

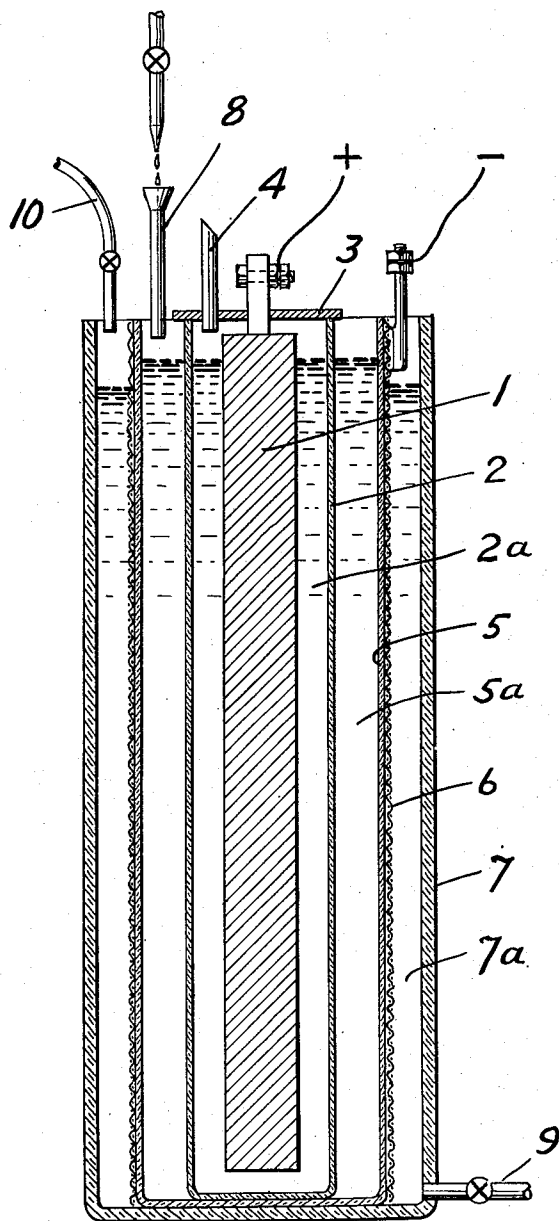
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ELECTROLYTIC PROCESS OF PREPARING QUATERNARY AMMONIUM HYDROXIDE

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ELECTROLYTIC PROCESS OF PREPARING
QUATERNARY AMMONIUM HYDROXIDE

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This invention relates to a new process for preparing quaternary ammonium hydroxides. In particular it deals with the electrolysis of quaternary ammonium salts in aqueous solution.

It is known that quaternary ammonium hydroxides may be formed by treating the corresponding quaternary ammonium halides with silver oxide, a process which is primarily of laboratory interest. It is also possible to convert quaternary ammonium sulfates to the hydroxides with barium hydroxide. The necessary quaternary ammonium sulfates are not, however, always available. McCoy and Moore (J. Am. Chem. Soc., 33, 273 (1911)) found that a tetramethyl ammonium amalgam could be prepared by electrolysis of tetramethyl ammonium chloride in absolute alcohol by the use of a mercury cathode. When the amalgam was treated with water, tetramethyl ammonium hydroxide was formed. This method is limited, however, to a relatively few compounds and requires conditions which are scarcely feasible on a commercial basis. On the basis of electrolysis of quaternary derivatives of aniline, which on electrolysis yielded benzene and a tertiary amine, it was reported that quaternary ammonium hydroxides could not be electrolytically formed. This broad conclusion, in view of applicant's findings, must now be modified.

It is an object to prepare quaternary ammonium hydroxides in a commercially practical manner. It is a particular object to prepare quaternary ammonium hydroxides having aliphatic or arylaliphatic N-substituents by electrolysis of the corresponding quaternary ammonium salts. It is a further object to prepare quaternary ammonium hydroxides essentially free from metallic ions and with a low content of salt-forming anions.

These objects are accomplished by electrolyzing with a cathodic overvoltage below about 0.6 volt an aqueous solution of a non-aromatic quaternary ammonium salt having N-substituents which are relatively stable and which are selected from at least one member of the class consisting of aliphatic and arylaliphatic groups. The electrolysis is desirably conducted in a cell having one or more inert porous diaphragms which serve to divide the cell into zones or compartments, thus insuring purity of product and preventing loss of product by anodic oxidation. With a cell having one or more diaphragms, the desired quaternary ammonium hydroxide is obtained in the compartment or zone about the

cathode although under some conditions with two diaphragms the hydroxide may also be obtained in the intermediate compartment.

