F. SPARRE.

PROCESS FOR CONVERSION OF LOWER OXIDS OF NITROGEN TO HIGHER OXIDS OF NITROGEN.

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1,008,383. Patented Nov. 14, 1911.

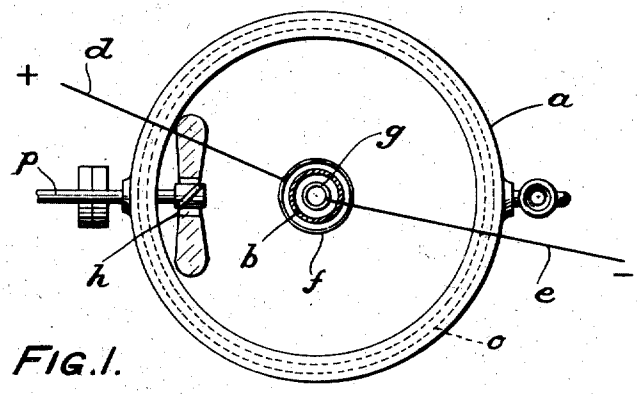

FIG. 1.

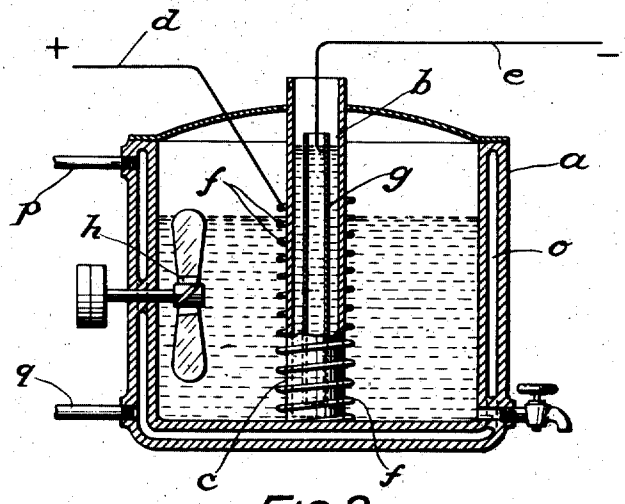

FIG. 2.

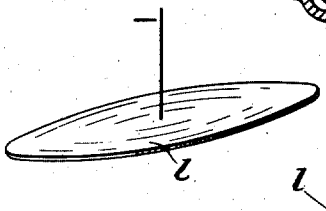

FIG. 4.

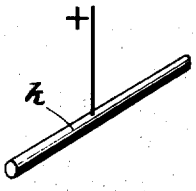

FIG. 5.

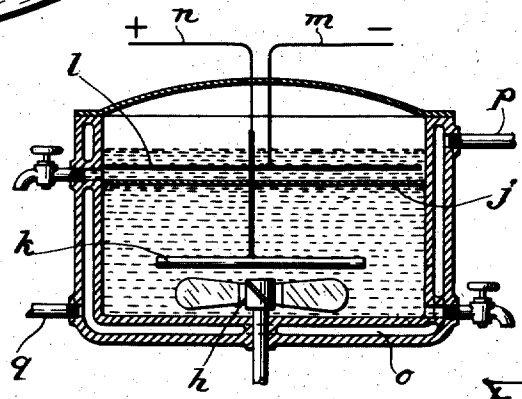

FIG. 3.

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PROCESS FOR CONVERSION OF LOWER OXIDS OF NITROGEN TO HIGHER OXIDS OF NITROGEN.

1,008,383. Specification of Letters Patent. Patented Nov. 14, 1911.

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To all whom it may concern:

Be it known that I, FIN SPARRE, a subject of the King of Norway, residing at Wilmington, county of Newcastle, and State of Delaware, have invented a new and useful Improvement in Processes for Conversion of Lower Oxids of Nitrogen to Higher Oxids of Nitrogen, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings, which form a part of this specification.

