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METHOD OF PREPARING URANIUM DEUTERIDE

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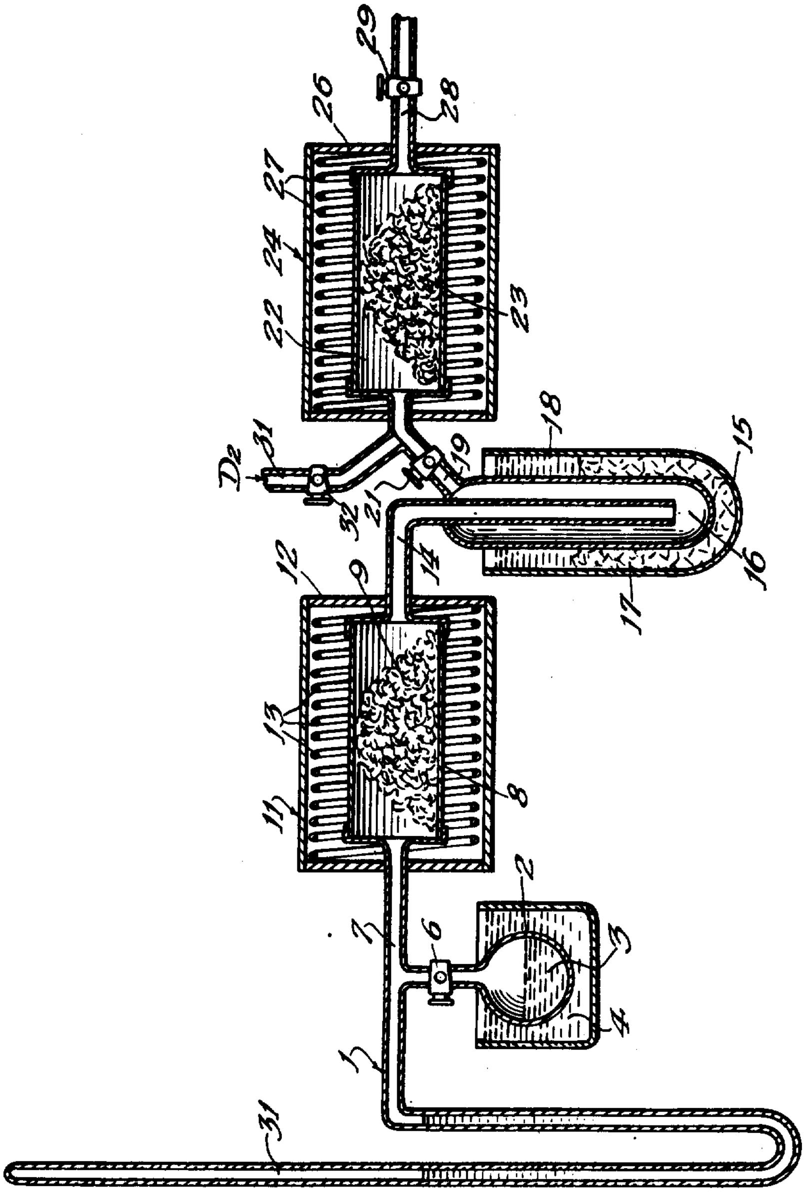

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METHOD OF PREPARING URANIUM DEUTERIDE

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7 Claims. (Cl. 23—204)

This invention relates to the production of compositions consisting of or comprising uranium deuteride and is particularly related to production of uranium deuteride in a highly purified state.

In accordance with the present invention, I have provided uranium deuteride substantially free from other impurities or in a concentrated state as a uranium hydride-deuteride composition in which the hydrogen content is preponderantly heavy hydrogen and preferably in which at least 90 per cent of the hydrogen is heavy hydrogen. The production of the deuteride is secured by reaction of deuterium with metallic uranium and must be conducted under conditions such that little or no deuterium is lost. It has been found that this may be effectively performed in a closed system in which deuterium oxide is introduced. and deuterium is generated from the deuterium oxide and directly used in the system to form the uranium deuteride. The process may be performed in a manner such that completion of the reaction may be automatically indicated as more fully described hereinafter.

