L. L. SUMMERS.

PROCESS OF PREPARING NITROGENOUS COMPOUNDS.

APPLICATION FILED FEB. 29, 1908.

1,013,460.

Patented Jan. 2, 1912.

2 SHEETS-SHEET 1.

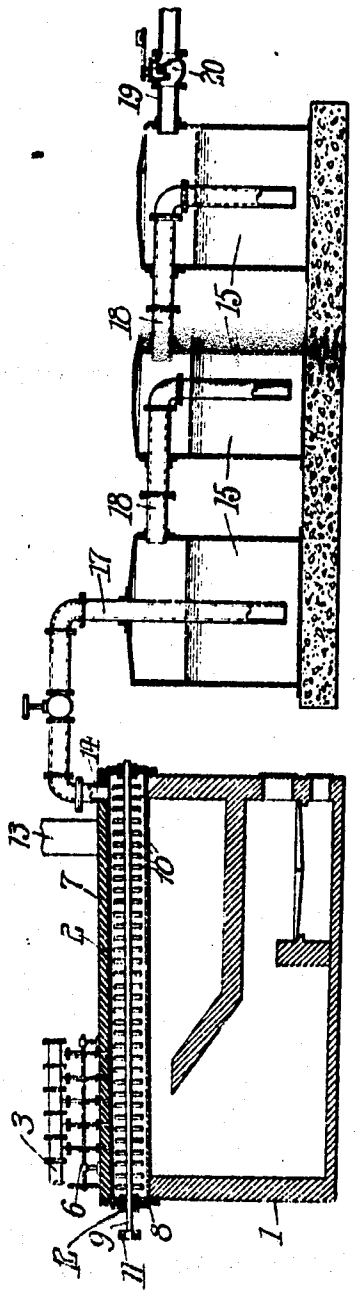

Fig. 1

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2 SHEETS-SHEET 2.

Fig. 3

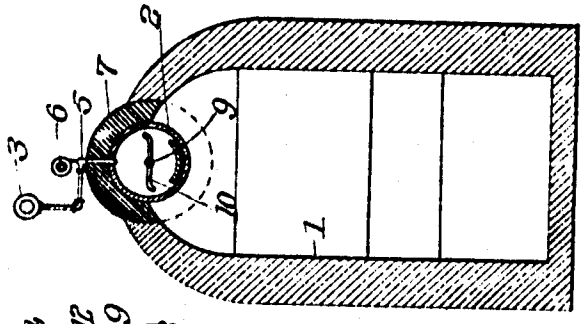
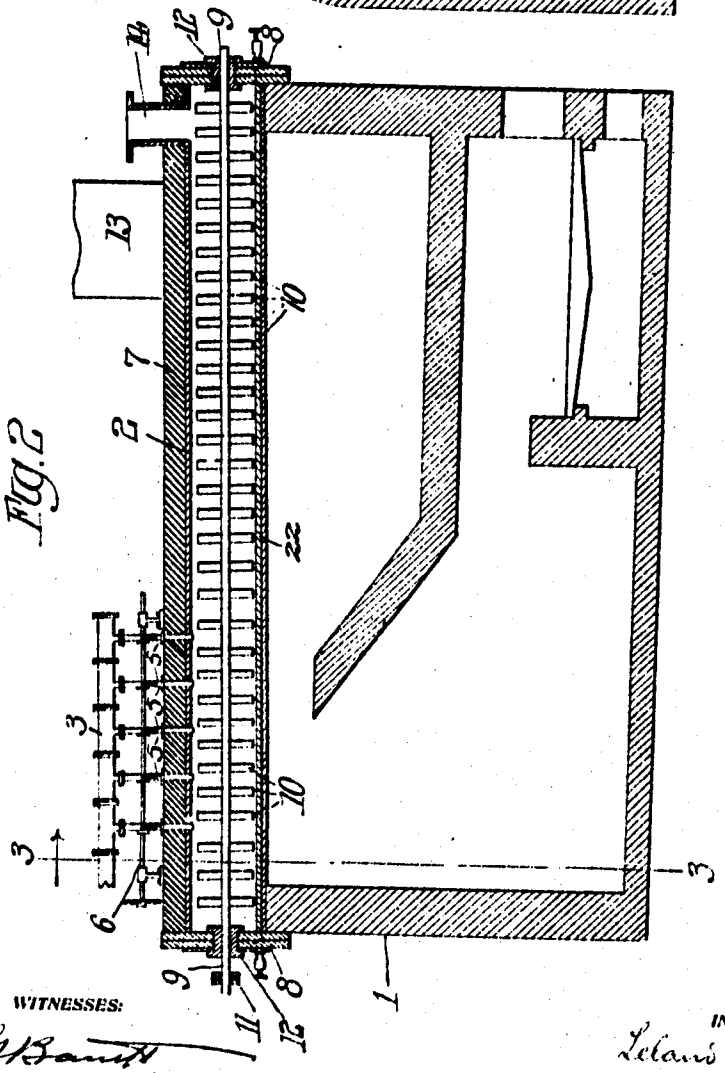


