March 4, 1924. 1,485,706

G. PLAUSON

METHOD OF CARRYING OUT ELECTROCHEMICAL REACTIONS AND APPARATUS FOR USE THEREIN

Filed March 13, 1922 2 Sheets-Sheet 1

Fig.1.

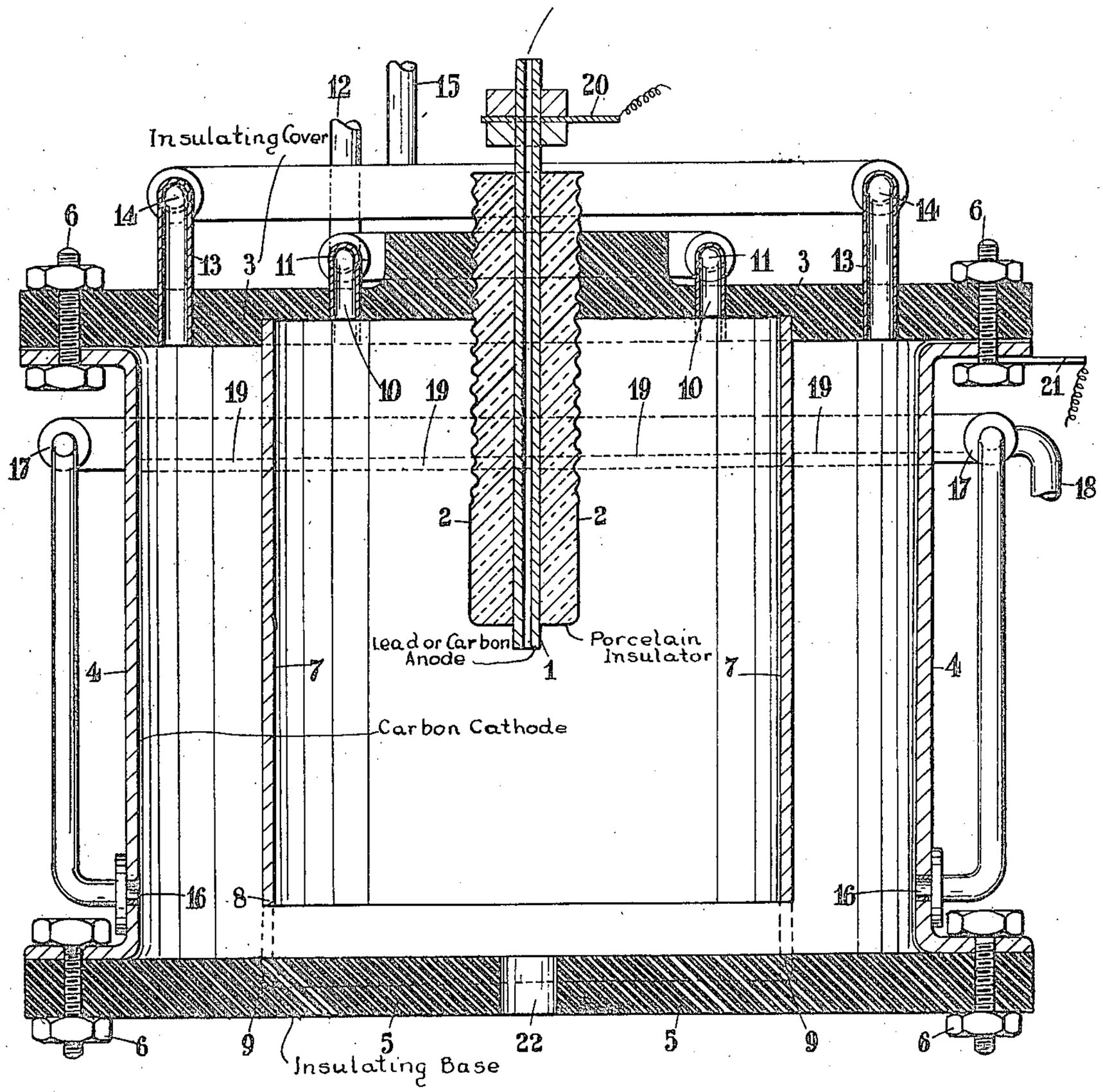

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Fig.2.

