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METHOD OF NITROGEN FIXATION.

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1,408,625. Patented Mar. 7, 1922.

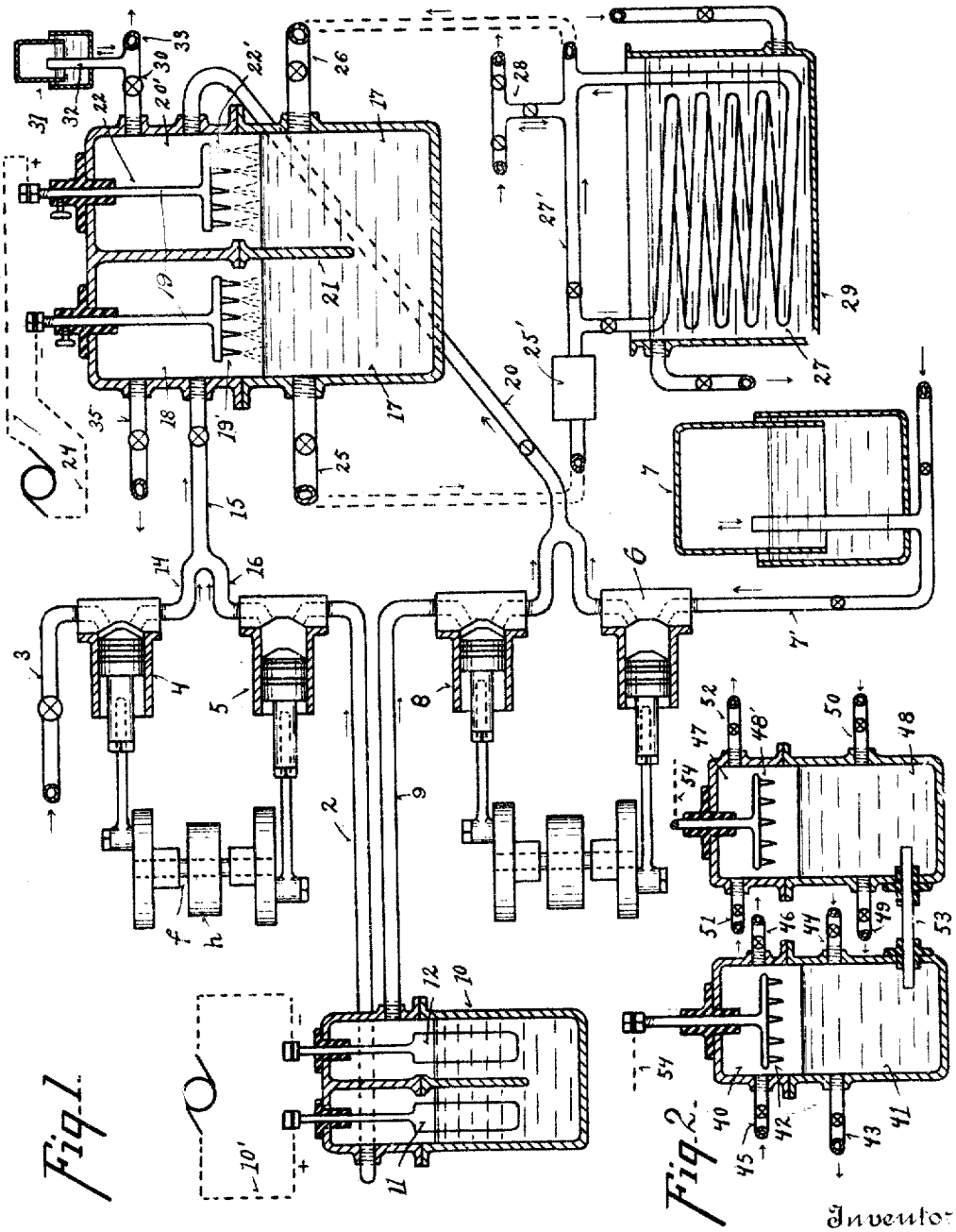


Fig. 1.

Fig. 2.

Witnesses

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METHOD OF NITROGEN FIXATION.

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To all whom it may concern:

Be it known that I, CASPER W. MILES, a citizen of the United States, residing at Anderson Township, in the county of Hamilton and State of Ohio, have invented certain new and useful Improvements in Methods of Nitrogen Fixation, of which the following is a specification.