Fig. 2



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PROCESS OF PREPARING NITROGENOUS COMPOUNDS.

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To all whom it may concern:

Be it known that I, LELAND L. SUMMERS, a citizen of the United States, residing at Chicago, Cook county, Illinois, have invented new and useful Processes of Preparing Nitrogenous Compounds, of which the following is a specification.

The object of my invention is to provide a new and useful process of preparing nitrogenous compounds, namely, those compounds of nitrogen and elements such as carbon and hydrogen, or a combination of these, producing as a result ammonia having the chemical formula NH_3, cyanogen C_2N_2, and hydrocyanic acid CHN, from all of which may be obtained numerous salts and chemical derivatives well known in the art.

I have discovered that by the use of cold or refrigerated nitrogen or a compound of nitrogen, such as ammonia, using it preferably in a liquid state certain chemical reactions may be more readily brought about.

Referring to the accompanying drawings, Figure 1 is a longitudinal sectional elevation of an apparatus for practicing my invention; Fig. 2 a similar sectional elevation of the furnace portion of the apparatus but on a larger scale than in Fig. 1, and Fig. 3 a cross section on the line 3—3 of Fig. 2.

Before describing the details of my apparatus I will state that no means or devices are herein shown for liquefying the ammonia or nitrogen inasmuch as such devices are now well-known in the arts.

Referring to the particular apparatus illustrated in the drawings, the same consists essentially of a suitable furnace 1, a retort 2 heated thereby and adapted to contain certain substances as hereinafter described, and a supply pipe 3 for supplying the nitrogenous liquid which is introduced in suitable manner by the instrumentalities hereinafter described. This supply pipe 3, it will be understood, communicates with a source of nitrogenous liquid which is either liquid nitrogen obtained as hereinbefore described, liquid ammonia or other nitrogenous product. This liquid pipe 3 is provided along its length with a series of delivery pipes or injectors entering the drum or retort 2 at different points along the length thereof but toward the front end thereof. Each of these delivery pipes or injectors is provided with an expansion valve 5 whereby the supply of the liquid nitrogen into the drum or retort may be accurately and minutely controlled. By preference these valves are arranged to be operated simultaneously and to this end the same are operated by the single controlling rod 6 whose rotation in one direction or the other opens or closes said valves.

The drum or retort 2 is arranged as shown at the upper portion of the furnace 1, so that the furnace heats only the lower portion of the drum throughout its entire length, the upper portion of the drum being provided with an insulating covering 7. The ends of the drum are provided with removable covers 8 which when the apparatus is in operation close the end openings through which is introduced the charge of carbon, hydrocarbon or various other substances. The drum is provided with a suitable stirring or mixing device such as the shaft 9 extending longitudinally through the drum or retort with bearings in the covers 8 and having the series of arms 10 for stirring or agitating the contents of the drum. This stirring device is rotated in any suitable manner through power which may be applied at one end, as the pulley 11. It will be understood that the covers 8 are provided with suitable stuffing boxes 12 through which the shaft 9 passes. The products of combustion from the furnace, after coming into contact with the drum, are discharged into the flue 13.

