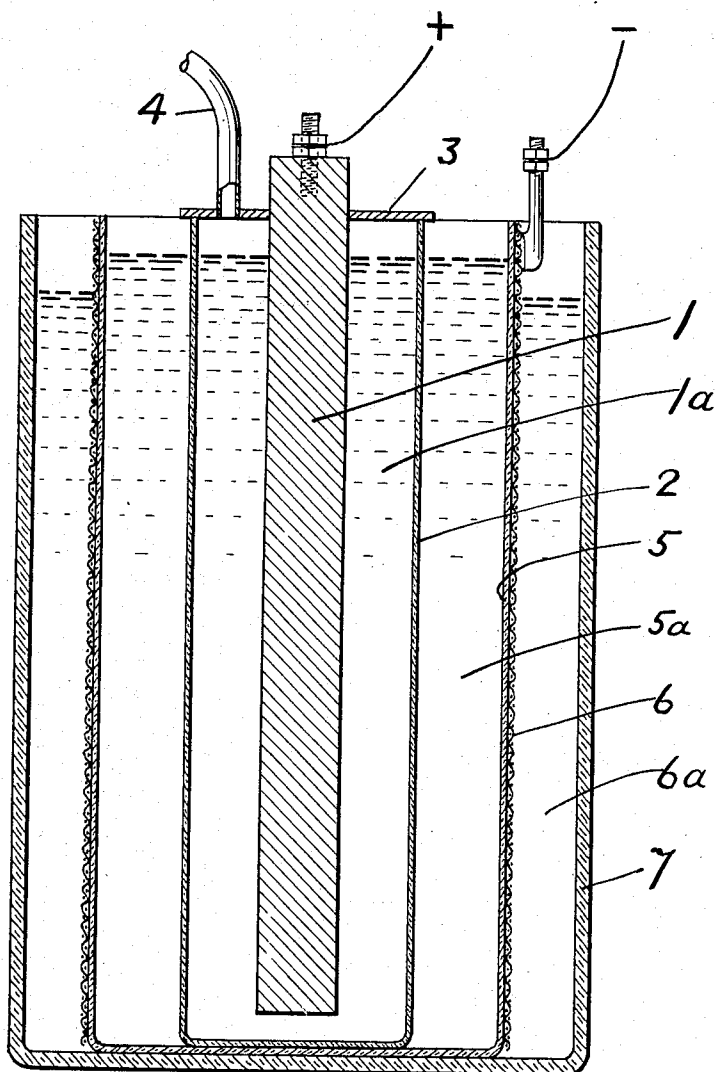


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L. H. BOCK
ELECTROLYTIC PREPARATION OF CAPILLARY-ACTIVE
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WITNESS:

Robert Mitchell

INVENTOR

Louis H. Bock

BY

John F. Bergin
ATTORNEY.

UNITED STATES PATENT OFFICE

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ELECTROLYTIC PREPARATION OF CAPILLARY-ACTIVE QUATERNARY AMMONIUM HYDROXIDES

Louis H. Bock, Huntingdon Valley, Pa., assignor to Röhm & Haas Company, Philadelphia, Pa., a corporation of Delaware

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This invention relates to a process for preparing quaternary ammonium hydroxides having capillary activity. In particular this invention deals with the preparation of quaternary ammonium hydroxides from corresponding salts having an N-substituent containing at least 10 carbon atoms.

In application Serial No. 310,360, filed December 21, 1939, of which this application is a continuation-in-part, there is described an electrolytic method for preparing quaternary ammonium hydroxides. This method is generally applicable to the conversion of quaternary salts to hydroxides when the groups in the molecule are not readily reduced and the molecules have sufficient stability to prevent decomposition to tertiary amines and hydrocarbons. By the use of porous refractory diaphragms good purity of the desired hydroxide may be attained with good yield. As one or more of the N-substituents is made large enough to give soap-like properties to the quaternary ammonium hydroxide, difficulties appear, however, in that coarse diaphragms become necessary and foam forms about the cathode. When a coarse diaphragm sets off the cathode, anions tend to diffuse into the cathode compartment to decrease the purity of the product. With evolution of hydrogen about the cathode the formation of foam as a result of capillary activity or soap-like properties creates a problem.

