readily adaptable to continuous operation.

Now, in accordance with the present invention, an electrolytic method has been discovered in which the reaction mechanism involving oxidative electrolysis of nitrocompounds, although difficult to define, proceeds with a certainty of behavior under continuous operation to yield a variety of uniform products accompanied with high yields and current efficiencies. In this method an active silver anode is electrolytically oxidized in an aqueous alkaline solution of a nitrocompound and nitrite ion. The oxidized silver reacts with the components of the solution in a repetitious manner to continuously form the corresponding gem-dinitrocompound in solution and silver metal wherein the latter repetitiously reprecipitates on the anode as the method proceeds and the dinitrocompound thus formed is continuously withdrawn.

Thus, a primary object of the present invention is to provide an electrolytic method for producing a variety of gem-dinitrocompounds accompanied with high yields and current efficiencies. Still another object of the invention is to accomplish the foregoing under conditions of continuous operation.

Other objects of the invention will appear hereinafter, the novel features and combinations being set forth in the appended claims.

Generally described, the present invention comprises in an electrolytic cell provided with a porous partition between the anode and the cathode, the method of passing an aqueous alkaline solution of a nitrocompound and inorganic nitrite with electrolysis thereof through a silver anode whereby the silver is electrolytically oxidized and reacts with the components of the solution to effect a conversion of the nitrocompound to a gem-dinitrocompound and silver metal, characterized in that the silver anode is disposed as a filter-like bed to receive the silver metal as it reprecipitates during passage of the electrolyzed solution therethrough.

Representative embodiments of the invention have been chosen for purpose of illustration and description and are shown in the accompanying drawings wherein reference symbols refer to like parts wherever they occur and wherein:

FIG. 1 is a diagrammatic, vertical, sectional view of one form of apparatus for carrying the invention into effect; and

FIG. 2 is a diagrammatic, vertical, fragmentary, sectional view of still another form of apparatus for effecting the invention.

In order to demonstrate the present invention, typical and preferred embodiments were utilized and are described in detail in the following examples with reference to the accompanying drawings.

Example 1

With reference to FIG. 1, an electrolytic cell **1** was assembled as follows for continuous operation. The anode compartment consisted of a jacketed, medium porosity, Pyrex glass Büchner funnel **2**, three inches in diameter, having a capacity of about 150 ml. The anode was a porous, filter-like bed **3** of powdered silver metal ¼ inch deep which completely covered the filter plate **4** or anode support of the funnel **2**. The powdered silver metal had a particle size of from 1 to 200 microns, which rendered the bed porous and permitted passage of electrolyzed solution therethrough. Electrical contact for the anode was a coil of platinum wire **5** buried in the silver powder bed **3**. The cathode compartment was a flat-bottomed porous alundum cup **6** of approximately 30 ml. capacity, supported so that its bottom was ½ inch above the porous bed of silver **3**. The cathode **7** was a cylinder of silver gauze 30 sq. cm. in area.

An anode solution containing 30 grams of nitroethane, 45 grams of potassium nitrite, adjusted to pH 11.5 with pellets of potassium hydroxide, was prepared in 500 ml. of water. The anode compartment was filled with a portion of this solution that had been preheated to 60° C. through line **8**. The cathode compartment was filled with 2% KOH as the cathode solution to the same liquid level as the anode solution through line **9**. A constant current of 10 amperes was passed through the cell **1** from a suitable E.M.F. as applied to wire **5** of the anode and a wire **10** connected to the cathode **7**. During the electrolysis the anode solution continuously passed through the bed of silver metal **3** and the filter plate **4**. The electrolyzed anode solution was collected in a beaker **11** or receiving flask set in an ice bath. Anode solution, preheated to 60° C., was continuously added to the top of the cell by way of line **8** to keep the liquid level constant. Temperature of the anode solution in the cell was maintained between 55° and 70° C. by cooling water passing through the jacketed funnel **2**. The applied potential was approximately 9 volts. The anode solution passed through the cell at a rate 350 ml. per hour. The electrolysis was carried out continuously with maintenance of the cathode solution by way of line **9** at approximately its original concentration to prevent the build-up of very concentrated KOH in the cathode compartment.