In operation the drum or retort 2 is charged with a mixture of carbon in the form of charcoal or coke and an alkali metal such as sodium the precise proportions being immaterial though I prefer to use an excess of carbon. Heat is supplied by the furnace and the mass in the drum or retort is agitated by the mixing or stirring device therein. When a suitable temperature is obtained in the charge, depending upon the reaction desired, the valve controlling rod 6 is operated and the valves 5 are permitted to discharge a small quantity of liquid ammonia into the heated charge through the series of injectors 4. A sudden and violent reaction occurs, and various compounds of nitrogen, hydrogen and carbon result. There is an instantaneous rise of pressure in the

drum or retort and a tendency for the gases formed to rush through the outlet pipe 14. A portion of the compound remains in the drum, being in a fixed combination with the highly heated carbon. The continual operation of the mixer insures an intimate contact between the injected material and the alkali metal and carbon. The temperature and the pressure in the drum 2 may be regulated by the amount or frequency of the injections of the nitrogenous material, the temperature being lowered and the pressure being increased by increasing the amount or frequency of such injections. The gasified portion of the contents of the drum 2 passes through the pipe or outlet 14 at the rearward end of the drum to the absorbing vessels 15. The outlet 14 may be provided with a valve so that communication with the absorbers can be shut off or a direct outlet may be maintained, as shown in Fig. 1. The absorbing vessels may contain any standard reagents for the absorption of the gaseous products, but on account of the chemical affinity of cyanogen compounds for minutely divided iron and also on account of the affinity of ammonia for sulfuric acid, the gases may be passed through an aqueous solution of ferrous sulfate, the product obtained being insoluble Prussian blue from the cyanogen and soluble ammonia sulfate from the ammonia. Or in the first absorbing vessel, for instance, may be placed hydroxid of potassium or sodium for the absorption of any hydrocyanic acid. The residual gases after passing through the absorbers may be washed to remove any traces of ammonia and the combustible products may be utilized in the ordinary manner as, for instance, providing heat to the furnace under drum 2. In the present instance I have shown a series of three of these absorbing vessels, but it will be understood that they may be of any desired number and of any suitable size and dimensions. These vessels communicate in series with each other, the first one thereof being connected with the outlet 14 of the drum by means of a pipe 17, while the vessels are arranged to communicate through suitable pipes 18. These pipes extend into the receptive absorbing vessels to a point near the bottom thereof and below the line of material, that is the line of the reagents introduced therein for the purpose hereinbefore stated. When a high pressure results from the discharge of the liquid nitrogenous material into the drum, it may be desirable to allow the liberated gases free exit from the drum through the outlet pipe 14, and the absorbing vessels would then be subjected to the pressure in the drum. In order to prevent any tendency of the solutions to be lifted out of the absorbing vessels, it is desirable to maintain them under pressure and to this end I provide the outlet pipe 19 leading from the last absorbing vessel with a back pressure valve 20 which reduces the pressure of the gases passing from the absorbing vessels to the pressure ordinarily carried in the gas washers or scrubbers or at which it is utilized.

In the above apparatus using a mixture in the drum 2 of carbon and metallic sodium, cyanid of sodium will be formed by the action of the ammonia at about 400° C., a sodium amid being first formed in accordance with the following equation

$$NH_3+Na=NaNH_2+H$$

The sodium amid in contact with the carbon will form the sodium cyanid at about 700° or 800° C. in accordance with the equation

$$NaNH_2+C=CNNa+H_2$$

In this reaction the fixed products in the drum will be sodium cyanid and the volatile products will be hydrogen. The proportion of material used in the drum may vary within wide limits for an excess of either has no effect on the reaction other than upon the quantity of the products of the reaction. If the drum be charged with charcoal only and this heated to incandescence, the reaction will take place in accordance with the equation