The quaternary ammonium salts, which are at present available and which are particularly suitable for the starting material for electrolysis, are the water-soluble quaternary salts having aliphatic or arylaliphatic groups as substituents of the pentavalent nitrogen. The aliphatic or arylaliphatic groups may consist of carbon and hydrogen or they may contain carbon, hydrogen, and other elements which form subsidiary functional groups. With a functional group which is not readily reduced, such as hydroxyl, amino, ether, etc., such group is found unaltered in the quaternary ammonium hydroxide.

Suitable N-substituents are aliphatic and arylaliphatic groups in a wide variety, including straight-chain, branched-chain, saturated, unsaturated, and cyclic groups. The term "non-aromatic" is here used to describe those compounds in which an aromatic cycle is not directly connected to the quaternary nitrogen. Typical of the N-substituents which may be used are such groups as methyl, ethyl, propyl, butyl, isobutyl, hexyl, capryl, decyl, dodecyl, and higher aliphatic groups including octadecyl and octadecenyl, allyl, methallyl, benzyl, methylbenzyl, butylbenzyl, chlorobenzyl, bromobenzyl, dimethylaminobenzyl, dimethylaminomethyl benzyl, hydroxyethyl, hydroxypropyl, aminoethyl, methoxymethyl, butoxymethyl, capryloxymethyl, dodecylloxymethyl, phenoxyethyl, terbutylphenoxyethyl, phenoxyethoxyethyl, naphthoxyethyl.

The quaternary ammonium salts which are now available and which are suitable for use in this invention are of the formula:



wherein R_1 , R_2 , R_3 , R_4 represent aliphatic or arylaliphatic groups and X represents the anion of an acid or a salt-forming anion, such as chloride, bromide, iodide, sulfate, phosphate, acetate, or other anion from an inorganic or organic acid. The halide salts are generally available and convenient for the electrolytic process, since the halogen may be removed from about the anode by volatilization. When non-volatile anions are used, it is generally necessary to dilute the anode liquor and remove some of it from time to time or continuously during electrolysis.

In the preferred form of this invention the solution of quaternary ammonium salt is elec-

trollyzed in a cell having two porous diaphragms. In such cell the anode and cathode are set off to form an anode compartment, a cathode compartment, and an intermediate compartment. A satisfactory type of such cell is shown in vertical cross-section in the drawing. The anode 1 is enclosed in a porous vessel 2 to form an anode compartment 2a which is provided with a cover or lid 3 of corrosion-resistant material, such as a carbon plate, through which a tube 4 serves to remove gases formed about the anode. A second porous diaphragm 5 surrounds diaphragm 2 to form the intermediate compartment 5a and together with the container 7 forms a cathode compartment 7a in which is placed the cathode 6. An inlet tube 8 is provided for introducing solution of quaternary ammonium salt into the compartment formed by diaphragms 2 and 5. An outlet 9 is conveniently provided for drawing off solution from the cathode compartment. By means of inlet 10 water may be added to the cathode compartment to adjust the concentration of the solution therein.

The materials used in the construction of an electrolytic cell should be resistant to quaternary ammonium salts or quaternary ammonium hydroxides. For the container glass or other ceramic material is satisfactory, although a container of a metal, such as iron, may be used and serve both as container and as cathode. The cathode is composed of any metal inert to a quaternary ammonium hydroxide and low in hydrogen overvoltage. Metals meeting these requirements are members of the group known in the art as metals of low overvoltage (less than about 0.2 volt at zero current density) and include iron, platinum, and palladium. The other electrode, the anode, should be composed of a material relatively inert to the products formed about it. Thus, carbon or graphite anodes are useful or such anodes impregnated with paraffin, linseed oil, or the like to minimize attack by oxygen or a halogen.