It is an object of this invention to prepare quaternary ammonium hydroxides having capillary activity. It is an object to prepare long-chained quaternary hydroxides with a minimum contamination of quaternary salts and decomposition products thereof. It is also an object to provide an electrochemical method of preparing long-chained, non-aromatic quaternary ammonium hydroxides, which is free from difficulties heretofore encountered.

These objects are accomplished by placing an aqueous solution of a capillary-active quaternary ammonium salt in the intermediate compartment of an electrolytic cell having an anode set off by a refractory diaphragm of defined porosity to form an anode compartment which contains an aqueous solution of a strong acid and having a cathode set off by a refractory diaphragm of defined porosity to form a cathode compartment which contains an aqueous solution of an alkali, said diaphragms forming the said intermediate compartment, and passing a unidirectional current through said cell whereby the salt-forming

anions of said salt are substantially replaced with hydroxyl ions.

The porosity of the diaphragms may be defined by the rate of flow therethrough. It has been found that diaphragms giving a flow between about 0.001 cc. and about 0.015 cc. of water at 20° C. per square centimeter per hour under a hydrostatic head of 20 cm. are suitable for preparation of quaternary ammonium hydroxides by this invention. The diaphragms are composed of a refractory material such as Carborundum, Alundum, porcelain, or other ceramic composition.

A suitable multi-compartment cell is illustrated in vertical cross-section in the drawing. The anode 1 is surrounded by a porous diaphragm 2 to form an anode compartment 1a which is sealed by a cover 3 having the tube 4 through which gases may be withdrawn from the anode compartment. A short distance from diaphragm 2 is located a second diaphragm 5, which sets off the cathode 6, forms a cathode compartment 6a, and at the same time in conjunction with diaphragm 2 forms an intermediate compartment 5a. The various parts described are assembled within a container 7.

As an anode there may be used any conducting material which is relatively inert to halogens or oxygen, such as carbon, carbon impregnated with oil or paraffin, or one of the platinum group metals. The cathode is composed of a metal which is not attacked by alkali, such as iron or platinum. The cathode 6 and container 7 may be one and the same unit, since an alkali-resistant metal serves satisfactorily as a container. With separate cathode and container, the latter may be composed of a material such as glass or vitreous ware.

It will be evident to those skilled in the art that the electrolytic cell used may take many shapes and dimensions. It is, of course, desirable to keep the cell as compact as possible to decrease internal resistance and increase efficiency.

As a quaternary ammonium salt there may be used any salt having N-substituents of sufficient size to impart capillary activity to the compound. Capillary activity is generally first noted with a substituent of 10 carbon atoms and is particularly marked in the case of quaternary ammonium compounds having at least one substituent of 12 to 18 carbon atoms. The N-substituents are preferably aliphatic or arylaliphatic, as these give stable hydroxides. Substituents of other types tend to cause decomposition of the quaternary type of compound, even under the favor-

able conditions encountered in the method here disclosed. The aliphatic or arylaliphatic substituents may be straight, branched, saturated, unsaturated, or may contain cycles, excluding aromatic cycles which are attached directly to the quaternary nitrogen atoms. The term "non-aromatic" is used herein to characterize compounds in which an aryl ring is not directly connected to the pentavalent nitrogen. These substituents may be hydrocarbon groups or they may be groups which contain stable functional groups such as hydroxyl, ether, or amino groups. Typical substituents imparting capillary activity are decyl, dodecyl, cetyl, octadecyl, octadecenyl, dodecyloxymethyl, octadecyloxymethyl, undecenyl, undecenylloxymethyl, butylbenzyl, diisobutylbenzyl, butylnaphthoxyethyl, diisobutylphenoxyethyl, diisobutylcresoxyethyl, diisobutylchlorophenoxyethyl, octylphenoxyethoxyethyl, etc. In addition to at least one such group which is capable of imparting capillary activity, other aliphatic or arylaliphatic groups are attached to the quaternary nitrogen atom, such as methyl, ethyl, hydroxyethyl, aminoethyl, propyl, isopropyl, butyl, capryl, ethoxyethyl, caproxymethyl, benzyl, benzyloxymethyl, etc.

