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ELECTROLYTE FOR THE MANUFACTURE OF HYDROGEN PEROXIDE

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This invention relates to processes of manufacture of hydrogen peroxide and more particularly refers to improvements in solutions to be used as electrolytes for the production of anolyte liquor from which the hydrogen peroxide is subsequently liberated by distillation.

In the manufacture of hydrogen peroxide, the product is generally obtained by the distillation of a solution containing among other ingredients persulphuric acid or a persulphate, preferably a persulphate of an alkali metal such as for instance, potassium.

The distillation of such a solution, the other ingredients of which are generally sulphuric acid and water, results in the liberation of hydrogen peroxide and water in the form of steam, which are led to a condenser where they are collected in the form of a solution of hydrogen peroxide in water.

Processes now in use result in a relatively low yield of peroxide, because of catalytic and other impurities which are contained in the mass and which cause an almost immediate dissociation of the peroxide as it is liberated, with loss of oxygen.

Hydrogen peroxide may either be obtained by the distillation of a solution of persulphuric acid in sulphuric acid and water, or else by the distillation of a solution of persulphate in a mixture of sulphuric acid and water.

The persulphuric acid or persulphate are obtained by the action of an electric current flowing through an electrolyte, composed of sulphuric acid and water only or else composed of a sulphuric acid salt, such as for instance, potassium bisulphate, in a mixture of sulphuric acid and water.

The latter type of electrolyte is preferable in practice, because of its greater conductivity and efficiency. One of the factors contributing to an increased efficiency is the greater viscosity of an electrolyte thus obtained, as against that of an electrolyte only composed of sulphuric acid diluted with water.

The electrolytic operation is conducted in the usual manner by passing a current through the electrolyte from the anode to the cathode, the container being divided into two chambers, an anodic chamber and a cathodic chamber, by means of a porous diaphragm. The electrolysis of the mixture results in the liberation of hydrogen at the cathode and oxygen at the anode, the hydrogen being lost and the oxygen being recombined with the sulphuric acid or the bisulphate, or both, forming a persulphuric acid or a persulphate.

The reactions taking place in the course of the electrolytic operation are as follows:—

If sulphuric acid only and water are used, the same are used in the proportions of 30% to 50% and 70% to 50% by weight, respectively. After approximately two hours operation, the liquid in the cathodic chamber is practically unchanged, while the liquid in the anodic chamber or anolyte will have acquired the composition of $H_2(SO_4)_2+H_2O$ that is, $H_2S_2O_8$ (persulphuric acid) $+H_2O$ (water).

If a bisulphate also is used in the composition of an electrolyte, for instance potassium bisulphate $KHSO_4$, the same is added to a mixture of 30% to 50% H_2SO_4, and 70% to 50% H_2O, so as to produce a saturated solution; this calls for an addition of between 55 to 60 parts of the bisulphate, to 100 parts of the sulphuric acid-water solution by weight.

The electrolyte will therefore originally have the composition

$$KHSO_4+H_2SO_4+H_2O.$$

After about two hours period during which the electric current is caused to electrolyze the solution, the composition of the catholyte will still be the same, while the anolyte will have acquired the composition

$$K_2S_2O_8+H_2SO_4+H_2O,$$

the first named ingredient, potassium persulphate, representing about 30% of the solution by weight.

The anolyte liquor is subsequently distilled under proper conditions, giving occurrence to the liberation of $H_2O_2+H_2O$, one of the atoms of oxygen going to form the peroxide being abstracted from the persulphate which will then acquire the formula $H_2S_2O_7$.

It is obvious that the best operating conditions are obtained when the electrolyte is highly responsive to the action of the electric current and when separation of the catholyte from the anolyte due to the electrolyte action having occurred, the possibility of mutual diffusion of the two bodies of liquid within each other through the porous diaphragm separating them, is impeded or eliminated.

A high conductivity of the electrolyte results in the possibility of using lower voltages with consequent savings of electric current, and the retarding or impeding of diffusion results in a greater quantity of anolyte liquor being formed in a given period of time.

As stated, an electrolyte containing a sulphuric acid salt in addition to a sulphuric acid-water solution, has a greater viscosity than a simple sulphuric acid-water solution, and similarly an anolyte containing a persulphate has a greater viscosity than an anolyte containing only persulphuric acid.

It is therefore obvious that due to the greater viscosity of the two bodies of liquid, the influence of the diffusion factor will be lessened to a considerable extent.

The primary object of this invention is to provide a novel and improved type of electrolyte adapted for use in the preliminary stages of a process of manufacture of hydrogen peroxide, whereby a higher yield of persulphate is obtained than is obtainable by means of electrolytes heretofore known, under the same conditions.

Another object is to provide an electrolyte for the purpose specified having a relatively high coefficient of viscosity and tending to reduce the diffusion losses to a minimum.

A further object is to provide a novel and improved type of electrolyte adapted for the electrolytic production of a persulphate solution, having a relatively high conductivity and permitting the employment of relatively low voltages with consequent savings in power costs.

A still further object is to provide an improved electrolyte of a relatively inexpensive nature, which may be compounded from readily available ingredients and which does not require any special experience either for its preparation or its operation.

Other objects and advantages of the present invention will more fully appear as the description proceeds and will be set forth and claimed in the appended claims.

In compounding my improved electrolyte, I take 150 parts of water by weight, and to these I add from 10 to 60 parts of potassium sulphate K_2SO_4 and from 5 to 40 parts of sulphuric acid, H_2SO_4, commercial grade, the preferred proportions being H_2O 150 parts by weight, K_2SO_4 45 parts, by weight, H_2SO_4 17 parts by weight. To this solution I add, from 5 to 70 parts of ammonium sulphate $(NH_4)_2SO_4$, the preferred proportion being 50 parts.