Difficulty is frequently encountered in effecting the reaction of deuterium with certain forms of uranium. Thus. when uranium powder is used the reaction is often difficult to control and may even occur with explosive violence. On the other hand when sintered uranium powder is used the uranium deuteride forms as a coating and the reaction ceases until the deuteride has been removed to expose a fresh uranium surface. In accordance with the present invention it has been found that many of the difficulties may be avoided by use of massive or dense uranium metal which is free or substantially free from oxide parting planes in the interior of the uranium mass. When such uranium is used. uranium deuteride is formed in a pulverulent state and crumbles and falls from the uranium body thereby continuously exposing fresh uranium to the deuterium. The reaction proceeds so long as metallic uranium is present and the temperature of reaction is maintained.

The metallic uranium used in accordance with this invention may be of high purity or may be mixed. contaminated or alloyed with other materials including tin. copper. bismuth. gold. silver or other metal. The uranium may be alloyed with these metals or merely physically mixed therewith. Moreover the uranium may contain other substances so long as it is substantially free from internal oxide parting planes. Such uranium or at least the uranium content of uranium mixtures has a melting point not in excess of about 1200° C. and in consequence has a density of above 18 grams per cubic centimeter.

Oxide free uranium in massive state suitable for use as herein contemplated may be prepared by reduction of metallic uranium under conditions such that the uranium becomes molten and drains or stratifies to form a molten pool of uranium from which the impurities separate as a slag layer. Upon solidification of the pool the uranium secured is dense and essentially massive. For example uranium tetrafluoride or similar halide may be reacted with an alkaline earth metal such as magnesium or calcium with consequent formation of an alkaline earth fluoride and uranium metal at a temperature sufficiently high to melt the uranium and cause it to separate from the fluoride into a molten uranium pool. Alloys or mixtures of this uranium with other metals, particularly those in which the uranium is the prepoderant component may be treated as herein contemplated.

The foregoing constitute the principal objects of the invention and will be more fully understood by reference to the specification and the accompanying drawing which is a diagrammatic sectional view of apparatus for carrying out the process.

The uranium deuteride produced in accordance with the invention can be considered to be an intermetallic compound between uranium and deuterium having the approximate composition UD_3. Analyses made on the basis of weight gain upon formation of the compound indicate a slightly varying deuterium content depending upon the manner in which the uranium deuteride is treated. Adsorption of the deuterium by the uranium deuteride tends to increase the deuterium content of the compound.

Broadly. the process embodying the invention comprises forming uranium deuteride by bringing deuterium in gaseous form into contact with massive uranium essentially free from internal oxide parting planes at temperatures sufficiently high to provide a reasonably rapid rate of reaction of the deuterium and uranium. Preferably the process includes preparing deuterium in gaseous form. as by the reduction of deuterium oxide, and then reacting such deuterium with uranium at elevated temperatures to form uranium deuteride, the reactions being carried out in a closed system.

The drawing illustrates one example of a suitable apparatus 1. for providing a closed system wherein gaseous deuterium is prepared and reacted with uranium. This apparatus includes a container for deuterium oxide such as receptacle 2 containing deuterium oxide 3 in an amount sufficient to yield, by reduction of the deuterium oxide, the quantity of deuterium in gaseous form required for the formation of uranium deuteride by the subsequent reaction of the deuterium and uranium. To increase the vaporization of deuterium oxide 3 over that obtained at room temperature, water bath 4 is provided. Water bath 4, heated by conventional heating means, not shown, raises the temperature of the deuterium oxide 3 above room temperature, as for example, to a temperature of approximately 30° C. The deuterium oxide in the form of vapor is admitted from receptacle 2 to the closed system 1 through stopcock 6.

For passage of the deuterium oxide vapor, tube 7 extends from receptacle 2 into reduction chamber 8 which is of sufficient size to contain a reducing agent 9. The reducing agent 9 may be iron, zinc, or other material which will combine with the oxygen of the deuterium oxide to form an oxide of the reducing agent 9 and release the deuterium in gaseous form. Metallic uranium has been found to be particularly suitable for this purpose as it is highly reactive with deuterium oxide vapor and causes a substantially complete reduction thereof. The reducing agent 9 is preferably in a form such as to have exposed a large surface area, as in the form of turnings or the like, and is so arranged in reduction chamber 8 as to readily contact the deuterium oxide vapor coming from tube 7. Where metallic uranium is used as a reducing agent, stable formation of uranium deuteride in the reduction chamber 8 is prevented by maintaining the uranium at a high temperature.

