UNITED STATES PATENT OFFICE.

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METHOD OF PREPARING HALOGEN-OXYGEN COMPOUNDS BY ELECTROLYSIS.

1,038,194. Specification of Letters Patent. Patented Sept. 10, 1912.

No Drawing. Application filed April 8, 1911. Serial No. 619,636.

To all whom it may concern:

Be it known that I, MATHIAS PIER, doctor of philosophy, subject of the Emperor of Germany, residing at Schlachtensee, near Berlin, Prussia, Germany, have invented a new and useful Improvement in the Method of Preparing Halogen-Oxygen Compounds by Electrolysis, of which the following is a full, clear, and exact description.

During the electrolysis of the alkalis and alkaline earths for the preparation of the corresponding halogen-oxygen compounds it has been found to be of advantage in order to obtain high yields of material on the current used to add to the electrolyte a chlorid of a metal which is precipitated by means of alkali from the salt solutions of same in the form of an oxid or hydroxid. In order to insure the efficiency of these additions, the presence of chromate was heretofore considered necessary. I have discovered that the technical chlorid of cerium forms an exception to this rule to such an extent that by means of the addition of same to the electrolyte high yields of material on the current used are obtained without the addition of chromate. This specific property, to prevent the reduction of hypohalogen acids, is also a property of other compounds of rare earth metals, but the use of cerium chlorid was found to be of special advantage.

All the compounds of the rare earth metals with which I have experimented separate at the cathode upon electrolysis in an insoluble form which adheres, forming a visible, effective diaphragm. That part which is not consumed for the formation of a cover for the electrode is precipitated as an insoluble substance. The electrolyte itself remains entirely free from impurities and entirely clear.

In the literature of the art, substances are repeatedly mentioned which, it is claimed, render possible an increase in the yield of chlorate in the same manner as the rare earth metals, *i. e.* without the addition of chromate. For instance, vanadium compounds are recommended as an addition in order to increase the yield, but it was found that the addition of vanadium compounds either does not increase the chlorate yield at all, or that this yield is unfavorably influenced by this addition. The vanadium compounds separate principally at the anode in thick crusts, which during continuous operation are bound to unfavorably influence the operation. The chlorate solutions, furthermore, are strongly colored.

Still more unfavorable results are obtained when operating with the addition of iron and copper compounds. In this instance also, as shown in the attached comparative tables, the yield of material obtained on the current is not increased but rather reduced. The examples cited below, on the other hand, prove that by means of an addition, as claimed in the present specification, of salts of the metals of the rare earths with the acid electrolytes, highly satisfactory technical results are obtained.

Examples: 1800 ccm. of a 28% sodium chlorid solution to which 4 grams of cerium chlorid had been added were subjected to a electrolysis between graphite and platinum electrodes, while HCl gas was introduced. The temperature of the bath was about 70° C. The experiments were continued to 1300 ampere hours and more. The losses during the electrolysis were determined by means of collecting and analyzing the gases developed and the total yield of material on the current used at the end of the experiment by determining the chlorate content. For the purpose of comparison parallel tests were carried out under exactly identical condition with and without making such additions as are mentioned above.

TABLE 1.—*Per cent. yield of sodium chlorate on current used.*

Experiment.	With cerium chlorid and hydrochloric acid.	Without any addition.	With chromate and hydrochloric acid.
I.	82	44	83
II.	84	41	84
III.	80	46	82

TABLE 2.—*Per cent. yield of sodium chlorate on current used.*

Time in ampere hours.	I. In weak acid solution.	II. Addition of 1 g. vanadium chlorid per liter.	III. Addition of 0.5 g. $CuCl_2$ per liter.	IV. Addition of 2 g. $FeCl_3$ per liter.	Addition of rare metals.		
					V. 2 g. erbium chlorid per liter.	VI. 2 g. lanthanum chlorid per liter.	VII. 2 g. yttrium chlorid per liter.
20	62.8	53.5	56.1	59.9	67.0	66.5	64.
300	54.8	56.4	41.7	28.	84.0	80.0	78.
430	54.6	54.4	45.9	27.6	87.0	81.0	77.5
900	52.5	55.0	.....	.....	86.0	82.0	80.0
1,242	.....	.....	.....	.....	86.5	83.3	81.3

The quantities of chlorids specified in the above tabulation are those which, in each instance, give the maximum yield.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

The method of preparing halogen-oxygen compounds of the alkalis and alkaline earths by electrolysis which consists in adding to the electrolyte in acid solution a compound of the rare earth metals.

In testimony of which invention, I have hereunto set my hand, at Berlin, Germany, on this 16 day of May, 1911.

MATHIAS PIER.

Witnesses:

HENRY HASPER,

WOLDEMAR HAUPT.