$$2NH_3+C=CNNH_4+H_2$$

The products therefore being volatile ammonium cyanid, and hydrogen, the fixed portion remaining in the drum being carbon. But if the action be continued until the carbon is largely utilized, the volatile products will also contain unspent ammonia as well as ammonium cyanid. These temperatures are well suited to the apparatus as shown. If, however, higher temperatures be used and the apparatus be heated to a temperature of from 1,200° C to 1,500° C. mixtures of alkali metal salts or salts of alkaline earth metals and carbon may be utilized, and nitrogenous compounds may then be formed either from ammonia or directly from nitrogen. Sodium is representative of the alkali metals whose compounds may be employed for this purpose and barium and magnesium are the alkaline earth metals. The particular compound employed may be any of a considerable number, of which nitrate or hydrate will serve as suitable examples. The formation of the nitrogenous compounds from contact of nitrogen or ammonia with carbon, hydrocarbons and salts of the alkali or alkaline earth metals may take place in accordance with various primary reactions from which compounds other compounds are formed in a secondary reaction. At a temperature of from 1,200° C. to 1,500° C. nitrogen may be caused to react with acety-

lene formed from hydrocarbons and hydrocyanic acid will be produced in accordance with the equation

$$2N+C_2H_2=2HCN$$

When an alkali or alkaline earth carbonate such as sodium carbonate, magnesium carbonate or barium carbonate is used, carbon monoxid will be formed through the reduction of the carbonate by the incandescent carbon. Ammonia can be caused to react with the carbon monoxid resulting in formamid in accordance with the equation

$$NH_3+CC=HCONH_2$$

and this may be decomposed into hydrocyanic acid and water in accordance with the equation

$$HCONH_2=HCN+H_2O$$

Contact of the metallic salts and the highly heated carbon effects a reduction of the metal from the salts of the alkali or alkaline earth metals, which may be acted upon by nitrogen or the nitrogenous compound injected into the drum 2. Thus metallic magnesium forms a nitrid in accordance with the equation

$$3Mg+2N=Mg_3N_2$$

which in the presence of water will form ammonia, thus

$$Mg_3N_2+3H_2O=2NH_3+3MgO$$

Certain of the alkali or alkaline earth metals when reduced from their salts in the presence of incandescent carbon will form a carbid. Thus barium reacts in accordance with the equation

$$Ba+2C=BaC_2$$

and this carbid will react with nitrogen forming the cyanid, in accordance with the equation.

$$BaC_2+2N=BaC_2N_2$$

For the purpose of securing a sufficiently high temperature to reduce the alkali or alkaline earth metals from their salts, it will be convenient to use a different method of heating the drum 2 in order to avoid excessive deterioration. This may readily be done by employing a resistor of any well known or approved type in the drum 2. Thus in Figs. 2 and 3 I have shown a longitudinally extending resistor 22 which may be connected up in any known manner to a source of sufficient current to effect the heating of the drum. The feature of my invention is not the particular means for providing for the heating of the drum 2 or means for cooling the nitrogen or nitrogenous substance injected into the drum 2, but the art of bringing in contact the highly heated substances in the drum 2 and the refrigerated nitrogen or nitrogenous compound in accordance with the above equations.

It is apparent that the process of forming the nitrogenous compounds may be varied widely without exceeding the scope of my invention. Thus, in using an alkali metal such as sodium in contact with carbon in the drum 2, of Fig. 1, the first application of heat will cause the metallic sodium to melt at a temperature of about 95° C., and at a temperature of from 750° C. to 900° C. the melted sodium vaporizes. As the cyanids are formed at a temperature of from 750° C. to 850° C., it follows that in the ordinary processes there is a separation of the vapor of sodium from contact with the carbon. In injecting the refrigerated compound into the drum 2 the immediate lowering of the temperature in the drum causes a condensation of the sodium vapor and in the case of ammonia an intimate reaction between the sodium and the ammonia forming the amid. As the cooled amid is condensed in contact with the highly heated carbon, the formation of the cyanid will take place without an escape of the vapor of metallic sodium. In this particular reaction, excess ammonia and hydrogen would be the only volatile products escaping. If the outlet 14 is closed until the action has been completed, the surplus of ammonia will be recovered in the absorber upon allowing the outlet 14 to communicate with the absorber. As ammonia is readily decomposed at a temperature of from 600° C. to 700° C., the reactions taking place in the drum 2 can be controlled by controlling the temperature and by admitting a sufficient quantity of the gases to the drum 2, the temperature can be lowered to a point where any excess of ammonia will not be decomposed, but may be caused to pass through the absorbers as combined nitrogen and hydrogen and thereby recovered, whereas, if the temperature of the drum is not lowered sufficiently to cause the nitrogen and hydrogen to recombine previous to discharging from the drum 2, they would pass through the solution in the absorbers, thereby wasting the nitrogen as an inert gas.