In general, suitable salts which may be converted by the herein-described process are of the formula:



wherein X is a salt-forming anion such as chloride, bromide, iodide, sulfate, acetate, phosphate, etc. and R₁, R₂, R₃, and R₄ are aliphatic or arylaliphatic groups at least one of which contains at least 10 carbon atoms. Suitable salts are decyl diethyl benzyl ammonium bromide, dodecyl dimethyl benzyl ammonium chloride, octadecyl trimethyl ammonium chloride, cetyloxymethyl dimethyl methylbenzyl ammonium chloride, dodecyl phenoxyethoxyethyl dimethyl ammonium chloride, or other water-soluble quaternary ammonium compound exhibiting surface activity.

In converting a salt of the above type to the corresponding hydroxide an aqueous solution of the salt is prepared and placed in a cell between two refractory diaphragms having a porosity permitting a flow of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head. Behind one diaphragm a solution of a strong acid, such as hydrochloric acid or sulfuric acid, is placed as the anolyte. Behind the other diaphragm a solution of an alkali, such as sodium or potassium hydroxide, or a quaternary ammonium hydroxide of low molecular weight, is placed to serve as the catholyte. Current is then passed through the cell. Neither voltage nor current density are critical factors in this process although it is, of course, desirable to establish and maintain conditions such that as good current efficiency as possible is obtained by keeping the voltage relatively low, four to twenty volts being suitable, and keeping the overvoltage also low by moderate to low current densities, values for which may be as high as three amperes per square decimeter. During the passage of electric current the temperature of the cell rises. Temperatures up to about 50° C. are often helpful in maintaining good solubility and low viscosity of the solutions. Excessive temperatures, however, in some cases cause

decomposition of the long-chained quaternary compounds but decomposition can be avoided by control of voltage and amperage or by cooling. Under the influence of the current the salt-forming anion migrates through the diaphragm about the anode and, in the case of such anions as chloride, chlorine is liberated at this pole. The quaternary ammonium ion is apparently present in a soap-like micelle which escapes only with difficulty into the cathode compartment through a diaphragm of the range of porosity above-specified. As a result, practically pure quaternary ammonium hydroxide is obtained in the intermediate compartment. The process is continued until the original anion is exhausted from this compartment or reduced to any required level.

The description of the preparation of long-chained quaternary ammonium hydroxides is amplified in the following illustrative examples.

Example 1

A solution of benzyl dimethyl octadecyl ammonium chloride in water, adjusted to a normality of 1.5, was placed in the intermediate compartment of a cell having a Carborundum cup surrounding a graphite anode and an Alundum jar separating the intermediate compartment from the cathode compartment. An iron screen served as a cathode. The porosity of the Carborundum cup allowed the flow of 0.001 cc. of water per square centimeter per hour under a 20 cm. head. The Alundum vessel permitted a flow of 0.008 cc. of water per square centimeter per hour. A 15% solution of hydrochloric acid was placed in the anode compartment while a 10% solution of sodium hydroxide was run into the cathode compartment. A current of two amperes at seven volts was passed through the cell. There was an increase in the volume of liquor in the intermediate compartment probably due to electroendosmosis. This necessitated occasional withdrawal of solution from between the diaphragms and adjustment of liquid levels in the other compartments by the addition of water. At the end of 47 hours the chloride content of the solution in the intermediate compartment was found to be nil and the normality of the hydroxide solution was found to be 0.52 normal with respect to benzyl dimethyl octadecyl ammonium hydroxide.

Example 2

The procedure described in Example 1 was repeated with a saturated solution of octadecyloxymethyl dimethyl benzyl ammonium chloride in place of the octadecyl dimethyl benzyl ammonium salt used above. The passage of current was continued until the liquor from the intermediate compartment was low in chlorine. The resulting solution contained octadecyloxymethyl dimethyl benzyl ammonium hydroxide, which formed a gel at a concentration of about 25%.

Example 3

The procedure of Example 1 was repeated with a solution of dodecyloxymethyl dimethyl benzyl ammonium chloride. Dodecyloxymethyl dimethyl benzyl ammonium hydroxide was obtained in solution.

Dodecyl dimethyl benzyl ammonium chloride was likewise converted electrolytically to dodecyl dimethyl benzyl ammonium hydroxide in aqueous solution.

The quaternary ammonium hydroxides of this

invention are useful as swelling agents for cellulose and finishing agents for cellulosic fabrics. They are peculiarly effective for treating regenerated cellulose. They are useful for making salts of various acids when no other means of producing such salts is known.