My invention relates to improvements in method and apparatus for the fixation of nitrogen. One of its objects is to provide a direct and economical method for the fixation of nitrogen. Another object is to provide a method of fixation whereby practically pure products may be directly obtained. Another object is to provide for the combined action of a plurality of forces all tending to the fixation of nitrogen. Another object is to provide an improved method for the production of ammonia and nitric acid separately, and also the product of their chemical union. Another object is to provide improved apparatus to carry out said method. My invention also comprises certain details of method and combination and details of apparatus, all of which will be fully set forth in the description of the accompanying drawings, in which:

Fig. 1 is a diagrammatic illustration of apparatus suitable to carry out my improved method, with the production as an end product of ammonium nitrate.

Fig. 2 is a diagrammatic illustration of a modification of a portion of said apparatus for the production of nitric acid and ammonia as end products.

In the accompanying drawings 4 represents a gas circulating pump to supply air or nitrogen gas received through conduit 3 to a nitrogen fixation chamber. A gas circulating pump 5 is designed to supply oxygen gas received through a conduit 2 to the same fixation chamber as the product of pump 4. The pumps 4 and 5 may be independently driven at relatively different speeds, but are illustrated as driven in unison from a common shaft *f* by means of a belt wheel or gear wheel *h*, and provision is made to adjustably vary the stroke and length of the connecting rods of said pumps so that the relative amount of gas pumped or circulated by the respective pumps may be accurately adjusted or predetermined to secure any desired proportion of oxygen and nitrogen in the mixture circulated to the fixation chamber.

A gas circulating pump 6 is designed to supply practically pure nitrogen gas, or other nitrogen containing gas, as for instance mixed hydrogen and nitrogen gas or nitrogen mixed with a chemically inert gas free from oxygen, to one of the fixation chambers from a storage gasometer 7 through a conduit 7′. The supply to the gasometer 7 may be the gaseous product of combustion freed from carbonic acid gas, or nitrogen from other sources.

The gas circulating pump 8 is designed to supply hydrogen gas through conduit 9 to the same fixation chamber as the product of pump 6, and the pumps 6 and 8 are preferably adjustable as described for pumps 4 and 5 to enable any desired ratio of nitrogen and hydrogen to be mixed and pumped together to a fixation chamber.

An electrolytic cell 10, or a battery of any desired number of such cells, is preferably employed to electrolize a liquid, as for instance water, and thereby provide a supply of oxygen for the pump 5 given off by the positive electrode 11 and hydrogen for the pump 8 from the negative electrode 12. A low tension electric circuit is indicated by 10′.

Air preferably first freed from dust, moisture and other objectionable impurities passes from pump 4 through the conduit 14 to conduit 15 while oxygen gas passes to the pump 5 through conduit 2 and from the pump through conduit 16 to conduit 15 where the two gases are intimately mixed in the desired proportions to produce a mixture rich in oxygen and preferably containing two or more parts of oxygen to one of nitrogen, depending upon the operating conditions. This mixture is conducted by conduit 15 to a fixation chamber 18 the lower portion of which is occupied by a body of liquid 17, as for instance water, which liquid is made one pole terminal or electrode of a high tension unidirectional electric current. The other pole or terminal 19 is located within the chamber 18 and insulated therefrom, being suspended in the oxygen enriched gas in said chamber, and is provided with one or more points 19′ from which either spark or silent electrical discharge may be directed through the gases in chamber 18 to the face of the liquid, terminal, or electrode 17.

Hydrogen gas circulated by pump 8, and nitrogen gas circulated by the pump 6

through the conduit 7' from gasometer 7, are intimately mixed in the conduit 20 and thence enter the fixation chamber 20' above the opposite section or leg of the body of liquid 17. A partition 21 separates the two legs of the liquid in the lower portion of the fixation chamber so that the body of liquid is U-shaped in cross-section with one end or surface in contact with mixed nitrogen and oxygen in chamber 18, and the other end or surface in contact with mixed nitrogen and hydrogen in chamber 20'. An electrode or pole 22 is admitted through and insulated from the walls of chamber 20' and has one or more points 22' from which either spark or silent electrical discharge may be directed upon the surface of the liquid 17 through the mixed hydrogen and nitrogen in chamber 20'.