In the nitration of cellulose and glycerin, by means of a mixture of nitric and sulfuric acid, there are produced lower oxids of nitrogen, such for instance as N_2O_4, which are of low value. These lower oxids are dissolved by the acid and for the larger part form nitrosyl-sulfuric acid, in which case one-half of the lower oxid is converted into nitric acid, and the other half into nitrosylsulfuric acid which has no nitrating value. Thus at least one-half of the nitrogen in the lower oxids is in useless form. If they could be cheaply and readily oxidized, so as to form nitric acid, they would at once become of the desired value. Usually the acids are used over and over again, only being strengthened up by the addition of some fresh strong acid before each new nitration. In this way the percentage of lower oxids increases continuously and at some time they have to be removed. These oxids can be removed and in part oxidized by certain, special distillations. Such operation and apparatus, however, are rather expensive and a loss of fixed nitrogen takes place. Furthermore such processes would fail in cases where the liquid to be treated was a solution with lower oxids as a principal component. I have discovered a new process whereby these low oxids of nitrogen in solution may be converted into nitric acid.

Speaking generally, the process by which I obtain the result is to subject the lower oxids of nitrogen in solution to the action of oxygen produced by an electric current. It would be impossible to produce the result by merely passing a current of electricity through the oxids of nitrogen to be treated in solution for the reason that while oxygen would be produced at one electrode of the source of current supply, hydrogen would be produced at the other electrode of the source of current supply and the actions of these two would neutralize each other, causing the oxids of nitrogen solution to remain constant, not considering possible secondary reactions. I have discovered that if I pass this current of electricity through water, made conductive to the electric current, for instance acidulated water, and oxids of nitrogen solution, when the acidulated water and the oxids of nitrogen solution are separated from one another but electrolytically communicating for instance by a diaphragm or semipermeable material, and when the positive electrode is placed in the chamber containing the oxids of nitrogen solution, that the oxygen produced will pass to the oxid of nitrogen solution, increasing its oxygen content. It is further advisable in this process that the pressure on opposite sides of the separating material shall be the same in order that there shall be no resistance to the free passage of the ions in each direction, and also to prevent material diffusion of the oxids of nitrogen solution into the chamber containing the negative electrode. By semipermeable material, I mean a porous material, with such pores as to permit passage of ions and to some extent of water, but refusing or making difficult passage of larger molecules, such as nitric acid and sulfuric acid. Such semipermeable material may be unglazed earthenware; if very porous it may be made less porous by methods known in the art, such as forming precipitates in the pores. There is no disadvantage that some water passes through the separating material and enters into the oxids of nitrogen solution. Usually it is of advantage to have the pressure on the water chamber a little higher than in the other chamber, thereby passage of oxids of nitrogen are prevented further. Furthermore, it is necessary that the oxids of nitrogen solution contain water. If the solution is very strong, say less than 5% water, it may be advisable to add water to assist the elec-

trolysis. As the electric current decomposes the water, dilution will not take place as the result of a moderate addition of water, say 10%. The voltage of the electric current should be high enough to produce oxygen, but not exceed this voltage materially. About 5 volts is found satisfactory, but the voltage may be lower or higher, and depends on the concentration of the solution, its temperature and upon the construction of the apparatus. The strength of the current depends on the apparatus, time of operation desired, and quantity of oxids of nitrogen, so that specific information cannot be given.

A high current density is necessary for the anodes or the proper oxidation will not take place, while the current density on the cathode should be quite low, for instance, anode density between three hundred and fifteen hundred amperes per sq. dm. preferably one thousand, while the current density on the cathode should be say, between five amperes and one tenth of one ampere to the sq. dm. preferably below one ampere. As the electrolytic liquid is heated by the current, means of cooling should be provided. The temperature should be below 40° C. or the oxidation may be lessened. Preferably it should be below 25° C., but above 10° C.

In the accompanying drawings apparatus is shown for carrying out my process.

In these drawings: Figure 1 is a plan view of one form of apparatus. Fig. 2 is a vertical section of the same on line 2—2, Fig. 1. Fig. 3 is a vertical section of another form of apparatus. Fig. 4 is a perspective view of the negative electrode. Fig. 5 is a perspective view of the positive electrode shown in Fig. 3.