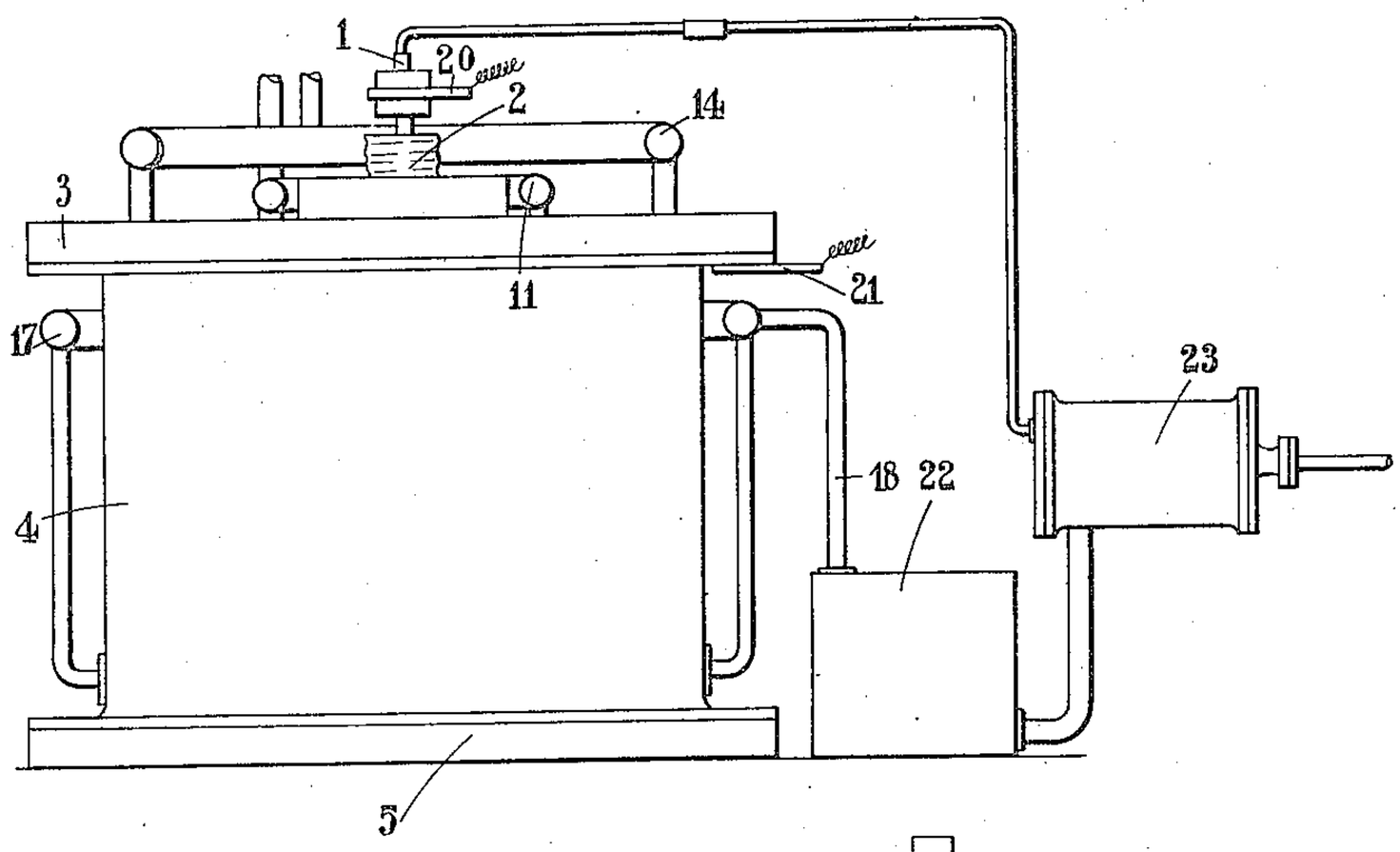


Fig.3.