The electrolyzed anode solution from the beaker **11** was passed through line **12** to a separator **13** wherein it was filtered to remove the crystalline potassium dinitroethane as represented by line **14**. The crystalline material was dried, weighed and analyzed. The weight obtained was 21.74 grams. This material obtained after separation analyzed 96% pure potassium dinitroethane by the polarograph. The filtrate was made up to 500 ml. with distilled water. There had been a loss of approximately 50 ml. in volume during the above operations. This filtrate solution was analyzed and found to contain 6.2 grams of potassium dinitroethane and 14.4 grams of nitroethane. This characterized filtrate solution was continuously recycled by way of line **15** to the anode feed line **8** and was continuously made up to maintain the original nitroethane, potassium nitrite concentration for continuous operation by addition of nitroethane and potassium nitrite with the pH adjusted to approximately 11.5 by addition of potassium hydroxide.

The solid material crystallized, utilizing continuous op-

eration with the recycled filtrate solution after drying and weighing, was found to weigh 27.10 grams. This material analyzed 94% pure potassium dinitroethane by the polarograph. The recycle filtrate when analyzed under continuous operation was found to contain 5.7 grams of potassium dinitroethane and 14.0 grams of nitroethane, thereby demonstrating the efficacy of the invention in respect to continuous operation.

Polarograms of the above two solids and of the filtrate showed no evidence of silver. The yield and current efficiency were determined as follows.

Yield:

Total potassium dinitroethane produced:

$$\begin{array}{r} 21.74\times.96=20.9 \\ 27.10\times.94=25.5 \\ \hline 5.7 \\ \hline 52.1 \text{ grams or} \end{array}$$

$$\frac{52.1}{158.2}=0.33 \text{ mole}$$

Total nitroethane consumed—32.6 grams:

$$\frac{31.6}{75}=0.42 \text{ mole}$$

$$\frac{0.33}{0.42}\times 100=79\% \text{ overall yield}$$

Current efficiency:

136 min.×60 sec.×10 amps.=71,600 coulombs

$$\frac{81,600}{96,500}=0.85 \text{ equivalent}$$

$$\frac{0.85}{2}\times 158.2=67 \text{ grams of potassium dinitroethane if 100\% current eff.}$$

$$\frac{52.1}{67}\times 100=78\% \text{ current efficiency}$$

Example 2

With reference to FIG. 2, an electrolytic cell was assembled substantially identical to that set forth for FIG. 1 with the exception of the cathode compartment. In this embodiment a flat-bottomed, cylindrical, alundum cup **16** was utilized having as the cathode a flat, circular piece of silver gauze **17** spaced approximately ¼ inch from the bottom of the cup wherein only the bottom of the cup was porous. A platinum wire **18** connected to the silver gauze **17** served as the electrical contact for the cathode. The cup **16** was spaced approximately ½ inch above the porous anode bed **3** and the gauze cathode **17** was substantially coextensive and parallel to the anode bed with, of course, sufficient area retained around the cup for passage of the anode solution into the cell. This cell was operated similar to the cell described in Example 1 with substantially the same results with certain improvements as to uniformity of current distribution indicated.

From the foregoing examples, it will be appreciated that electrolytically oxidized powdered or particulate silver as an anode can be used to prepare the aci-salt of gem-dinitrocompounds from the corresponding nitrocompound and nitrite ion. The silver behaves essentially catalytically in the reaction as is most evident from the examples which demonstrated no evidence of silver consumption or loss.

The desired reaction for gem-dinitrocompounds will occur between the pH's of 13 and 9. Above pH 13, no appreciable gem-dinitrocompound is formed. With pH's less than 9, the nitrocompounds are only partially converted to the aci-form. A molar excess of from 30 to 150% nitrite ion can be used as well as stoichiometric proportions, but as the higher nitrite concentrations are approached, reduced yields and current efficiency result. Concentrations of the nitrocompounds may run at least as high as 12%, and with a corresponding increase in nitrite and time of electrolysis, satisfactory yields and current efficiencies are obtained.