An electrolyte of the above composition has a greater conductivity and results in a greater yield of persulphate than an electrolyte of the ordinary composition

$$KHSO_4 + H_2SO_4 + H_2O$$

previously mentioned. In order to further improve the solution. I then add from ½ to 10 parts of potassium dichromate $K_2Cr_2O_7$, the preferred proportion being 5 parts.

To the above, I can also finally add a relatively small proportion of cerium sulphate, $Ce_2(SO_4)3$, namely ½ to 10 parts, preferably about 3 parts by weight. I have found that the latter ingredient materially assists the electrolytic action, speeding up the electrolytic dissociation and consequently speeding up the formation of persulphates; but the addition should not be excessive because it might otherwise result in a pronounced catalytic effect during the subsequent process of distillation which might cause dissociation and consequent loss of oxygen.

The preferred type of solution should have substantially the following composition:

	Parts by weight
Water	150
Potassium sulphate	10 to 60
Sulphuric acid	5 to 40
Ammonium sulphate	5 to 70
Potassium dichromate	½ to 10
Cerium sulphate	½ to 10

and upon analysis, it should yield the following ingredients and proportions.

	Parts by weight
Hydrogen	17.00 to 22.00
Oxygen	142.00 to 221.06
Potassium	4.48 to 29.15
Sulphur	4.65 to 42.56
Nitrogen	1.05 to 14.81
Chromium	0 to 3.53
Cerium	0 to 4.92

It will be understood that a solution analyzing as above may be compounded otherwise than hereinbefore set forth, and that therefore the invention is not limited to the stated manner of compounding.

It will also be understood that although potassium sulphate has been specifically mentioned, another metallic salt of sulphuric acid may be used, preferably a salt of the same or of another alkali metal; similarly another salt containing chromium may be used, such as for instance sodium chromate, or else a sulphuric acid salt of chromium, or a chrominum alum instead of potassium dichromate, and another salt of cerium with sulphuric acid may be substituted for the cerium sulphate mentioned, as long as quantities of chromium and cerium equivalent to those

mentioned are carried into solution. Therefore it may be broadly stated that not only the substances mentioned but their substitutes or homologues fall within the scope of my invention.

The advantages inherent to an electrolyte of the type specified are a very high conductivity permitting of either reducing the voltage or the time factor, a high amperage capacity, that is, a capacity to quickly absorb the oxygen produced at the anode in relatively large volumes per unit of time, a high yield of persulphates, and minimized diffusion losses.

The latter advantage is due to the fact that the solution has a relatively high coefficient of viscosity. In addition to this, the solution can be prepared and operated with the greatest ease, the various ingredients being readily mixable with one another, to form a stable and uniform mixture.

I have also found that an electrolyte of the composition stated permits of conducting the electrolytic operation at relatively high temperatures without causing a reduction of the persulphate to sulphate. If temperatures higher than 30 to 35° C. are used in connection with electrolytes heretofore in use, a considerable proportion of the persulphate will be reduced to sulphate so that the yield becomes unsatisfactory.

On the other hand, if a true cyclic process is to be employed throughout the use of relatively high temperatures is desirable in order to prevent crystallization of the persulphate.

My improved electrolyte as stated permits of using temperatures sufficient to prevent the crystallization of the persulphate, and prevents at the same time a diminution of the persulphate yield through reduction.

The solution is practically self sustaining because no losses of active materials occur during the process of distillation; so that the residues of the processes of distillation may be returned over and over again to the electrolytic container or containers, making it necessary only to add water each time the electrolytic process is started.

I claim:

1. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with a sulphuric acid salt of an alkali metal, an ammonium salt, cerium, and an alkali metal salt containing chromium.

2. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with a sulphuric acid salt of an alkali metal, an ammonium salt, cerium, and an alkali metal salt containing chromium.

3. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of potassium, ammonia and cerium, and an alkali metal salt containing chromium.

4. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of potassium, ammonia and cerium and a salt of potassium containing chromium.

5. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of an alkali metal, and cerium, ammonium sulphate, and a salt containing chromium.

6. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with a sulphuric acid salt of an alkali metal, ammonium sulphate, cerium sulphate, and a salt containing chromium.

7. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of potassium and cerium, ammonium sulphate, and a salt of potassium containing chromium.

8. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with a sulphuric acid salt of potassium, ammonium sulphate, cerium sulphate and a salt of potassium containing chromium.

9. An electrolyte for the preparation of an alkali persulphate, comprising, in water solution, sulphuric acid, together with a sulphuric acid salt of potassium, ammonium sulphate, cerium sulphate, and a salt of potassium containing chromium.

10. An electrolyte for the preparation of an alkali persulphate analyzing as follows: hydrogen, 17.00 to 22.00 parts; oxygen, 142. to 221.06 parts; potassium, 4.48 to 29.15 parts; sulphur, 4.65 to 42.46 parts; nitrogen, from 1.05 to 14.81 parts; chromium, from 0 to 3.53; cerium, from 0 to 4.92 parts, by weight.

11. An electrolyte for the preparation of a compound including in its composition the group S_2O_8, containing cerium.

12. An electrolyte for the preparation of a compound including in its composition the group S_2O_8, containing chromium and a sulphuric acid salt of cerium.

13. An electrolyte for the manufacture of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of an alkali metal, ammonia and cerium, and a salt containing chromium.

14. An electrolyte for the manufacture of an alkali persulphate, comprising, in water solution, sulphuric acid, together with sulphuric acid salts of an alkali metal, ammonia, and cerium, and a potassium salt containing chromium.

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