The reduction chamber 8 is surrounded by heating means 11 which, for example, may be of conventional electric furnace construction and in the simplest form may comprise furnace casing 12 containing electric heating elements 13. Heating means 11 is adapted to maintain reduction chamber 8 at a suitable temperature sufficiently high to cause the iron or other metal to react with the deuterium oxide to form deuterium, such as, for example, at a temperature between 600° C. and 800° C., for the reduction of the deuterium oxide vapor by reducing agent 9. Heating means 11 includes suitable control means, not shown, for maintaining reduction chamber 8 at the desired temperatures.

The gaseous deuterium resulting from the reduction of the deuterium oxide is conveyed from reduction chamber 8 into trap 16 by tube 14 which extends into the trap. The trap 16 removes unreduced deuterium oxide vapor carried by the gaseous deuterium, the purification being effected by maintaining the trap at low temperatures, thereby causing condensation of any deuterium oxide vapor present. Trap 16 is cooled by suitable cooling means such as, for example, solid carbon dioxide 17 and acetone 18 contained in receptacle 15. The purified deuterium is conveyed from trap 16 into reaction chamber 22 through tube 19 and stopcock 21.

Where it is found desirable to effect the preparation of uranium deuteride by the reaction of previously prepared deuterium and uranium metal or to supplement deuterium prepared in chamber 8, supply tube 31 may be provided for introducing previously prepared gaseous deuterium from a source of gaseous deuterium, not shown, through tube 19 and into reaction chamber 22. Supply tube 31 may be opened and closed by stopcock 32. If the process comprises preparing gaseous deuterium and reacting such deuterium with uranium in the closed system 1, stopcock 32 is closed, thereby shutting off supply tube 31. If the process includes reacting previously prepared deuterium with uranium in reaction chamber 22, stopcock 21 may be closed to shut off supply tube 19, and stopcock 32 is opened, thereby admitting previously prepared deuterium to reaction chamber 22 or deuterium may be supplied from both sources.

Reaction chamber 22 contains metallic uranium 23 in massive or dense state and free from internal oxide parting planes with which the gaseous deuterium reacts to form uranium deuteride. Preferably, the uranium metal 23 is in a form presenting a large surface area, as in the form of turnings or the like. The reaction chamber 22 is surrounded by heating means 24 such as a conventional electric furnace comprising casing 26 containing electric heating elements 27. Heating means 24 is adapted to maintain reaction chamber 22 at a suitable temperature, such as, for example, between 150° C. and 400° C. for causing a reasonably rapid rate of reaction between the gaseous deuterium and the metallic uranium. Heating means 24 includes suitable and conventional control means for maintaining reaction chamber 22 at the desired temperature.

As it is desirable to remove residual atmospheric oxygen from the system before carrying out the process, reaction chamber 22 is provided with outlet tube 28 which is connected to a conventional type of mechanical exhaust means, not shown, capable of obtaining a vacuum in the system of the order of .1 millimeter mercury pressure and the system is evacuated while stopcock 6 is closed. After evacuation, stopcock 29 is closed thereby closing the entire system.

The various elements of the apparatus are suitably formed of a material, such as heat resistant glass, stainless steel, glass lined iron, etc., that withstands elevated temperatures, resists corrosion, and does not contaminate or react with the substances present in the system. Manometer 33 or equivalent pressure indicating means may be connected to the system on an extension of tube 7 to indicate visually the pressures developed during the process.

Where it is desired to obtain uranium deuteride by a process in which previously prepared deuterium is reacted with uranium to form uranium deuteride, stopcock 21 is closed, thereby shutting off reaction chamber 22 from the remainder of the system, and previously prepared deuterium is admitted under pressure from a deuterium supply chamber, not shown, to reaction chamber 22 through supply tube 31 by opening stopcock 32. Reaction chamber 22, containing massive uranium metal in the form of turnings or other convenient form presenting a large surface area is heated by furnace 24 to a favorable temperature for the reaction between the uranium and deuterium, as, for example, between 200° C. and 400° C. In general, the reaction proceeds more rapidly as the temperature and pressure of reaction chamber 22 is increased, the pressure of reaction chamber 22 being automatically controlled by the rate of generation of the deuterium in the closed system.