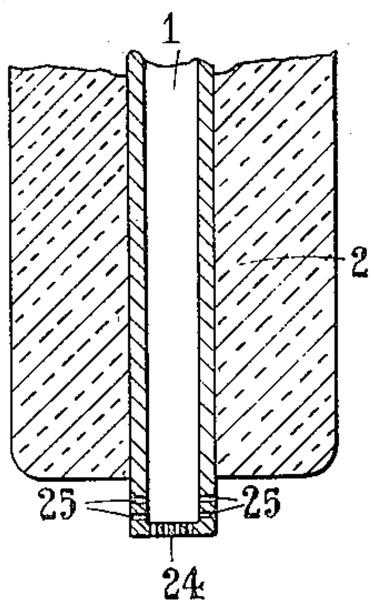
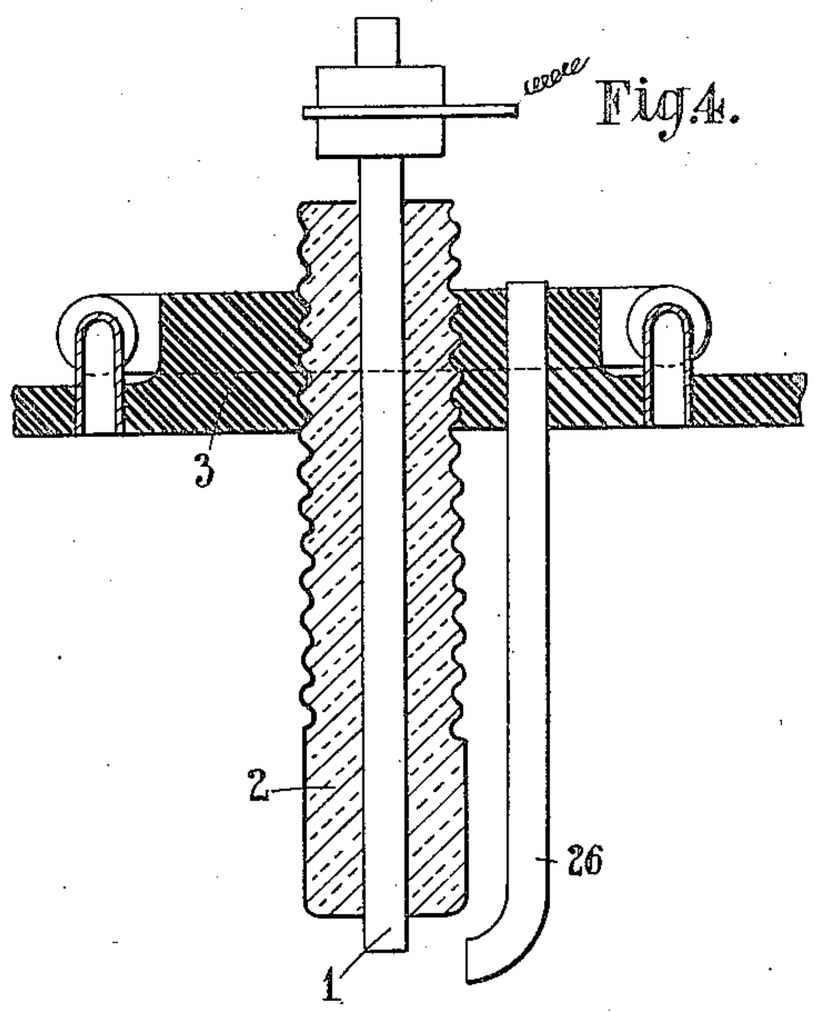


Fig.4.



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UNITED STATES PATENT OFFICE.

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METHOD OF CARRYING OUT ELECTROCHEMICAL REACTIONS AND APPARATUS FOR USE THEREIN.

Application filed March 13, 1922. Serial No. 543,408.

To all whom it may concern:

Be it known that I, GERTRUD PLAUSON, an Esthonian citizen, and resident of Huxter 14, Hamburg, Germany, have invented certain new and useful Improvements in Methods of Carrying Out Electrochemical Reactions and in Apparatus for Use Therein (for which I have filed an application in England dated March 24th, 1921, and an application in Germany, in part only, dated August 1st, 1917), of which the following is a specification.