It will be noted that maximum current density was not obtained in respect to the examples since the true anode area of the silver bed was difficult to accurately obtain as will be the case with all powdered or particulate beds used for the anode. Nevertheless, in the examples it was demonstrated that 10 amperes of current when passed using a bed of overall area of approximately 10 sq. in. gave a current efficiency of 78%. The silver in powdered or particulate form utilized as the anode bed should have a particle size of from about 1 to about 500 microns.

Moreover, the electrolysis of nitrocompounds in accordance with this invention should be carried out at a temperature of from about 20° to about 75° C., and preferably in a vessel jacketed for cooling since the electrolysis reaction generates heat. At temperatures in the order of 80° C. and above, undue decomposition of the gem-dinitrocompound product formed by the electrolysis occurs.

The cathode in respect to the present invention serves the ordinary function of a cathode in an electrolytic cell. The use of an identical alkali metal for the anode and cathode solutions is merely a matter of convenience. However, some advantage is obtained when using the same strong alkali metal for the anolyte and catholyte since the catholyte by diffusion through the porous partition tends to fortify the reactive anolyte as the electrolysis proceeds. Solutions of other electrolytes may be employed as catholytes and the cathode may be an inert metal such as platinum or it may be silver which is only active from the viewpoint of reaction when used as the anode. Nevertheless, regardless of the particular metal used as the cathode, important advantages accrue when having the silver metal in particulate form for the anode. With the metal in particulate form, layer thickness and gradations may be selected to assist in obtaining optimum passage of electrolyzed solution through the anode bed, it being appreciated, of course, that other factors must be considered such as porosity of the bed support, viscosity of the electrolytes used, and the like, which factors are best determined empirically to arrive at optimum gradation and thickness of bed. The rate of diffusion for the catholyte may be controlled simply by valving means applied to line **9**, for example. It is essential, however, that particulate silver be employed as the anode since it is electrolytically oxidized silver that reacts with the components of the anode solution to form the corresponding salt of dinitrocompound as shown by the examples. Thus, it is quite preferable to use either potassium or sodium consistently as the alkali metal for the anolyte, catholyte and source of inorganic nitrite ion. Generally, an electrical current at a density of from about 0.02 to about 0.20 ampere per square centimeter of active electrode surface will be found adequate for effecting a variety of electrolytic reactions yielding gem-dinitrocompounds in accordance with this invention, with the only known requirement being that the starting compound form a stable, soluble aci-salt in aqueous alkali.

Although nitromethane does not react to produce a gem-dinitrocompound, other suitable starting materials include nitroethane, 1-nitropropane, 1-nitrobutane, 1-nitropentane, 1-nitrohexane, 2-nitropropane, 2-nitrobutane, 2-nitro-1-propanol, 1-nitro-2-propanol and 2-nitro-1,3-propanediol.

The product obtained from the electrolysis in accordance with the present invention is a gem-dinitrocompound either as a salt or the compound itself which may be separated from its electrolyzed anode solution by conventional procedures. Preferred procedures for the salts involve crystallization in a cooling bath followed by filtration, while for the gem-dinitrocompounds themselves, extraction followed by distillation. In this respect, it will be appreciated that in the utilization of a secondary

nitrocompound for the reaction, the product obtained is not a salt but is the gem-dinitrocompound itself. Moreover, the gem-dinitrocompound, per se, may be separated from the salt by conventional procedures such as acidification followed by ether extraction.

Although it is not intended that the invention shall be limited to any particular theory of operation, the reactions that appear to take place may be written as follows wherein nitroethane, a preferred material, is used as an example.

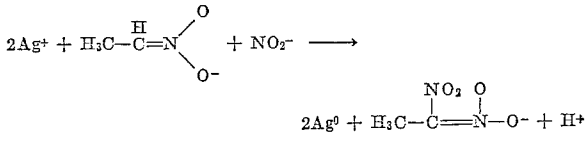
Cathode reaction:

$$2H_2O + 2e \rightarrow 2OH^- + H_2\uparrow$$

Anode reaction:

$$2Ag \rightarrow 2Ag^+ + 2e$$

The oxidized silver, either as free silver ion or as an insoluble silver compound, reacts as follows:



Under the conditions, as shown in the examples, the silver metal is precipitated on or within the anode without consumption or loss thereof and, accordingly, the silver may be considered to behave catalytically.