In carrying out the process in which gaseous deuterium is prepared in the system and then reacted with uranium, stopcock 6 is closed, stopcocks 21 and 29 are opened, and the system is evacuated through exhaust tube 28. After a sufficient vacuum has been obtained, stopcock **29** is closed, thereby closing the system. Water bath **4** is brought to a temperature of approximately 30° C. and stopcock **6** is opened to admit deuterium oxide vapor to the reduction chamber through tube **7**. The reduction chamber containing reducing agent **9** is maintained by furnace **11** at a suitable temperature, such as between 600° C. and 800° C., for the reduction of the deuteride oxide vapor. The gaseous deuterium resulting from the reduction of the deuterium oxide in the reduction chamber passes through tube **14** into the trap in which deuterium oxide vapor carried by the deuterium is condensed and removed.

The dried deuterium is conveyed by tube **19** from the trap into reaction chamber **22**, maintained at a suitable temperature by furnace **24**, in which the deuterium reacts with metallic uranium **23** to form uranium deuteride. Reaction chamber **22** is preferably maintained at a temperature similar to that maintained in reaction chamber **22** when previously prepared deuterium is reacted with uranium, such temperature being, for example, between 150° C. and 400° C. As the reaction takes place, the uranium deuteride tends to fall away from the uranium metal thereby exposing additional uranium metal for further reaction. The reaction continues until all of the uranium is converted to uranium deuteride. At a temperature of 300° C. in reaction chamber **22**, 100 grams of uranium turnings have been converted to uranium deuteride in less than thirty minutes and a 100 gram lump of uranium metal has been converted to uranium deuteride in less than two hours.

After conversion of the uranium metal to uranium deuteride is substantially completed, the pressure in the system increases rapidly as the supply of deuterium to the system continues, such increased pressure in the system being visibly indicated by manometer **33**. Stopcock **21** is then closed to seal off reaction chamber **22** from the remainder of the system and to permit removal of the uranium deuteride. Stopcock **6** is also closed to prevent further generation of deuterium in reduction chamber **8**. The uranium deuteride is preferably partially cooled in the atmosphere of gaseous deuterium present in reaction chamber **22** in order to prevent or minimize thermal decomposition of the deuteride at the end of the reaction. Where stopcock **21** is not provided, reduction chamber **8** should be maintained at a lower temperature than that of reaction chamber **22** during the cooling of the uranium deuteride to prevent distillation of deuterium from reaction chamber **22** to reduction chamber **8** and the consequent decomposition of the uranium deuteride during cooling.

The pressure established in reaction chamber **22** during hydrogenation and cooling is maintained at or somewhat above the decomposition pressure of the uranium deuteride. Thus where a temperature of approximately 300° C. is maintained in the reaction chamber, the decomposition pressure of the uranium deuteride is approximately 27 millimeters and the uranium deuteride formed will decompose at this temperature into deuterium and uranium metal whenever the deuterium pressure falls below this value. Continued introduction of deuterium into the reaction chamber tends to increase the pressure until it exceeds the decomposition pressure, thereby causing formation of uranium deuteride. As the deuterium combines with the uranium, the pressure in the reaction chamber tends to decrease and if the pressure goes below the decomposition pressure the formation of uranium deuteride is retarded until further supply of deuterium to the reaction chamber increases the pressure above the decomposition pressure whereupon deuteride formation proceeds.

This affords a simple and effective means for controlling the rate of deuteride formation and for determining the time at which the reaction is completed. Thus, at the start of the reaction deuterium is supplied to chamber **22** in an amount sufficient to establish a deuterium pressure in excess of the decomposition pressure but insufficient to cause the hydrogenation reaction to occur more or less explosively. Usually a pressure which is not over about 150 millimeters above the decomposition pressure is established. In general deuterium is introduced substantially as rapidly as it is consumed and at a rate sufficient to replace consumed hydrogen and to maintain the deuterium pressure within the system above the decomposition pressure at the reaction temperature.

After the reaction has been completed, the deuterium introduced causes the pressure to increase thus affording a simple method of determining the time at which the hydride formation is completed since the pressure increase will be visually indicated by the manometer.

In order to secure uranium deuteride in substantial concentration, it is necessary to prepare the deuteride from a composition in which the deuterium content is high. Normal hydrogen gas contains but a small quantity of deuterium and is not suitable for this purpose and therefore a deuterium concentrate which may consist substantially wholly of deuterium or may comprise a mixture of light and heavy hydrogen wherein the heavy hydrogen content is preponderant. Preferably the deuterium content of the deuterium enriched hydrogen should be at least 90 per cent by weight of the total hydrogen. Such deuterium may be prepared from deuterium oxide enriched water containing similar concentrations of deuterium oxide.