The capillary-active quaternary ammonium hydroxides have not heretofore been available in view of the fact that conventional metatheses fail to give products which can be separated with isolation of capillary-active quaternary ammonium hydroxides free from soluble or insoluble salts, which might result from attempted metathesis. Thus, the method herein described, which may be considered one of electrodialysis, yields capillary-active quaternary ammonium hydroxides which are substantially free from non-quaternary products.

I claim:

1. A process for the preparation of a capillary-active quaternary ammonium hydroxide in an electrolytic cell having an anode inert to oxygen and halogens set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having an intermediate compartment between said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing about the anode of the cell an aqueous solution of a strong acid, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in a compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of a quaternary ammonium compound having salt-forming anions and having its N-substituents selected from at least one member of the class consisting of aliphatic and arylaliphatic groups, at least one of which substituents contains at least 10 carbon atoms, and passing a unidirectional electric current through said cell until the salt-forming anions of the quaternary ammonium compound have been substantially replaced with hydroxyl ions.

2. A process for the preparation of a capillary-active quaternary ammonium hydroxide in an electrolytic cell having an anode inert to halogens set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing about the anode of the cell an aqueous solution of a halogen acid, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of a capillary-active quaternary ammonium halide, the N-substituents of which are selected from at least one member of the class consisting of aliphatic and arylaliphatic groups, and passing a unidirectional electric current through said cell until the halogen of the quaternary ammonium halide

has been substantially replaced with hydroxyl ions.

3. A process for the preparation of a capillary-active quaternary ammonium hydroxide in an electrolytic cell having an anode inert to halogens set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.15 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing about the anode of the cell an aqueous solution of a halogen acid, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of a quaternary ammonium halide, the N-substituents of which are selected from at least one member of the group consisting of aliphatic and arylaliphatic groups and one N-substituent being an aliphatic group having 12 to 18 carbon atoms, and passing a unidirectional current through said cell until halogen is essentially removed from the intermediate compartment.

4. A process for the preparation of a capillary-active quaternary ammonium hydroxide in an electrolytic cell having an anode inert to halogens set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing about the anode of the cell an aqueous solution of a halogen acid, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of a quaternary ammonium chloride, the N-substituents of which are selected from at least one member of the group consisting of aliphatic and arylaliphatic groups and one N-substituent being an aliphatic group having 12 to 18 carbon atoms, and passing a unidirectional current through said cell until chlorine is essentially removed from the intermediate compartment.

5. A process for the preparation of benzyl dimethyl octadecyl ammonium hydroxide in an electrolytic cell having an anode inert to chlorine set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing an aqueous solution of hydrochloric acid about the anode of the cell, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of benzyl dimethyl

octadecyl ammonium chloride and passing a unidirectional electric current through said cell until the chlorine ions have been substantially removed from the intermediate compartment.

6. A process for the preparation of benzyl dimethyl octadecyloxymethyl ammonium hydroxide in an electrolytic cell having an anode inert to chlorine set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing an aqueous solution of hydrochloric acid about the anode of the cell, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of benzyl dimethyl octadecyloxymethyl ammonium chloride and passing a unidirectional electric current through said cell until the chlorine ions

have been substantially removed from the intermediate compartment.

7. A process for the preparation of benzyl dimethyl dodecyl ammonium hydroxide in an electrolytic cell having an anode inert to chlorine set off by a porous refractory diaphragm to form a compartment about the anode, having a cathode set off by a second porous refractory diaphragm to form a compartment about the cathode, and having a compartment intermediate to said anode and cathode, the porosity of said diaphragms permitting the flow therethrough of about 0.001 cc. to about 0.015 cc. of water at 20° C. per square centimeter per hour under a 20 cm. head, which comprises placing an aqueous solution of hydrochloric acid about the anode of the cell, placing about the cathode of the cell an aqueous solution of an alkali yielding hydroxyl ions, placing in the compartment of the cell intermediate to the anode and cathode thereof an aqueous solution of benzyl dimethyl dodecyl ammonium chloride and passing a unidirectional electric current through said cell until the chlorine ions have been substantially removed from the intermediate compartment.

LOUIS H. BOCK.