This invention relates to processes for carrying out electro-chemical reactions and to apparatus for use therein. According to this invention such reactions are carried out in an apparatus wherein an anode is used having a small surface in relation to that of the cathode so that it can be heated to a high temperature, preferably a glowing temperature. The heating of the onode can be regulated by increasing to a greater or less extent, and controlling the voltage at which the current is supplied to the electrodes, and a series of new chemical reactions can be produced such as it has not been possible to produce hitherto with any known electro-chemical process or apparatus, or which could only be produced with a great deal of trouble and expenditure. By the use of an anode in an electrolytic apparatus according to this invention, together with suitable electrolytes, it is possible to evolve either oxygen alone or oxygen and halogens at the anode; further, parafins and other hydrocarbons can be converted into fats or materials of the class of naphthene acids; again, it is possible to change substances such as brown coal or lignite into materials having a consistency resembling that of montan wax. Resin oils can be converted in a similar way into bodies of the nature of resinous acids, and other oils or hydrocarbons can be converted into their corresponding acids or salts. In alkaline electrolytes it is possible in a similar manner to carry out oxidizing reactions giving acids, aldehydes or ketones. The invention is not limited to reactions upon electrolytes, but substances which are not electrolytes such as fluids or solid matters dissolved in organic solvents can be oxidized by this process with a high output. Gases can also be treated by the process as indicated in the examples mentioned hereinafter, and here again a high output can be obtained. For instance, the same can be oxidized to yield either formaldehyde, methyl alcohol or formic acid, and acetylene can be oxidized to give acetaldehyde or acetic acid. If electrolytes are used which evolve halogens at the anode and if the material to be acted upon is supplied in a fine stream, preferably through the interior of a tubular anode, there are evolved chloro-hydrocarbons as well as halogens in a nascent condition. In this manner gaseous hydrocarbons can be halogenated as well as fluid hydrocarbons. By variation of the voltage employed the evolution of halogens or the formation of halogenated hydrocarbons can be varied as required. Again, the formation of nitro-compounds is possible.

The apparatus employed for these reactions is preferably one in which the anode which is to be heated to a high temperature is formed as a rod or tube, the latter form being preferable because the material to be treated can be supplied directly through the anode. The anode may be arranged to project through an insulator into a central chamber wholly or partially enclosed by a porous diaphragm, while the cathode which is very much larger than the anode, may consist of the wall of the outer chamber surrounding the diaphragm, or may be disposed in any suitable manner in this chamber. If the electrodes are in chambers entirely separated by a porous diaphragm the two chambers must be suitably connected by a pipe or passage supplying the electrolyte. The gases evolved at the electrodes can then be kept separate, and valves can be used to control the speed of flow of the electrolytes.

The invention will be best understood by reference to the following description taken in conjunction with the annexed drawings, in which:—

Figure 1 is a central vertical section showing diagrammatically an electrolytic cell constructed in accordance with the present invention;

Figure 2 is an elevation to a reduced scale showing electrolyte circulating means;

Figure 3 is a fragmentary view showing an alternative form of anode on an enlarged scale; and

Figure 4 is a similar view showing a further modified form of anode.

In the embodiment illustrated in Figure 1, the anode 1 consists of a tube supported in a porcelain plug 2 in the cover 3 of the cell. The lower end of the tube 1 projects a little beyond the porcelain plug 2 as shown. The cathode 4 forms the surrounding wall of the cell, and may be made of compressed carbon or of any suitable metals. The cathode wall 4 is formed with flanges, and is secured in a fluid-tight manner to the cover 3 and base 5 by means of bolts 6. Suitable packing rings or washers of india rubber or the like may be inserted to render the joints fluid-tight. The base 5 and cover 3 may be formed of any suitable insulating material such as vulcanite, glass, asbestos or the like. The cover plate 3 has depending from it a porous diaphragm 7 in the form of a cylinder of earthenware, fireclay, cement, asbestos, or other suitable material fitting into a recess in the cover plate in a fluid-tight and gas-tight manner. This diaphragm extends down nearly to the bottom of the cell as shown in full lines at 8, leaving a gap at the bottom through which alone fluid can pass between the inside and outside of the diaphragm although ions can pass through the porous wall of the diaphragm. Gases generated in the anode space inside the diaphragm 7 or in the cathode space outside it can escape through pipes 10 and 13 respectively in the cover plate. The pipes 10 communicate with an annular pipe 11, and this communicates with a pipe 12 through which the gases from the anode space can pass off or can be drawn off under reduced pressure if required. Similarly the pipes 13 lead into an annular pipe 14 communicating with a gas outlet 15 for the gases from the cathode space. The required level of liquid in the cathode space is maintained by outlet pipes 16 communicating with the cathode space near the bottom, and leading up to an annular pipe 17 with an overflow 18. The liquid level is maintained at the line 19 in this case. The overflow pipe 18 may lead to a vessel 22 from which the liquid may be carried by a circulating pump 23 (Figure 2) back to the anode chamber through the bore of the tubular anode 1, when circulation of the liquid is required in order to subject it repeatedly to the electrolytic action. The anode has a terminal 20, and the cathode a terminal 21. For reactions in which it is necessary to keep the anode and cathode chambers quite separate the diaphragm 7 may extend down into a groove in the bottom 5 of the cell as indicated in dotted lines at 9. An aperture at 22 in the base of the cell is normally closed by a plug, but can have a tube inserted if required for circulating purposes, for example when the diaphragm 7 extends to the bottom of the cell, separate circulation of liquid in the cathode chamber may also be provided for by suitable pipes disposed at a distance from the outflow pipes 16.