In order to conduct away any excess of heat from the liquid 17 and to keep the liquid 17 of uniform temperature and composition, a portion of the liquid 17 is taken through conduit 25 from the fixation chamber to a circulating pump 25' and circulated partly through a coil 27 and partly through a by-pass 27' or entirely through the cooling coil 27 and thence returned by a conduit 26 to the fixation chamber, thereby also causing a more or less rapid liquid circulation as may be required in said fixation chamber, and keeping the liquid in said chamber at any desired temperature below its boiling or extensive vaporization temperature. Artificial refrigeration may if desired be employed to cool the coil 27. A pipe connection 28 enables a portion of the liquid to be withdrawn for the purpose of recovering the product and replacing it with fresh liquid. The pipe connection 28 also provides for varying or adjusting the surface level of the liquid 17 by adding to or removing a portion of the liquid 17 through the pipe connection 28. Coil 27 is immersed in a tank 29 of cooling medium.

A gas exit conduit 30 leads from the chamber 20' to a storage gasometer 31 through a branch conduit 32, while the branch 33 may be employed to supply mixed nitrogen and hydrogen to the fixation chamber 20' of one or more additional fixation elements such as illustrated in Fig. 1, and in which the gasometer 31 serves to maintain a uniform gas pressure and gas supply. I also preferably provide an exit cock from the last of said fixation chambers whereby a small percentage of gas may be bled and wasted or stored for other purposes, which serves to eliminate from the fixation chambers 20' and gasometer 31 any gas impurities which may slowly accumulate therein. A conduit 35 is employed in like manner to the conduit 30 to lead mixed nitrogen and oxygen gas from the chamber 18 to a storage gasometer and the fixation chambers of other fixation elements as heretofore described for conduits 30, 32 and 33, and including an exit cock to lead away accumulating gas impurities.

The effect of the high tension unidirectional current of circuit 24 is to polarize the two end surfaces of the liquid 17 oppositely to the polarizing effect exerted by said circuit at the electrodes 19' and 22' so that to a greater or less extent nascent oxygen appears at the surface of the liquid in chamber 18 and hydrogen in nascent state appears at the surface of the liquid in chamber 20', while the gases in the respective chambers are subjected by the current to an ionizing effect, a local heating effect, and a polarizing or electrolytic effect tending to bring nascent oxygen in chamber 18 at the contact surface of the liquid into a chemical union and fixation product with the mixed gases in said chamber, while at the same time nascent hydrogen at the contact surface of the liquid in chamber 20' and the polarized gases of chamber 20' tend to a union whereby ammonia gas is formed and immediately absorbed in the liquid 17, as are also the nitrogen and oxygen fixation products. Thus the fixation products in both chambers are promptly absorbed into the liquid 17 so as to effect a separation of the fixed nitrogen from the unfixed nitrogen and gases mixed therewith in the respective chambers, leaving the mixed gases practically pure or free from fixation products, and in condition to undergo the fixation operation free from complications. The fixation products from the respective fixation chambers promptly enter into chemical union one with the other to produce ammonium nitrate in solution in the liquid 17 from which it is removed and recovered from time to time, or by a continuous operation. The oxygen enrichment of the nitrogen gas, the solution energy or tendency of the liquid, and the chemical combination energy, all tend to a fixation of nitrogen with oxygen with an exothermic result. In a similar manner the reciprocal tendencies of nitrogen and hydrogen to combine and disassociate, and to establish an equilibrium between the ammonia and mixed gases is upset by the solution tendency or capacity of the liquid, thereby maintaining a constant potential toward the extensive formation of ammonia by its rapid absorption and removal, which is further facilitated by the tendency of the ammonia to chemically combine with the nitric acid products, which also prevents the liquid from becoming even partially saturated with ammonia in solution. Gases from sources other than electrolytic may be fed to chambers 18 and 20'.

The container or containers for the liquid 17 require to be of insulating material, and of chemical resisting nature, as for instance of glass or porcelain, and the apparatus for

cooling the liquid 17 requires to be suitably insulated one unit from another to provide for conducting the high tension current along the prescribed path or circuit. It is not requisite that the high tension circuit should be strictly unidirectional, but the flow of current over a unit of time should predominate in one direction to provide the desired polarity at the surfaces of the liquid 17. The primary object of the high tension current is to maintain an ionizing, polarizing and local heating effect as distinguished from a purely electrolytic effect, but the electrolytic effect may be varied within considerable limits, as may also the rapidity or mass of the reaction in the fixation chamber. The electrodes 19′ and 22′ may be composed of metals resistant to the chemical reactions and substances present, or of non-metallic conductors having the necessary chemical resisting properties. Gas pressures in the fixation chambers may be either above or below atmospheric pressure.

