

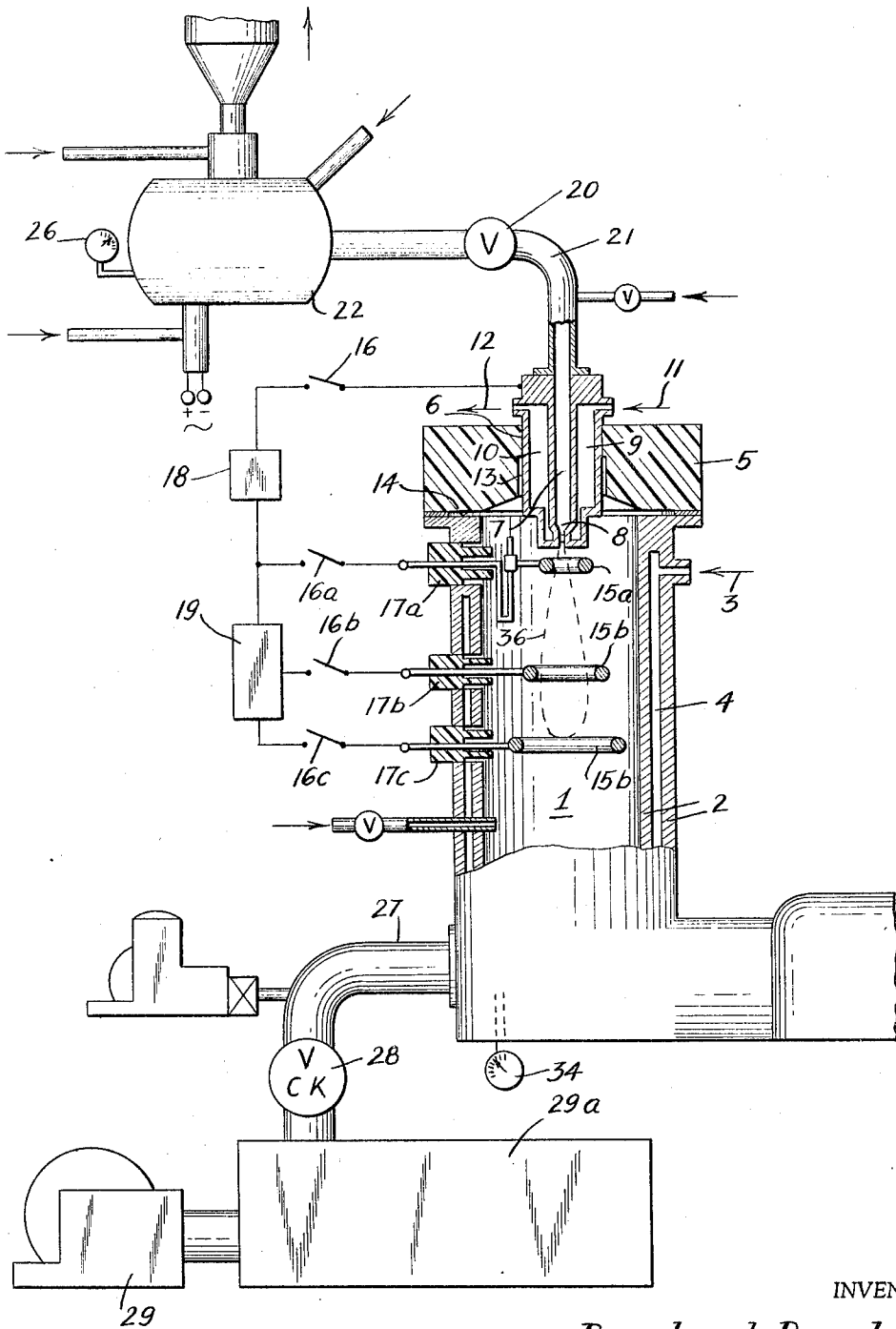
Sept. 13, 1966

B. BERGHAUS ETAL

3,272,730

PROCESS OF PREPARING HYDRAZINE-AMMONIA ADDITION COMPOUNDS

Filed Aug. 24, 1964



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3,272,730

PROCESS OF PREPARING HYDRAZINE-AMMONIA
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Filed Aug. 24, 1964, Ser. No. 391,387

13 Claims. (Cl. 204-177)

This application is a continuation-in-part of application Ser. No. 27,212, filed May 5, 1960, now Patent No. 3,152,056, dated October 6, 1964.