Representative gem-dinitrocompounds obtainable in accordance with this invention include 1,1-dinitroethane, 1,1-dinitropropane, 1,1-dinitrobutane, 1,1-dinitropentane, 1,1-dinitrohexane, 1,1-dinitro-2-propanol, 2,2-dinitropropane, 2,2-dinitrobutane, 2,2-dinitro-1-propanol and 2,2-dinitro-1,3-propanediol.

The aforementioned compounds are valuable intermediates in chemical synthesis and more recently, the specific compound demonstrated by the examples, namely, 1,1-dinitroethane, has found considerable utility as an ingredient in the preparation of rocket fuels.

The advantages of this invention are multifold in that gem-dinitrocompounds can be produced continuously by electrolysis and without separation and subsequent reoxidation of large amounts of silver such as required using known chemical reactions. With these known chemical reactions, at least 2 moles of silver must be separated and reoxidized for each mole of dinitrocompound produced. Additionally, the electrolytic method of this invention can be continuously conducted to give high yields of the desired products and at high current efficiencies. As the examples have demonstrated, yields of at least 79% and current efficiencies of at least 78% have been obtained. Moreover, the use of an active anode, which may be readily controlled with respect to porosity, offers advantages in respect to electrolytic cells which heretofore have not been available.

In view of the foregoing, it will be evident that this invention may be carried out by the use of various modifications and changes without departing from its spirit and scope. Although the invention has been described hereinabove for the preparation of certain specific gem-dinitrocompounds, it is to be understood that these specific embodiments are but representative of my improved method for the preparation of compounds of the broad class of gem-dinitrocompounds and, accordingly, the invention is to be broadly construed in the light of the defining language of the appended claims.

What I claim and desire to protect by Letters Patent is:

1. In the electrolytic method of passing an aqueous alkaline solution of a nitrocompound and inorganic nitrite, during the electrolysis thereof, through a silver anode whereby the silver is electrolytically oxidized and reacts with the components of the solution to effect a conversion of the nitrocompound to a gem-dinitrocompound and silver metal, the improvement which comprises disposing the silver anode as a filter-like bed of particulate silver to receive the silver metal as it reprecipitates during passage of the electrolyzed solution therethrough.

2. The method of claim 1 wherein the filter-like bed of particulate silver is substantially horizontally disposed.

3. The method of claim 1 wherein the filter-like bed is particulate silver of gradated particle size.

4. The method of claim 3 wherein the filter-like bed of particulate silver of gradated particle size is substantially horizontally disposed.

5. In the electrolytic method of passing an aqueous alkaline solution of a nitrocompound and inorganic nitrite, during the electrolysis thereof, continuously through a silver anode whereby the silver is electrolytically oxidized and reacts with the components of the solution to effect a conversion of the nitrocompound to a gem-dinitrocompound and silver metal, the improvement which comprises disposing the silver anode as a filter-like bed of particulate silver to receive the silver metal as it continuously reprecipitates during passage of the electrolyzed solution therethrough, and further characterized in that the cathode is disposed substantially parallel and coextensive with the anode.

6. The method of claim 5 wherein the filter-like bed is particulate silver and is substantially horizontally disposed.

7. The method of claim 5 wherein the filter-like bed is particulate silver of gradated particle size and is substantially horizontally disposed.

8. In the electrolytic method for effecting oxidative nitration of a nitrocompound by silver ion into its corresponding dinitrocompound, the improvement which comprises passing the nitrocompound, during the electrolysis thereof, into contact with and through a filter-like bed of particulate silver metal as the anode to reprecipitate and receive silver metal serving as the source of said silver ion.

9. The method of claim 8 wherein the anode has a cathode disposed substantially parallel and coextensive thereto.

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