In the modification Fig. 2, the fixation is carried on in two independent chambers or chamber sections. In section 40 is a mixture of nitrogen and oxygen gas, a liquid 41 and a suspended electrode 42, and liquid circulating conduits 43 and 44 for cooling and circulating the liquid, and gas supply and exit conduits 45 and 4 . Nitric acid is formed in chamber 40 an may be recovered as nitric acid. Chamber 47 contains a mixture of nitrogen and hydrogen gas, a liquid 48 and suspended electrode 48′, and has liquid circulating and cooling conduits 49 and 50, and gas supply and exit conduits 51 and 52. Ammonia gas is formed in chamber 47 and is absorbed in the liquid 48 and recovered as ammonia. An insulated electric conductor 53 serves to conduct the high tension current of unidirectional electrical circuit 54 from one of the liquids 41 and 48 to the other. The electrolytic effect at the opposite ends of electrode 53 would ordinarily be relatively small, but may if desired be masked by a porous division or other means so as not to act electrolytically directly upon the fixation products. An "X" within a circle indicate the several controlling valves in the respective conduits.

The apparatus herein illustrated may be extensively modified and is designed merely to illustrate a means for carrying the method into effect. The method is capable of considerable modification without departing from the principle of my invention.

What I claim is:

1. The method of nitrogen fixation comprising producing oxygen gas and hydrogen gas electrolytically, mixing said oxygen gas with nitrogen gas in one fixation chamber, mixing said hydrogen gas with nitrogen gas in a separate fixation chamber, and independently fixing said oxygen gas and hydrogen gas with nitrogen to each produce a nitrogen compound.

2. The method of nitrogen fixation comprising producing oxygen gas and hydrogen gas electrolytically, feeding said oxygen gas and nitrogen gas as a mixture in predetermined proportions to a fixation chamber, feeding said hydrogen gas and nitrogen gas as a mixture in predetermined proportions to a separate fixation chamber, and independently fixing said oxygen gas and hydrogen gas with nitrogen to each produce a nitrogen compound.

3. The method of nitrogen fixation comprising producing oxygen gas and hydrogen gas electrolytically, mixing said oxygen gas with atmospheric air in one fixation chamber to provide a gas mixture of high oxygen contents, mixing said hydrogen gas with nitrogen gas in a separate fixation chamber, and independently fixing said oxygen gas and hydrogen gas with nitrogen to each produce a nitrogen compound.

4. The method of electrolytic synthesis which comprises passing a unidirectional electrical current through an electrolyte, and from a circuit terminal through a gaseous body to said electrolyte where the current enters the electrolyte, and through a gaseous body to a circuit terminal where the current leaves the electrolyte.

5. The method of nitrogen fixation comprising producing oxygen gas and hydrogen gas electrolytically, mixing said oxygen gas with nitrogen gas in one fixation chamber, mixing said hydrogen gas with nitrogen gas in a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to electric currents of high tension in the presence of a liquid adapted to absorb the fixation product.

6. The method of nitrogen fixation comprising producing oxygen gas and hydrogen gas electrolytically, mixing said oxygen gas with nitrogen gas in one fixation chamber, mixing said hydrogen gas with nitrogen gas in a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers in the presence of a liquid to electric currents of high tension in which current of one polarity predominates.

7. The method of electrolytic synthesis which comprises passing an electrolyzing electric current through an electrolyte, and respectively through a confined gaseous body at each terminal of said electrolyte.

8. The method of nitrogen fixation comprising mixing oxygen gas with nitrogen gas in one fixation chamber, mixing hydrogen gas with nitrogen gas in a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to electric current of high tension.

9. The method of nitrogen fixation comprising mixing oxygen gas with nitrogen

gas in one fixation chamber, mixing hydrogen gas with nitrogen gas in a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to electric current of high tension in the presence of a liquid adapted to absorb the fixation product.

10. The method of nitrogen fixation comprising mixing oxygen gas and nitrogen gas in one fixation chamber, mixing hydrogen gas and nitrogen gas in a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers in the presence of a liquid to electric current of high tension in which current of one polarity predominates.

11. The method of nitrogen fixation comprising introducing a mixture of oxygen gas and nitrogen gas into one fixation chamber introducing a mixture of hydrogen gas and nitrogen gas into a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers in the presence of a liquid to electric current of high tension in which current of one polarity predominates, and in which said liquid element constitutes one electrode in contact with the gaseous mixture.