The present invention relates to the synthesis of hydrazine-ammonia addition compounds and more particularly to such a synthesis by means of an electrical jet discharge.

Hydrazine-ammonia addition compounds have not had any previous commercial application. It was presumed, on the basis of the high exothermic heat to be expected on their reaction, that hydrazine-ammonia addition compounds would be particularly well suited for rocket propellants. The problem lying at the base of the present invention was, therefore, to find a convenient commercial process for preparing hydrazine-ammonia addition compounds.

The process of preparing hydrazine-ammonia addition compounds according to the invention is carried out by conducting and subjecting a gas comprising nitrogen and hydrogen and consisting of one or more gases of the group consisting of ammonia, nitrogen and hydrogen, preferably ammonia alone, through a jetlike glow discharge, and subsequently separating the reaction products, preferably by means of a cooling trap in which the hydrazine-ammonia addition compounds accumulate. The gas containing nitrogen and hydrogen preferably consists of ammonia and hydrogen.

The gas comprising nitrogen and hydrogen is fed through a nozzle into a reaction chamber, and the jetlike glow discharge is produced in the gas stream issuing from the nozzle. The latter preferably is connected as an electrode of the glow discharge, suitably as the cathode.

Further, the process conveniently is carried out in a reaction vessel by means of one or more annular electrodes of which preferably one at least is operated as anode of the glow discharge. The glow discharge suitably is carried out at a gas pressure from 1 to 30 millimeters Hg, preferably from 2 to 6 mm. Hg, and at potentials from 200 to 400 v. Liquid air or liquid nitrogen is preferably used for cooling the cooling trap.

The present invention is more clearly described with the aid of the apparatus for carrying out the process of the invention as shown in the accompanying figure, which is a schematic representation of a suitable jet discharge reaction chamber and accompanying apparatus. In the apparatus shown, the reaction chamber 1 is enclosed on all sides by metal walls 2 which are formed as double-walls and adapted to receive a coolant which flows in the direction of the arrow 3 through the intermediate space 4. The top of chamber 1 is hermetically closed by a cover 5 which is composed of electrically insulating material, and carries annular feed means 6 made of metal of which the interior duct 7 terminates in a nozzle 8 communicating with chamber 1. The wall enclosing the interior duct and the nozzle, is provided with coolant ducts 9 and 10 through which flow a coolant such as water or liquid air in the direction from inlet 11 to outlet 12. The points of transition from metal to insulating material on cover 5 are protected by slots 13, 14 in a manner known per se.

In front of that portion of annular feed means 6 with nozzle 8 which projects into the discharge chamber, an electrical field is to be produced. To such end a ring 15a is perpendicularly disposed as counterelectrode immedi-

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ately in front of nozzle 8 and is adjustable along the nozzle axis, said ring being adjustably held by the interior conductor of the insulated current inlet bushing 17a. The clear diameter of ring 15a which is coaxial to the nozzle axis is sufficient to not hamper the gas jet issuing from the nozzle mouth. Ring 15a is connected via switch 16a to one pole of a voltage source 18 of which the other pole is connected via a switch 16 to said feed means 6. Preferably a direct-voltage source 18 is used, of which the negative pole via switch 16 energizes said means 6. On the other hand, one pole of a voltage source 19, suitably a direct voltage source, is connected to switch 16a, which by a center tap via a switch 16b and a bushing 17b is connected to ring 15b. The other pole of voltage source 19 is connected via a switch 16c and a bushing 17c to ring 15c. It has proved of advantage to have electrode 15b positive with respect to electrode 15a.

The initial products are delivered to said inlet means perhaps together with a carrier gas, through a line 21 that may be closed by a valve 20. If desired, the initial products may be mixed beforehand in a mixer 22. The pressure P_2 in mixer 22 may be read from a manometer 26.

An outlet pipe 27 is connected to the lower end of reaction chamber 1 which communicates via a shut-off valve 28 with an absorption unit 29a to which is connected a pump unit 29. Line 27 is so dimensioned that chamber 1 and the mouth of line 27 may be maintained a predetermined pressure P_1 that may be read from manometer 34. It is possible to raise the pressure ratio $P_2:P_1$ to high values. The hydrazine-ammonia addition compound accumulates in the absorption unit 29a which is a cooling trap cooled by liquid air or other suitable means.

