The present invention pertains to a method of preparing cathodes for use in the electrolytic reduction of ketones and generally in all types of carbon to carbon reductive condensation reactions.

Specifically, our invention is concerned with the preparation of cathodes which are particularly suitable for the reduction of acetone electrolytically to sym-tetramethyl-ethylene glycol.

It is known that the electrolytic reduction of ketones can take place at the cathode surface according to any one of the following reactions:

\[ 2R_1C\textsubscript{3}O\textsubscript{3}R_2 + 2\text{H}^+ \rightarrow R_1\textsubscript{1}O\textsubscript{2}H + OH^{-} + \textsubscript{2}R_2 \]

\[ R_1C\textsubscript{3}O\textsubscript{3}R_2 + 2\text{H}^+ \rightarrow CH\textsubscript{2}OH \]

\[ R_1C\textsubscript{3}O\textsubscript{3}R_2 + 4\text{H}^+ \rightarrow CH_3 + H_2O \]

Other side reactions result in the formation of metal alkyls, especially when the reduction is effected in acid medium with lead cathodes.

An electrolytic method for effecting the reductive condensation reaction whereby acetone is converted to pinacol (sym-tetramethylethylene glycol) using a lead cathode and an acid catholyte is described in German Patent 113,719 (1899). The claims of the German patent were verified by Elbs in Z. Electrochemie, 7, 844 (1901).

Several German patents pertaining to the electrolytic reduction of acetone to pinacol were issued in the period 1912-1920. Among these patents were DRP. 306,304 (1917), 306,523 (1918) and 324,919 (1920). The principal developments made in this period appear to have used the mixtures of mixed metal and alloy cathodes, such as 4 to 10% copper-96 to 90% lead mixtures and 10% tin-90% lead alloy, and the use of horizontally suspended cathodes to prevent the metal alkyls formed from accumulating on and decreasing the activity of the electrode surface.

All of the prior processes for electrolytically converting acetone to pinacol have been unsatisfactory either because pinacol current efficiency or the overall current efficiency or both were too low. The current efficiency (C.E.) is the ratio of the theoretical quantity of electricity required for a given reduction to that actually used. Thus, the per cent pinacol C.E. = \[ \frac{\text{grams of pinacol hydrate} \times 55.6 \times 100}{\text{mol. wt. of pinacol hydrate} \times \text{total ampere hours}} \]

It is the object of the present invention to provide the art with a novel method of preparing electrodes, for effecting the electrolytic reduction of organic compounds.

It is also the object of this invention to provide the art with a method of preparing lead coated cathodes of high activity in carbon to carbon reductive condensation reactions.

These and other objects will appear more clearly from the detailed description and claims which follow.

We have now found that by electrodepositing a thin film of lead on a base of low hydrogen overvoltage metal from a lead salt electrolyte containing a low concentration of other metal ions it is possible to obtain cathodes which minimize the formation of toxic lead alkyls that tend to diminish the effectiveness of the cathode and effect the reduction of ketones to \( \alpha,\beta \) glycols with good current efficiency and high ratio of glycols to other reduction products. The metal ion content of the electrolyte may be provided by adding up to about 25 gm. per liter of a salt thereof to the electrolyte or may be advantageously formed in situ by making a sheet of the metal the anode in the electrolyte for a brief period and then reversing polarity of the cell making the metal plate the cathode and electrodepositing a thin layer of lead thereon. Specifically, we have found that cathodes consisting of a base of copper having a thin film of lead electrodeposited thereon from an electrolyte containing a low concentration of copper ions are particularly effective.

The metals of low hydrogen overvoltage that may be used as the base for our cathode include copper, nickel, silver, gold and platinum or alloys such as Monel metal and brass.

The film of lead is preferably electrodeposited on the low overvoltage metal base in the following manner: Plates of the metal which are to serve as the base of the cathode are treated for a few minutes with one part of nitric acid to
three parts of distilled water. The plates are washed with water to remove nitric acid and are then ready for lead plating. The plating bath contains about 50 to 100 grams of lead nitrate per liter of distilled water. Lead sheets are used as the other electrodes and upon assembly of the cell, the plates which are to receive the lead plating are made the anodes and the lead sheet is made the cathode at a current density of about 1.55 amperes/sq.dm, for ½ minute. The current flow is then reversed, so that the plates are cathodes and the lead sheets the anodes. Plating is continued for about 2 minutes at about the same or at a higher current density. The lead coated plates are then removed from the plating bath and immediately washed with hot water and dried, whereupon they may be used directly without any further conditioning treatment. Alternatively, relatively small amounts of metal salts other than lead salts are added to the electrolyte whereupon the lead is electrodeposited on the base metal without any reversal of polarity of the base.

It is to be understood that this method of preparing our lead coated cathodes is merely illustrative and that other methods can be utilized. For example, the lead can be deposited on the base plates from fluosilicate, fluoroborate and perbromate baths. The important factor in the preparation of the cathode is that the lead deposit must be kept very thin, preferably within the range of from 0.02 to about 0.5 gram/sq.dm.

The following examples serve to illustrate our invention but it is to be understood that our invention is not limited thereto.