12. The method of nitrogen fixation comprising introducing a mixture of oxygen gas and nitrogen gas in which the oxygen gas exceeds in proportion that normally found in the atmosphere under substantially uniform pressure to one fixation chamber, introducing a mixture of hydrogen gas and nitrogen gas substantially free from exygen to a separate fixation chamber under substantially uniform pressure, and subjecting said gas mixtures in the respective fixation chambers to electric current of high tension in the presence of a liquid adapted to absorb the fixation product.

13. The method of nitrogen fixation comprising introducing a mixture of oxygen and nitrogen gas under substantially uniform pressure into one fixation chamber, introducing a mixture of hydrogen gas and nitrogen gas under substantially uniform pressure to a separate fixation chamber under substantially uniform pressure, and subjecting said gas mixtures in the respective fixation chambers to electric current of high potential in which current of one polarity predominates.

14. The method of nitrogen fixation comprising introducing a mixture of oxygen gas and nitrogen gas to one fixation chamber introducing a mixture of hydrogen gas and nitrogen gas to a separate fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to electric current of high tension in the presence of a liquid adapted to absorb the fixation product, and maintaining a substantially uniform temperature in said absorbing liquid.

15. The method of nitrogen fixation comprising introducing a mixture of oxygen gas and nitrogen gas to one fixation chamber introducing a mixture of hydrogen gas and nitrogen gas into a separate fixation chamber, subjecting said gas mixtures in the respective fixation chambers to electric current of high tension in which current of one polarity predominates and in the presence of a liquid adapted to absorb the fixation product, and maintaining said absorbing liquid at a substantially uniform temperature.

16. The method of nitrogen fixation comprising circulating a mixture of oxygen gas and nitrogen gas through one fixation chamber, circulating a mixture of hydrogen gas and nitrogen gas through a separate fixation chamber, subjecting said gas mixtures in the respective fixation chambers to electric current of high tension in which current of one polarity predominates and in the presence of a liquid adapted to absorb the fixation product, and maintaining the absorbing liquid at a substantially uniform temperature.

17. The method of nitrogen fixation comprising circulating a mixture of oxygen gas and nitrogen gas through one fixation chamber, circulating a mixture of hydrogen gas and nitrogen gas through a separate fixation chamber, subjecting said gas mixtures in the respective fixation chambers in the presence of a medium to absorb the fixation product to electric current of high tension.

18. The method of nitrogen fixation comprising mixing oxygen gas and nitrogen gas in one fixation chamber, mixing hydrogen gas and nitrogen gas in a separate fixation chamber, interposing a liquid to separate said fixation chambers one from the other and to present a liquid surface in each fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to an electric current of high tension.

19. The method of nitrogen fixation comprising mixing oxygen gas and nitrogen gas in one fixation chamber, mixing hydrogen gas and nitrogen gas in a separate fixation chamber, interposing a liquid to separate said fixation chambers one from the other and to present a liquid absorbing surface in each fixation chamber, and subjecting said gas mixtures in the respective fixation chambers to an electric current of high tension in which current of one polarity predominates.

20. The method of nitrogen fixation comprising subjecting oxygen gas and nitrogen gas in one fixation chamber and hydrogen gas and nitrogen gas in a separate fixation chamber, with an interposed liquid constituting a liquid electrode surface in each fixa-

tion chamber to an electric current of high tension in which current of one polarity predominates.

21. The method of nitrogen fixation comprising subjecting oxygen and nitrogen in one fixation chamber and hydrogen and nitrogen in a separate fixation chamber with an interposed liquid to separate one fixation chamber from the other and to present a liquid absorbing surface in each chamber to an electric current of high tension.

22. The method of nitrogen fixation comprising subjecting oxygen and nitrogen in one fixation chamber and hydrogen and nitrogen in a separate fixation chamber with an interposed liquid to separate one fixation chamber from the other and to present a liquid absorbing surface in each chamber to an electric current of high tension, and maintaining said liquid at a substantially uniform temperature.

23. An electrolytic apparatus comprising a cell, an electrolyte in said cell, a gas chamber to confine a body of gas in contact with the upper face of said electrolyte and electrodes one of which electrodes terminates in said body of gas above and out of direct contact with said electrolyte.

24. The method of electro-chemical synthesis which comprises passing an electrical current of high potential from one electrical terminal to another electrical terminal through an interposed body of gas, one of said terminals being a nonmetallic body of liquid adapted to absorb the synthetic product.

25. The method of electro-chemical synthesis which comprises passing an electrical current of high potential from one electrical terminal to another electrical terminal through an interposed body of gas, one of said terminals being an electrolyte adapted to absorb the synthetic product.

In testimony whereof I have affixed my signature.

CASPER W. MILES.