An essential feature of the present process is the fact that a jetlike glow discharge 36 is maintained in chamber 1. To such end, a pressure P_1 of suitably 1 to 30 millimeters Hg, preferably from 2 to 6 mm. Hg, is produced in chamber 1 and maintained at least in the immediate vicinity of the mouth of line 27, and simultaneously a gas stream is introduced under a pressure P_2 through the nozzlelike opening 8 in said feed means 6. By suitably balancing the pressure P_2 at the mouth of nozzle 8, and the pump performance on line 27, and by a compatible adjustment of the clear width of the nozzle, a steady state is obtained in which prevails a pressure difference (P_2-P_1) in the reaction chamber between the mouth of nozzle 8 and the outlet line 27. Thereby, the entering gas stream then assumes at the mouth of nozzle 8 the form of a high ion density gas jet the exact configuration of which may be varied depending on the nozzle shape. In FIG. 1 a jet that is essentially spheroidal with respect to the nozzle axis, is schematically indicated by the dotted lines 36, but the radial extent of the spindlelike limiting surfaces is exaggerated in comparison with the actual shape for the sake of clarity. Further and for the same reason, the deformations of the jet which mostly arise immediately at the mouth, are not shown. When the gas stream spreads freely in chamber 1, the individual gas particles will pass over the major portion of the distance between nozzle opening 8 and the counterelectrodes 15 at high velocity. By a suitable choice of the total pressure head (P_2-P_1) the velocity and thus also the flow time of the reactants may be adjusted within wide limits to the desired value.

Inside the jet, a luminous phenomenon develops from the ordinary glow appearance, mostly in the form of an illuminating ray of which the structure is different from all the gas and glow discharge phenomena known so far. The appearance and shape of the illuminating zone apparently is determined by the gas jet, but occasionally there is also observed a stratification within the luminous phenomenon. The spectral range of the light-emission is determined to a certain extent by the reactions taking

place in the ray or jet. In this connection, the light-emitting regions in the jet are not, of course, the sole space portions which can energize reactions, as the reaction zone proper also may comprise non-luminous portions of the jet as well as the immediate vicinity thereof and may extend into nozzle opening 8.

The shape of the reaction zone is governed to a high degree by the flow velocity of the jet, although the reaction zone does not have to extend entirely across the same. An essential feature of the present form of discharge is the sharp demarcation thereof from its surroundings, which may be due to the steep pressure drop from jet core to jet rim. Since, according to the well-known relationship in which the energy turnover of gas discharges increases with the gas pressure in an approximately cubic function, and further, since the pressure at the jet rim is already the prevailing pressure P_1 of the vessel, one may safely assume that the reaction is most vigorous in the interior of the jet where simultaneously the maximum ion density at relatively low temperature is present. In accordance with all observed experience, the reactants are already dissociated by the electrical action shortly after leaving nozzle 8. The reaction of the individual ions takes place during their passage through jet 36.

The length of time in which the reactants remain in the jet, normally lies in the range from fractions of milliseconds to fractions of seconds. This short, regulable duration of action of the electric field and the fact already mentioned that the reactants leaving the jet move at once into a space sector which is at another pressure and perhaps also at another temperature, is considered the reason for the surprising chemical effect of the present process.

When pure ammonia is supplied through nozzle 8 into the apparatus described above, and when the resulting products are cooled in liquid air, non-decomposed NH_3 and a liquid is recovered on thawing which melts at about -20°C . and smells intensively like ammonia but which gives the hydrazine reaction with p-dimethylamino-benzaldehyde. Said liquid slowly volatilizes at room temperatures and more quickly at $+30$ to 40°C ., but in either case is completely volatilized. In the fresh state, said liquid develops a high gas pressure.

Said liquid also is formed by the reaction of a mixture of H_2 and N_2 and of mixtures of NH_3 and N_2 , or NH_3 and H_2 , or NH_3 and H_2 and N_2 . The liquid comprises the desired hydrazine-ammonia addition compounds which correspond to the general formula $\text{N}_2\text{H}_4 \cdot n\text{NH}_3$ where n is the number of ammonia molecules added to a hydrazine molecule. It was found that hydrazine-ammonia additive $\text{N}_2\text{H}_4 \cdot 4\text{NH}_3$ preferably is formed in which, n is 4 in this case. Also recovered, however, were a series of other such addition compounds where n varies from 1 to 20.