**EXAMPLE 1**

Copper sheets about 21 x 30 cm. and about 0.2 cm. in thickness were treated for a few minutes with a mixture of one part of nitric acid to three parts of distilled water. The copper sheets were washed and then placed in a solution of lead nitrate containing 100 grams of lead nitrate/liter and made the anode while a lead or carbon electrode was made the cathode. Current was passed through the resultant cell for ½ minute at a current density of about 1.55 amperes/sq.dm. for ½ minute. The polarity of the electrodes was then reversed, making the copper sheet the cathode and current was passed at a current density of about 4.5 amperes per sq.dm. for 2 to 3 minutes.

The resultant lead coated copper electrode was then used as the cathode in a diaphragm cell wherein the catholyte consisted of a 4/1 acetone 15-20% sulfuric acid solution. The anolyte was 20% sulfuric acid. The electrolysis was conducted at 0-10° C. at a current density of 1.55 to 2 amperes/sq.dm. The run was conducted for 21 hours. Upon conclusion of the electrolysis, isopropyl alcohol and unreacted acetone were stripped from the catholyte under reduced pressure at low temperatures (below 20° C.) and the sym-tetramethylene glycol was separated from the residue as the hexahydrate by cooling and filtering the crystals.

655 grams of pinacol hydrate corresponding to 343 grams of sym-tetramethylene glycol and 16.9 grams of isopropyl alcohol were obtained. This corresponds to an overall current efficiency of 37% based on pinacol and 3.8% based on isopropyl alcohol. The mol ratio of pinacol hydrate to isopropyl alcohol was 10/1.

When using lead or 4% copper-96% lead, or 10% copper-90% lead mixtures in sheet form as the cathode in lieu of the lead deposited on copper cathodes with the same anolyte and catholyte and the same conditions of temperature and current density, current efficiencies based on pinacol of 12.7% and 13.8%, respectively, and a mol ratio of pinacol hydrate/isopropyl alcohol of 0.4/1 and 0.9/1, respectively were obtained.

**EXAMPLE 2**

A number of cathodes were prepared by electrodeposition lead onto copper plates in accordance with the present invention. The first cathode in the table set out below was prepared by arranging a copper sheet and a carbon electrode in a bath containing 100 grams per liter of lead nitrate and no copper. The copper sheet was made anode and the carbon cathode for less than a minute whereupon the polarity was reversed and lead was deposited on the copper sheet cathode at a current density of about 1 amp/sq.dm. for a period of 10 minutes. The other electrodes listed in the table were prepared from electrolytes containing 100 grams per liter of lead nitrate and different amounts of other metal salts. These electrodes were prepared without reversing the polarity of the copper sheet, the current density used in each case being the same as above, i.e., 1 amp/sq.dm.

The several cathodes were then used for the reduction of acetone to pinacol and pinacalone in a diaphragm cell under the following conditions. The anode used was made of chemical lead and had an area of 79 sq.dm. while the several cathodes used had an area of 258 sq.dm. each.

The catholyte volume was 830 c.c. and consisted of acetone and 30 wt. per cent sulfuric acid in a 3:1 ratio. The anolyte volume was 63 c.c. and consisted of 30 wt. per cent sulfuric acid. The current density used in the electrolysis was 1.0 amp/sq.dm. except in the first case wherein a current density of 1.6 amp/sq.dm. was used, other experiments having shown that no substantial alteration in current efficiency is brought about by increasing current density from 1.0 to 1.5 amp/sq.dm. The electrolysis was effected at a temperature between 19 and 23° C. The quantity of reduction products formed was determined and the current efficiency based on pinacol and pinacalone was determined. The results obtained are summarized in the following table:

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Salt Added to Electrolyte</th>
<th>Current Efficiency (% based on pinacol and pinacalone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4 g./l. cupric nitrate</td>
<td>60.5</td>
</tr>
<tr>
<td>2</td>
<td>5 g./l. cupric nitrate</td>
<td>41.5</td>
</tr>
<tr>
<td>3</td>
<td>10 g./l. cupric nitrate</td>
<td>44.5</td>
</tr>
<tr>
<td>4</td>
<td>15 g./l. cupric nitrate</td>
<td>48.0</td>
</tr>
<tr>
<td>5</td>
<td>20 g./l. cupric nitrate</td>
<td>44.0</td>
</tr>
<tr>
<td>6</td>
<td>30 g./l. cupric nitrate</td>
<td>44.5</td>
</tr>
<tr>
<td>7</td>
<td>50 g./l. cupric nitrate; 5 g./l. mernic acid</td>
<td>44.5</td>
</tr>
</tbody>
</table>

The ketones which may advantageously be reduced electrolytically to pinacol and pinacalone. The conditions of electrolysis etc. are disclosed in considerable detail in an application Serial No. 449,718, filed July 1923.
2,485,208

4, 1942, now Patent 2,422,468, of which the present application is a continuation in part.

The foregoing description contains a limited number of embodiments but it will be understood that our invention is by no means limited to the specific details described since numerous variations are possible without departing from the scope of the subjoined claim.

What we claim and desire to secure by Letters Patent is:

A process for preparing cathodes suitable for the electrolytic reduction of organic compounds which comprises electrolytically depositing a thin film of lead weighing between about 0.02 and 0.5 gram per square dm. on copper from an aqueous electrolyte consisting essentially of 100 grams per liter of lead nitrate and from 1 to about 20 grams per liter of cupric nitrate at a current density of about one ampere per square dm.

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