From the above reactions it will be apparent that part of the nitrogen may be combined with carbon or other fixed material and part may be combined in a gaseous state generally resulting in a union of nitrogen and hydrogen, or nitrogen and carbon. By varying the fixed or incandescent element in the retort or drum, various compounds may thus be obtained. As the gases formed are passed to the absorbing vessels and brought into intimate contact with various solutions, chemical combinations are effected and products may be extracted for use as hereinbefore stated. By means of the apparatus and un-

der the process described cyanogen products, ammonia, amid and cyanamid products are obtained, but it will be understood that with a change of materials in the retort the nitrogen, carbon and hydrogen may be compounded with other products, the process being general in its application for the fixation of atmospheric nitrogen, the production of cyanogen, etc.

In certain of the claims I have used the term "carbonaceous material" to refer to that portion of the charge of the drum which furnishes the carbon, whether it be coke, other form of carbon or a hydro-carbon.

I claim:

1. The process of preparing nitrogenous compounds which consists in introducing into heated carbonaceous material liquefied gas containing nitrogen.

2. The process of preparing nitrogenous compounds which consists in introducing into heated hydrocarbons liquefied nitrogen.

3. The process of preparing nitrogenous compounds which consists in introducing into heated carbonaceous material refrigerated gas containing nitrogen.

4. The process of preparing nitrogenous compounds which consists in introducing into heated hydrocarbons refrigerated nitrogen.

5. The process of preparing nitrogenous compounds which consists in introducing into heated carbonaceous material, mixed with an alkali, a liquefied nitrogeneous gas.

6. The process of preparing nitrogenous compounds which consists in introducing into heated hydrocarbons mixed with an alkali, a liquefied nitrogenous gas.

7. The process of preparing nitrogenous compounds which consists in introducing into heated carbonaceous material, mixed with an alkali, refrigerated nitrogen.

8. The process of preparing nitrogenous compounds which consists in introducing into heated hydrocarbons, mixed with an alkali, refrigerated nitrogen.

9. The process of preparing nitrogenous compounds which consists in introducing into carbonaceous material under high heat and pressure a liquefied nitrogenous gas.

10. The process of preparing nitrogenous compounds which consists in introducing into hydrocarbons under high heat and pressure a liquefied nitrogenous gas.

11. The process of preparing nitrogenous compounds which consists in introducing into carbonaceous material under high heat and pressure refrigerated nitrogen.

12. The process of preparing nitrogenous compounds which consists in introducing into hydrocarbons under high heat and pressure refrigerated nitrogen.

13. The process of preparing nitrogenous compounds which consists in introducing into carbonaceous material under high heat and pressure a liquefied nitrogenous gas, the degree of heat and pressure of the carbons being regulated by the amount of the nitrogen or liquefied nitrogenous gas introduced.

14. The process of preparing nitrogenous compounds which consists in introducing into hydrocarbons under high heat and pressure a liquefied nitrogenous gas, the degree of heat and pressure of the hydrocarbons being regulated by the amount of the nitrogen or liquefied nitrogenous gas introduced.

15. The process of preparing nitrogenous compounds which consists in introducing into carbonaceous material under high heat and pressure a liquefied nitrogenous gas, the degree of heat and pressure of the carbons being regulated by the frequency of introduction of the nitrogen or liquefied nitrogenous gas introduced.

16. The process of preparing nitrogenous compounds which consists in introducing into hydrocarbons under high heat and pressure a liquefied nitrogenous gas, the degree of heat and pressure of the hydrocarbons being regulated by the frequency of introduction of the nitrogen or liquefied nitrogenous gas introduced.

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