UNITED STATES PATENT OFFICE.

OTTO LIEBKNECHT, OF FRANKFORT-ON-THE-MAIN, GERMANY, ASSIGNOR TO ROESSLER & HASSLACHER CHEMICAL CO., OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

PROCESS FOR THE MANUFACTURE OF GLYCOLIC ACID.

1,013,502. Specification of Letters Patent. Patented Jan. 2, 1912.

No Drawing. Application filed March 1, 1911. Serial No. 611,586.

To all whom it may concern:

Be it known that I, OTTO LIEBKNECHT, a subject of the German Emperor, and a resident of Frankfort-on-the-Main, Germany, have invented a certain new and useful Improvement in Processes for the Manufacture of Glycolic Acid, of which the following is a specification.

This invention relates to a more economical and effective process of manufacturing glycolic acid by the electrolytic reduction of oxalic acid than heretofore.

I have described a process for the manufacture of glycolic acid by the electrolytic reduction of oxalic acid in my United States Patent No. 837,083 patented November 27, 1906, in which process there is a cathodic overvoltage and the conduction of the current is through a suitable inorganic acid, such as dilute sulfuric or hydrochloric acid, rather than through the oxalic acid. In my patented process the oxalic acid to be electrolytically reduced is concentrated to a certain degree and I have found, in practicing the same, that it is easy to carry the degree of concentration too far whereby the oxalic acid is caused to participate in the conduction of the current and to go to the anode where it is oxidized into carbonic acid.

I have discovered by experiment and research that the slow addition of solid or dissolved oxalic acid to the catholyte during the electrolysis, so that oxalic acid is always present for reduction by the hydrogen developed at the cathode, permits a much higher concentration of glycolic acid than heretofore, that is up to 40% and more, resulting in a much more favorable and economical method of making glycolic acid because of working with such higher concentration. In such case there is no fear of going too far in cathodic reduction and anodic decomposition of the oxalic acid by oxidation and an almost voluntary progressive enrichment of the catholyte in glycolic acid is obtained. An explanation of this surprising fact, quite contrary to the communications in the literature (see *Claus Annals B.* 145 p. 256), lies in the circumstance that the glycolic acid, even at the higher degree of concentration, is not further reduced to acetic acid and, as a mono-basic and much weaker acid, offers more resistance to the electric current. I have further discovered that the conversion of oxalic acid into glycolic acid can be carried out in a quicker and more favorable manner, by starting with a considerably concentrated solution of oxalic acid, (20 to 30% and more), the current density at the same time being proportionally increased from 250 to about 500 amperes per square meter of cathode surface and higher. This results in the unforeseen circumstance that the concentration of the inorganic acid employed may be decreased to less than 10% and even to 2 or 3%, or the acid may be omitted entirely, without the fear of the anodic oxidation going too far. This is particularly true if it be arranged so that the level of the liquid in the anode compartment is higher than the level of the liquid in the cathode compartment, for this will prevent the oxalic acid from entering the anode compartment. In this manner solutions of glycolic acid may be obtained up to a concentration of 40% and more with but 3% or less of inorganic or mineral acid. Particularly favorable results are obtained by the use of cathodes having a large effective surface, such as those used in accumulators of the "Planté" plate type.

As an example of one way of carrying out my new process I give the following: Twenty-five parts by weight of crystallized oxalic acid are dissolved in about eighty parts by weight of water to which is added seven parts by weight of a suitable inorganic or mineral acid, sulfuric acid of a specific gravity of 1.6 having been found satisfactory. This solution forms the catholyte, which should be placed in the cathodic compartment of a suitably electrolytic apparatus provided with a suitable diaphragm. The cathodes should preferably be in the form of accumulator electrodes as above described. The anolyte comprises a twenty five to thirty per cent. sulfuric acid for example, as such gives a good conductivity. The density of the current at the cathode in the example given should be from five hundred to six hundred amperes per square meter of cathode surface. When the larger part of the oxalic acid has been converted into glycolic acid, which fact is ascertained by test, solid or dissolved oxalic acid is slowly added to the catholyte to bring the same up to the degree of concentration of oxalic acid desired. This operation is repeated until the solution contains glycolic acid in the desired degree of concentration. Of course por-

tions of the catholyte could be removed from time to time, enriched with oxalic acid and returned to the cathode chamber instead of introducing the oxalic acid directly into the cathode chamber. I have found that by thus slowly adding seventy five parts by weight of crystallized oxalic acid to the above solution, a solution is finally obtained which contains but little mineral acid and over forty grams of glycolic acid in each one hundred grams of catholyte. The concentration may easily be carried to a still greater degree if desired.

As above stated the amount of mineral acid may be decreased especially if the anolyte stands at a higher level than the catholyte. The oxalic acid may be added continuously if desired rather than intermittently. Hydrochloric acid may be substituted for sulfuric acid if desired. I refer to my Patent No. 837,083 for other details common to the two processes.

As it is obvious that the process herein described may be practiced in a number of different ways with considerable variation, I do not restrict myself to the steps or proportions described further than the scope of the claims demand but—

What I claim and desire to secure by Letters Patent of the United States is:

1. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus in the presence of electrodes having a cathodic overvoltage, while maintaining the quantity of oxalic acid in the solution at such a point that it is always present for reduction by the hydrogen developed at the cathode.

2. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in a solution of a suitable inorganic acid in the cathode compartment of an electrolytic apparatus in the presence of electrodes having a cathodic overvoltage, while maintaining the quantity of oxalic acid in the solution at such a point that it is always present for reduction by the hydrogen developed at the cathode.

3. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus by a current having a density of over approximately 250 amperes per square meter of cathode surface.

4. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus by a current having a density of over approximately 250 amperes per square meter of cathode surface, the initial concentration of the oxalic acid solution being increased proportionally to the increase of current density.

5. A process for the manufacture of glycolic acid from oxalic acid, consisting in the elctrolytic reduction of oxalic acid dissolved in a suitable dilute inorganic acid of less than 10% concentration in the cathode compartment of an electrolytic apparatus, by a current having a density of over approximately 250 amperes per square meter of cathode surface, the initial concentration of the oxalic acid solution being increased proportionally to the increase of current density.

6. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus by a current having a density of over approximately 250 amperes per square meter of cathode surface, the initial concentration of the oxalic acid solution being increased proportionally to the increase of current density and maintaining the anolyte at a higher level than the catholyte.

7. A process for the manufacture of glycolic acid from oxalic acid, consisting in the elctrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus in the presence of accumulator electrodes having a cathodic overvoltage, while maintaining the quantity of oxalic acid in the solution at such a point that it is always present for reduction by the hydrogen developed at the cathode.

8. A process for the manufacture of glycolic acid from oxalic acid, consisting in the electrolytic reduction of oxalic acid in solution in the cathode compartment of an electrolytic apparatus by a current having a density of over approximately 250 amperes per square meter of cathode surface, the initial concentration of the oxalic acid solution being increased proportionally to the increase of current density and the quantity of oxalic acid in the solution being maintained at such a point that it is always present for reduction by the hydrogen developed at the cathode.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

OTTO LIEBKNECHT.

Witnesses:
JEAN GRUND,
CARL GRUND.