In Figs. 1 and 2, *a* is a cylindrical tank, having a central chamber *b*, the wall *c* of which is formed of the semipermeable material described. In the tank *a* is placed the oxids of nitrogen solution to be treated, and in the chamber *b* is placed acidulated water. Preferably the tank *a* is closed; a stirring arrangement *h* may be placed in tank *a* with a view of bringing fresh untreated solution to the positive electrode. The water is acidified preferably with sulfuric acid, say 50% by weight. As the specific gravity of the oxids of nitrogen solution is greater than the specific gravity of the water, the wall *c* of the chamber *b* is extended above the main tank *a* to a height sufficient to give a pressure on that side of the wall *c* equal to the pressure of the oxid of nitrogen solution on the opposite side, or even a little higher pressure. The wall *c* of the chamber *b* should be impermeable to the solutions above the level of the oxids of nitrogen solution so as to prevent the dilute sulfuric acid from passing through the wall where no counter pressure exists. While the specific gravity of the acidified water is only about, say 1.40, the specific gravity of nitrating acids containing oxids of nitrogen is about 1.7 to 1.8. From a suitable source of current supply, electric wires *d* and *e* are carried, the wire *d* leading from the positive pole of the source of current supply and the wire *e* from the negative pole of the source of current supply. The wire *d* terminates in an electrode *f* in a tank *a*, extending into the oxids of nitrogen solution and is preferably of platinum. The area of the positive electrode or anode is governed by a number of amperes used and may, as a rule, be merely a coiled platinum wire or other arrangement giving a relatively small area. The wire *e* terminates in a cylindrical sheet of lead or aluminum *g*, graphite may also be used as cathode material in the chamber *b*. The area used is to be governed by the current and, as a rule, a coiled sheet is used so as to give a large area. When current is generated, the oxygen ions produced pass through the wall *c* and increase the oxygen content of the oxids of nitrogen, transforming them into nitric acid, while the hydrogen ions pass into the chamber *b* and produce no counter-effect upon the oxids of nitrogen, but escape from the chamber *b* as hydrogen gas. Platinized platinum has been found advantageous as anode material, as it allows the use of a low voltage. The temperature during the electrolysis should neither be too high nor too low; it may be allowed to raise to say 30° C., while 10° C. is rather low for economical work. The higher temperature causes smaller resistance to the current and less formation of persulfuric acid. By taking samples from time to time, it can be determined when all the lower oxids of nitrogen have been converted to the higher oxid, or N_2O_5, at which time the operation is stopped and the acid removed, now consisting only of nitric acid and the solvent.

In the construction shown in Fig. 3 the vessel or tank *i* is formed into two chambers by the semipermeable partition *j* which is removable from the vessel *i*. The vessel is first filled with the oxids of nitrogen solution to the level of the point where the semipermeable partition rests. Then the partition is put into position and the upper portion of the vessel *i* filled with the acidulated water. The electrode *k* in the oxids of nitrogen solution and the electrode *l* in the acidulated water solution are similar to those used in the apparatus shown in Fig. 1. The wire *m* leads to the electrode *l* while the wire *n* leads to the electrode *k*. This wire *n* is insulated where it passes through the acidulated water solution.

In order to maintain the oxids of nitrogen solution at the desired temperature, I provide the water jacket *o*.

p is an inlet pipe to the water jacket and *q* an outlet or discharge pipe. Water or other cooling liquid is circulated by these pipes *p* and *q* through the water jacket surrounding the tank *a*.

To prevent or reduce undesirable polarization the anode or electrode in the oxids of nitrogen solution may be provided with means for rotation.

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

1. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being high.

2. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being high.

3. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, the current density on the electrode in the water being low.

4. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the acidulated water being low.

5. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being above one hundred amperes to the sq. dm.

6. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being above one hundred amperes to the sq. dm.

7. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, and current density on electrode in the water being below ten amperes to the sq. dm.

8. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on electrode in the acidulated water being below ten amperes to the sq. dm.

9. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being high, and the current density on the electrode in the water low.

10. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being high and the current density on the electrode in the acidulated water low.

11. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being above one hundred amperes to the sq. dm. and the current density on the electrode in the water below ten amperes to the sq. dm.

12. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, between electrodes in the respective solutions, the current density on the electrode in the oxids of nitrogen solution being above one hundred amperes to the sq. dm. and the current density on the electrode in the acidulated water below ten amperes to the sq. dm.

13. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and water, containing an electrolyte while the solutions are in electrolytic

connection with each other and maintaining the temperature of the oxids of nitrogen solution between 15° C. and 40° C.

14. The method of treating oxids of nitrogen in solution to increase their oxygen content, which consists in passing a current of electricity through said oxids of nitrogen solution and acidulated water, while the solutions are in electrolytic connection with each other, and maintaining the temperature of the oxids of nitrogen solution between 15° C. and 40° C.

In testimony of which invention, I have hereunto set my hand, at Philadelphia, on this 3rd day of September, 1907.

FIN SPARRE.

Witnesses:
M. M. HAMILTON,
A. M. URIAN.