The diaphragms setting off the electrodes should likewise be resistant to the products formed. Organic materials are not in general satisfactory as they are attacked by halogens, oxygen, and quaternary ammonium hydroxides. Porous diaphragms of ceramic ware are most suitable. The materials useful for such diaphragms include porcelain, Alundum, Carborundum, and other refractory materials. The diaphragms may have a considerable range of porosity, although it has been noted that the yield and purity of the quaternary ammonium hydroxide is related to this factor. With less porous diaphragms the yield is good and the purity is excellent, but the rate of electrolysis may be slow. Highly dense diaphragms increase the resistance of the cell and lower current efficiency. Less dense or more porous diaphragms are permissible when freedom of the hydroxide from salt is not of prime importance and may become necessary when the size of an N-substituent is large and it is desired to collect the quaternary ammonium hydroxide about the cathode. In a cell having two diaphragms it is generally desirable that the diaphragm about the anode have a low porosity to prevent migration of quaternary ammonium ions into the anode compartment with resultant loss. A highly porous diaphragm about the cathode merely permits contamination of the quaternary ammonium hydroxide solution there with the salt. The diaphragms, therefore, should be selected with these factors in mind and with the object of giving as

pure a product as required with the maximum efficiency.

It has been found that diaphragms which have the most favorable balance of properties for electrolyzing quaternary ammonium salts having N-substituents of less than 12 carbon atoms possess porosities which are best defined in terms of flow therethrough. For best results the porosity should be such that a flow between about 0.001 cc. and about 0.020 cc. of water at 20° C. per square centimeter of surface results in one hour under a 20 cm. head.

In converting a quaternary ammonium salt to hydroxide the cell may be filled at the start with aqueous solution containing the salt, and a unidirectional current passed through the cell. The anions migrate to the region of the anode and a halogen or oxygen, depending upon the particular salt used, is evolved there. Quaternary ammonium ions are carried toward the cathode yielding quaternary ammonium hydroxide which may be removed either continuously or from time to time. By proper selection of diaphragms the liquor from the cathode compartment may be obtained essentially free from the quaternary salt. The concentration of the cathode liquor may be adjusted by adding water thereto and drawing off liquor as desired.

In the preferred procedure with a three-compartment cell the anode compartment is filled with a solution of a strong inorganic acid, preferably corresponding to the anion of the salt. A dilute solution of the desired quaternary ammonium hydroxide is placed in the cathode compartment. This hydroxide may have been prepared in a previous electrolysis or by a method other than electrolysis. The intermediate compartment is filled with an aqueous solution of quaternary ammonium salt. In this way there is the maximum utilization of quaternary ammonium salt with immediate production of hydroxide of high purity.

In another method of procedure the anode compartment may be filled with a solution of a strong acid and the rest of the cell filled with aqueous solution of a quaternary ammonium salt.

Conditions of electrolysis may be considerably varied. For example, voltages across the electrodes from about 2 volts to about 20 volts may be used, although it is desirable to maintain conditions such that as low voltages as possible are used in order to keep efficiency high. Current densities may also be considerably varied so long as excessive overvoltages do not result thereby and the cell is not excessively heated by the current flowing through it. It is desirable that the temperature be maintained below 50° C. to 60° C. to minimize decomposition of the hydroxide. Temperature may be controlled by rate of electrolysis and/or by cooling. In order to obtain as high efficiency as possible, it is desirable to work with fairly concentrated solutions of quaternary ammonium salts but any concentration up to saturation may be used by proper balancing of conditions. In general, all variables are in good balance when the hydrogen overvoltage does not exceed about 0.6 volt.

Further details of this invention are presented in the following illustrative examples.

Example 1

A rectangular cell of the type described above and illustrated in the drawing was built with anodes consisting of four graphite bars 25 mm. x 10 mm. x 300 mm. These bars were im-

pregnated with hot paraffin. The anode diaphragm was a porous porcelain vessel, 34 mm. wide, 198 mm. long, and 300 mm. high, the porosity of which allowed a flow of 0.001 cc. of water per hour per square centimeter of surface with a hydrostatic head of 20 cm. The diaphragm (corresponding to 5 in the diagram) setting off the cathode was a rectangular Alundum vessel, 80 mm. wide, 230 mm. long, and 300 mm. high, the porosity of which allowed a flow of 0.008 cc. of water per hour per square centimeter at a head of 20 cm. The cathode was a screen of iron wire fitted snugly but not tightly about the outer diaphragm. The porous vessels and electrodes were contained in a glass jar, 110 mm. x 200 mm. x 300 mm.