The following are examples as to the reactions which can be effected according to the invention:—

Example I.—Saponifiable fatty acids or soap solutions can be produced from the oils obtained from brown coal, lignite and so forth. For this purpose an anode is used which may consist of platinum, graphite or lead, and current is supplied at from about 20–50 volts, while the surface of the anode should only be about 0.1 to 1 or 2 sq. centimeters in area. The electrolyte may consist of sodium bi-sulphate alone or together with per-sulphates. When the current is supplied the anode is heated steadily and after about 20 minutes its temperature is sufficiently high. The oil can then be introduced through the tubular passage of the anode. The oil may be in the form of an emulsion containing say 50 parts of gas tar oil in 50–100 parts of concentrated sodium bi-sulphate or sodium bi-chromate. If care is taken that the temperature of the bath does not rise above 30° C. a practically complete oxidation of the tar oil to products of the nature of fatty acids is effected.

Example II.—Petroleum of a boiling point of 150–260° C. obtained from Caucasian mineral oil may be substituted for the gas tar oil of Example I, while the electrolyte may consist of a mixture of 5 parts sulphuric acid and 1 part hydrochloride acid, together with 5 parts of a concentrated solution of sodium bi-sulphate. The anode may consist of lead or platinum. The oil may be emulsified with dilute sulphuric acid. With a voltage of from 60–75 volts or more the oil is converted partly into a naphthene di-sulphonic acid and partly into compounds resembling the naphthene acids. The acids can be drawn off directly and subjected to further treatment. For example, the naphthene acids and the naphthene di-sulphonic acids can be separated from one another by known methods and can be saponified with alkalis or alkaline earths. When an oil of the character of solar oil is treated, if the temperature of the bath is kept down to 30–90° C. the conversion of the oil is effected up to 70–90%. It is advantageous in this process to supply oxygen gas to the anode together with the oil emulsion. Instead of bi-sulphates it is also possible to employ perchromates, and instead of sulphuric acid it is possible to use nitric acid for the same purpose at 10–25% concentration. If nitric acid is used it is possible

to obtain adipic acid practically quantitatively. The Caucasian naphtha fractions boiling between 80–105° C. will also give adipic acid up to 50% or even 75%.

Example III.—The products of the nature of Montan wax can be obtained from brown coal as follows: 100 parts of brown coal are introduced into an autoclave with 300 parts of caustic alkali lye of 30° at a pressure of 2–10 atmospheres. The product obtained is mixed with a solution of 50–80 parts of sodium per-chlorate in 500 parts of water and this is introduced into the apparatus. At a voltage of 10–20 volts on a square centimeter of the anode surface the electrolyte is oxidized giving products of the nature of montanic acids and partly also products of the nature of ketones. If the temperature is allowed to rise to 90–95° C. the acids obtained form an oil which floats on the surface of the electrolyte and which can be allowed to flow out at the overflow of the vessel which determines the height of the liquid therein. This oil solidifies giving a mass of the nature of Montan wax which melts at between 65 and 85° C.

Example IV.—The apparatus can be used to form oxides of nitrogen from mixtures of nitrogen and oxygen, or from nitrogen contained in air, and the fixation of atmospheric nitrogen by this process forms an important part of this invention. An electrolyte may be used containing 10–20 parts of an aluminium, magnesium, calcium or barium salt, such as the chloride, either with or without a per-sulphate such as those of chromium, tungsten and vanadium. The anode may consist of platinum or of silicon, or of alloys of silicon and the like, and the superficial area of the anode subjected to heating should be small, preferably from 0.1 to 0.5 square centimeters. The anode in this case is preferably made not with a single tubular passage through it, but as seen in Figure 3, it may be tubular with a closed end 24 through which a number of very small opening as indicated at 25 are provided for the gas to flow through. These openings may be of a diameter, for example, of 0.5 to 0.05 m. m. The voltage may be 100 volts or more. A stream of nitrogen gas or air is now allowed to flow slowly through the anode and nitrates or other nitrogen compounds are formed directly with the aluminum, calcium or other kations contained in the electrolyte. The yield of these compounds is quite good. The nitrogen compounds are separated by known methods from the other salts present and may be purified and concentrated for use.