The hydrazine-ammonia addition compounds prepared in accordance with the process described above, on account of their exothermic heat and relatively low specific weight, are very suitable for rocket propellants in particular as substitute for pure hydrazine still used today. As compared with the latter, the exothermic heat and the volume of the additives prepared according to the present process are much more favorable at comparable weights.

The invention is illustrated, but not limited, by the following specific example of preparation of hydrazine-ammonia addition compounds.

Example

An apparatus similar to that shown in FIG. 1 was used, comprising a water-cooled feed means 6 having a nozzle bore of abt. 1 mm. clear width. Pure NH_3 gas was supplied to nozzle 8 through valve 20 and line 21, and injected as a jet into reaction chamber 1. The pressure in the latter was first adjusted to $P_1=1$ millimeter Hg, the switches 16, 16a then closed, and the regulable direct-voltage source 18 adjusted in steps from 200 v. to higher values until the field intensity between the cathodic nozzle 8 and the anodic counterelectrode 15a

was sufficiently high and there appeared a gas or glow discharge between nozzle mouth and counterelectrode. There was formed a jet about 1 meter long which emitted a brightly bluish and reddish light. By adjusting the pump performance and the pressure in line 21, the gas-throughput then was adjusted to 3 liters per minute, pressure P_1 being about from 20 to 30 mm. Hg. The voltage across current source 18 then was abt. 340 v. and the wattage from 300 to 400 w., mostly from 350-360 w. The intensely luminous jet could be maintained for any length of time with these adjustments.

Now the cooling device, comprising 2 tubes of 200 mm. leg length and 20 mm. diameter, was immersed in liquid air and removed therefrom after 10 minutes. After distilling-off the NH_3 , there were recovered in the first tube 1.29 grams and in the second tube 0.20 gram, or a total of 1.49 grams of a liquid melting at -20°C ., which liquid according to the analysis comprised addition compounds of ammonia and hydrazine.

It should be understood of course that the foregoing disclosure relates only to a preferred embodiment of the invention and that numerous modifications, additions or alterations may be made therein without departing from the spirit and the scope of the invention as set forth in the appended claims.

What we claim is:

1. A process for the production of addition compounds of hydrazine and ammonia comprising subjecting a gas selected from the group consisting of (1) ammonia and (2) at least two gases of the group consisting of ammonia gas, nitrogen and hydrogen to an electric glow discharge in the form of a jet discharge to form a reaction mixture containing addition compounds of hydrazine and ammonia and removing the formed reaction mixture rapidly from said discharge zone.

2. A process according to claim 1 in which the addition compounds are of the formula $\text{N}_2\text{H}_4 \cdot n\text{NH}_3$ where n is an integer from 1 to 20.

3. A process according to claim 2 in which n is 4.

4. A process according to claim 1 in which the hydrazine-ammonia addition compounds are separated from the reaction mixture by cooling.

5. A process according to claim 1 in which the gas comprises ammonia.

6. A process according to claim 5 in which the gas comprises ammonia and hydrogen.

7. A process according to claim 1 in which the reaction is conducted at a pressure of 1 to 30 mm. Hg.

8. A process according to claim 7 in which the pressure is 2 to 6 mm. Hg.

9. A process according to claim 1 in which the potential difference across the current source of the discharge is from 200 to 400 volts and the power from 300 to 400 watts.

10. A process according to claim 9 in which the potential difference is 340 volts and the power 350 to 360 watts.

11. A process for the production of an addition compound of hydrazine and ammonia comprising introducing at high velocity under pressure through a metallic nozzle shaped restricted inlet into a reaction zone at reduced pressure a member selected from the group consisting of (1) ammonia gas and (2) at least two gases of the group consisting of ammonia gas, nitrogen and hydrogen, generating an electric glow discharge in said introduced gas in the form of a jet discharge radiating into the reaction zone axially from said metallic nozzle as one electrode toward an area of lower pressure and an electrode of opposite polarity disposed in said reaction zone to form a reaction mixture containing addition compounds of hydrazine and ammonia; removing the formed reaction mixture rapidly from said zone and separating the addition compound of hydrazine and ammonia from the withdrawn reaction mixture.

12. A process according to claim 11 in which the restricted inlet has a clear width of about 1 mm.

13. A process according to claim 11 in which the metallic nozzle electrode is cathodic.

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