An aqueous solution which was 2.528 normal in dimethyldibenzyl ammonium chloride was run into the compartment between the diaphragms. The cathode compartment was filled with an aqueous solution containing 0.66 mol of dimethyldibenzyl ammonium hydroxide. The anode compartment was filled with 2 *n* hydrochloric acid solution. Electrolysis then proceeded with 10 amperes passing through the cell with a potential drop across the electrodes of 5.5 volts. The cell warmed up to 40–42° C., where the temperature remained constant. The solution of quaternary ammonium chloride was constantly replenished by trickling fresh solution into the central compartment. Water was added to the cathode compartment gradually and the cathode liquor was continuously drawn off at such a rate that the cathode liquor was maintained about 18 mm. below the level of the liquid between the diaphragms. By control of the rate at which water was added and solution removed, the concentration of the quaternary ammonium hydroxide solution drawn off was kept about 0.77 *n*. At the end of 128 hours of electrolysis 9.1 mols of dimethyldibenzyl ammonium hydroxide had been taken off in a solution which was found on analysis to be 0.775 *n*. Analysis for quaternary ammonium chloride showed the solution to be 0.0075 *n* in the chloride. Hence, the separation of chloride ion was over 99% complete.

In this preparation of quaternary ammonium hydroxide 18.05 mols of dimethyldibenzyl ammonium chloride were added in all and at the start 0.66 mol of dimethyldibenzyl ammonium hydroxide was added to the cathode compartment, making a total input of 18.71 mols. At the end of 128 hours of electrolysis there remained 2.83 mols of hydroxide in the cell and 4.11 mols of dimethyldibenzyl ammonium chloride in the intermediate compartment. These quantities, together with the 9.11 mols of the hydroxide removed, accounted for 16.05 mols. By difference, the loss of quaternary ammonium ion was 2.66 mols. The yield was, therefore, 81.7% at a current efficiency of about 30%. The loss is considered low in view of the fact that the quaternary ammonium ion can be oxidized at one electrode and decomposed at the other into amine. The loss can be made smaller by electrolysis at a lower current density.

Example 2

A 25% solution of di-(butoxy methyl) dimethyl ammonium chloride was placed in the intermediate compartment of a three-compartment cell. The cathode compartment was filled with a 5% aqueous solution of the same salt while the anode compartment was filled for reasons of economy with a 15% solution of hydrochloric acid. Direct

current was passed through the cell at a 6 volt potential drop with a current density of 0.7 ampere per square decimeter. The hydrogen overvoltage under such conditions was below one-half volt. At the end of 48 hours the cathode liquor was removed from the cell and evaporated under reduced pressure at 50° C. until it was 1.588 normal in hydroxide and 0.28 normal in quaternary ammonium salt. This solution was quite stable at room temperatures. The hydroxide was found to behave as a strong base. It was a very active swelling agent for cellulose.

Example 3

The method described in Example 2 was applied to the electrolysis of benzyl capryloxymethyl dimethyl ammonium chloride. Electrolysis was carried on at about 6 volts for two days. At the end of this time most of the chloride ion had been removed from the cathode compartment and the quaternary salt converted to the corresponding hydroxide. This solution was applied to rayon fabric which was then heated to 120° C. The resulting fabric was stabilized in dimensions against shrinking on laundering.

In place of the quaternary ammonium salts shown in the above examples there may be electrolyzed in the same way other salts, such as trimethyl benzyl ammonium chloride, dimethyl dibenzyl ammonium bromide, triethyl benzyl ammonium bromide, hydroxyethyl dimethyl benzyl ammonium chloride, benzyloxymethyl dimethyl benzyl ammonium chloride, trimethyl ethyl ammonium ethyl sulfate, etc.

These salts are converted by passage of electric current with low hydrogen overvoltage at the cathode into strong organic bases which are suitable as analytical reagents, solvents for cellulose and proteins, reagents for the syntheses of new compounds, etc.

The present case is a continuation-in-part of application Serial No. 310,360, filed December 21, 1939.

I claim:

1. A process for preparing in a cell having a cathode of low hydrogen overvoltage a quaternary ammonium hydroxide from a quaternary ammonium compound yielding salt-forming anions, the N-substituents of which compound are selected from at least one member of the class consisting of aliphatic groups and arylaliphatic groups attached through the aliphatic portion thereof to the quaternary nitrogen atom of said compound, which comprises passing a unidirectional electric current through an aqueous solution of said quaternary ammonium compound in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form quaternary ammonium hydroxide in aqueous solution about said cathode.