The above axamples will suffice to indicate the practical uses of an electrolytic apparatus having an anode which is small in relation to the cathode and is highly heated. It will be understood that the apparatus may be provided with a plurality of anodes in parallel, each having a small effective surface area and that in general the cathode will be very much larger than the anode. In general the cathode may consist of any suitable metal or alloy, or of graphite and the like. Although a hollow anode has been referred to for the introduction of the material to be treated, it will be understood that if preferred, as seen in Figure 4, the anode 1 may be a solid rod and the material to be acted upon may be introduced through a suitable passage in a tube 26 opening close to the anode so as to direct the stream or liquid or gas upon the same. An anode with fine holes in it has been referred to above particularly for use in the oxidation of atmospheric nitrogen. Instead of this, an anode having a surface of a porous conductive material or a metallic alloy, or even of carbon or graphite may be used in suitable cases, but the anode is always kept very small in relation to the surface area of the cathode, in order that good results may be attained. In some of the reactions with the apparatus the results which are found may be explained by the fact that the heating of the anode may be intermittent. It may rise to a high temperature at which an evolution of gas occurs, and then the gas forcing back the electrolyte may break the continuity of the electrolysis so that a cooling takes place until the gas is absorbed or liberated and the electrolyte again comes in contact with the anode. Such alternate sudden cooling and heating which may take place very rapidly, may be of the utmost importance for the preservation of products which would break up again when they are formed except for these alterations of temperature. This method of working is of especial importance in the case of the production of nitro-compounds from nitrogen and oxygen mixtures.

Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. A method of carrying out an electrochemical reaction consisting in passing current through an electrolytic cell such that the surface of the anode exposed to the electrolyte which is of relatively small area is heated to a high temperature and introducing a substance, which it is required to act upon, into the reaction zone at said anode.

2. A method of carrying out an electrochemical reaction consisting in heating to a high temperature the relatively small surface of the anode exposed to the electrolyte in an electrolytic cell and subjecting a reagent to an oxidizing action in the reaction zone at said anode.

3. A method of carrying out an electrochemical reaction consisting in heating to a high temperature the relatively small surface of the anode exposed to the electrolyte in an

electrolytic cell, generating a nascent oxidizing agent at the surface of said heated anode and introducing a substance, which it is required to act upon, into the reaction zone at said anode so as to be acted upon by said oxidizing agent.

4. A method of carrying out an electrochemical reaction consisting in heating to incandescence the surface of the anode exposed to the electrolyte in an electrolytic cell and introducing a substance to be treated into the reaction zone of said incandescent anode.

5. A method of carrying out an electrochemical reaction consisting in heating to a high temperature the relatively small surface of the anode exposed to the electrolyte in an electrolytic cell and passing a fluid required to be acted upon through the anode into the reaction zone around said exposed surface of the anode.

6. A method for the oxidation of nitrogen consisting in passing current through an electrolytic cell such that the relatively small surface of the anode exposed to the electrolyte is heated to a high temperature and nascent oxygen is evolved at said anode and passing a gaseous current containing nitrogen through the anode into the reaction zone around said exposed surface of the anode.

7. A method for the fixation of atmospheric nitrogen consisting in heating to incandescence by the passage of current the relatively small surface of an anode exposed to the electrolyte in an electrolytic cell and introducing a current of air to the reaction zone at said anode.

8. A method for the fixation of atmospheric nitrogen consisting in passing current through an electrolytic cell such that the relatively small surface of the anode exposed to the electrolyte is heated to a high temperature and passing a current of air through small perforations in the wall of said anode into the reaction zone adjacent said exposed surface.

9. A method for the electro-chemical oxidation of reagents consisting in applying such a potential difference to the electrodes of an electrolytic cell that the anode of relatively small effective surface is heated to a high temperature and the reagent to be oxidized is conducted through a tubular duct to the reaction zone at said anode.

10. A method of carrying out an electrochemical reaction, consisting in passing current through an electrolytic cell such that the relatively small surface of the anode exposed to the electrolyte is heated to a high temperature, alternately causing gas to be evolved at said anode to interrupt the passage of current momentarily and dissipating said gas to restore the passage of current and introducing a substance to be acted upon into the reaction zone at said anode.

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