2. A process for the electrolytic preparation of a quaternary ammonium hydroxide from a quaternary ammonium compound yielding salt-forming anions, the N-substituents of said compound being selected from at least one member of the class consisting of aliphatic groups and arylaliphatic groups attached through the aliphatic portion thereof to the quaternary nitrogen atom of said compound, said preparation being conducted in an electrolytic cell having an inert anode set off by a porous ceramic diaphragm and a cathode of a metal having low hydrogen overvoltage set off by a second porous refractory diaphragm to form an intermediate compartment, which comprises passing a unidirectional current

through an aqueous solution of said quaternary compound in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form quaternary ammonium hydroxide in aqueous solution about said cathode.

3. A process for the electrolytic preparation of a quaternary ammonium hydroxide from a quaternary ammonium halide, the N-substituents thereof being selected from at least one member of the class consisting of aliphatic groups and arylaliphatic groups attached through the aliphatic portion thereof to the quaternary nitrogen atom of said compound, said preparation being conducted in an electrolytic cell having an anode substantially inert to halogens set off by a porous ceramic diaphragm and a cathode of a metal having low hydrogen overvoltage set off by a second porous refractory diaphragm to form an intermediate compartment, which comprises passing a unidirectional current through an aqueous solution of said quaternary compound in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form quaternary ammonium hydroxide in aqueous solution about said cathode.

4. A process for the electrolytic preparation of a quaternary ammonium hydroxide from a quaternary ammonium compound yielding salt-forming anions, the N-substituents thereof being selected from at least one member of the class consisting of aliphatic groups and arylaliphatic groups attached through the aliphatic portion thereof to the quaternary nitrogen atom of said compound, said preparation being conducted in an electrolytic cell having an inert anode set off by a porous ceramic diaphragm and a cathode of a metal having low hydrogen overvoltage set off by a second porous refractory diaphragm to form an intermediate compartment, which comprises passing a unidirectional current through an aqueous solution of said quaternary compound in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form quaternary ammonium hydroxide in aqueous solution about said cathode, adding aqueous solution of the quaternary ammonium compound to the intermediate compartment, and withdrawing from about the cathode an aqueous solution containing a quaternary ammonium hydroxide.

5. A process for the electrolytic preparation of a quaternary ammonium hydroxide from a quaternary ammonium compound yielding salt-

forming anions, the N-substituents of said compound being selected from at least one member of the class consisting of aliphatic groups and arylaliphatic groups attached through the aliphatic portion thereof to the quaternary nitrogen atom of said compound, said N-substituents containing from one to ten carbon atoms each, said preparation being conducted in an electrolytic cell having an anode substantially inert to halogens and set off by a porous refractory diaphragm and having a cathode of a metal characterized by low hydrogen overvoltage and set off to form an intermediate compartment by a second porous refractory diaphragm of a porosity which permits the flow of 0.001 cc. to 0.020 cc. of water at 20° C. per square centimeter per hour under a head of 20 cm. of water, which comprises passing a unidirectional current through an aqueous solution of said quaternary compound in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form quaternary ammonium hydroxide in aqueous solution about said cathode.

6. A process for the electrolytic preparation of dimethyl dibenzyl ammonium hydroxide in a cell having a cathode of low hydrogen overvoltage, which comprises passing a unidirectional electric current through an aqueous solution of a dimethyl dibenzyl ammonium salt in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form an aqueous solution of said hydroxide about said cathode.

7. A process for the electrolytic preparation of trimethyl benzyl ammonium hydroxide in a cell having a cathode of low hydrogen overvoltage, which comprises passing a unidirectional electric current through an aqueous solution of a trimethyl benzyl ammonium salt in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form an aqueous solution of said hydroxide about said cathode.

8. A process for the electrolytic preparation of capryloxymethyl dimethyl benzyl ammonium hydroxide in a cell having a cathode of low hydrogen overvoltage, which comprises passing a unidirectional electric current through an aqueous solution of a capryloxymethyl dimethyl benzyl ammonium salt in said cell while maintaining the cathodic hydrogen overvoltage below about 0.6 volt to form an aqueous solution of said hydroxide about said cathode.

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