The following example is illustrative.

Example

2016 grams of powdered uranium tetrafluoride having a particle size such that 90 per cent passes a 60 mesh screen, 85 per cent passes an 80 mesh screen and 50 per cent passes a 200 mesh screen was mixed with 400 grams of metallic magnesium having a particle size of about 20 mesh, the charge packed in an iron crucible lined with calcium oxide and the crucible closed. The crucible was gradually heated until it reached an outside temperature of about 640° C. Molten metallic uranium and magnesium fluoride formed and the temperature of the mixture was maintained sufficiently high to retain the uranium in molten state until the uranium and the magnesium fluoride separated into separate layers whereby upon cooling massive uranium having a melting point of 1100° C.—25° and a density of 19—0.1 grams per cubic centimeter was secured.

This uranium was formed into turnings and was placed in reaction chamber **22**. 100 grams of uranium metal, also in the form of turnings, were placed in reaction chamber **8**. Flask **3** was partially filled with deuterium oxide concentrate containing 99 per cent by weight of D_2O and water bath **4** heated to approximately 30° C. Receptacle **15** was filled with dry ice and acetone. With stopcock **6** closed and stopcocks **21** and **29** open, a vacuum of the order of .1 millimeter was obtained in the system by evacuating means attached to outlet tube 28. Stopcock 29 was then closed, reaction chamber 8 heated to approximately 700° C. and reaction chamber 22 heated to approximately 250° C. by furnace 24. Thereupon cock 6 was opened and deuterium oxide vapor delivered to chamber 8 for deuterium formation and the process conducted as previously described. The conversion of uranium to uranium deuteride was substantially complete in two and a half hours, the completion being indicated by manometer 32. Stopcock 21 was closed, the apparatus cooled and disassembled, and the uranium deuteride in the amount of 102.54 grams was removed.

Uranium deuteride is a black powder which has been found to be a convenient means of storing or handling deuterium in a form from which the deuterium can be made readily available as a pure gas. One gram mole of uranium deuteride of a bulk density from 3 to 4, that is, 60 to 80 cubic centimeters of the compound, contains approximately 35 liters of deuterium at atmospheric pressure. Deuterium in gaseous form is released from the uranium deuteride by heating the compound above its decomposition temperature at the existing pressure.

The approximate decomposition temperature of the uranium deuteride at various pressures in millimeters of mercury is given in the following table:

Temperature, ° C.	Uranium Deuteride Decomposition Pressure mm. of Hg	Uranium Hydride Decomposition Pressure mm. of Hg
260	4	3
270	9.5	6.5
285	17	11
300	27	19
330	75	53
345	130	100
360	195	150
390	460	330
413	800	600
438	--------------	808

The term "uranium" as used in the following claims is intended to include metallic uranium, physical mixtures of uranium with other materials such as tin or other metallic dendrites, and alloys in which uranium is the predominant constituent.

The above detailed description is for purposes of illustration and the invention is to be limited only by the scope of the following claims.

This application is generally related to my copending application, Serial No. 546,178, filed July 22, 1944, now Patent No. 2,446,780 dated August 10, 1948, which is directed to a process of preparing uranium hydride.

What is claimed is:

1. The process of preparing uranium deuteride which comprises reducing deuterium oxide in a closed system to obtain gaseous deuterium and then reacting the deuterium with uranium in said system.

2. The process of preparing uranium deuteride which comprises passing deuterium oxide vapor over a reducing agent in a first reaction zone to obtain gaseous deuterium and then passing the generated deuterium over uranium in a second reaction zone which is in intercommunication with the first reaction zone.

3. The process of preparing uranium deuteride which comprises introducing a composition in which the preponderant aqueous compound is deuterium oxide into a closed system generating deuterium oxide vapor at a constant rate in said system, reacting said deuterium oxide vapor and a reducing agent in a first reaction zone in said system at a temperature sufficient to reduce the deuterium oxide vapor to gaseous deuterium, and then reacting the deuterium with uranium in another reaction zone in said system at a temperature between 150° C. and 400° C.

4. The process of preparing uranium deuteride which comprises introducing a composition in which the preponderant aqueous compound is deuterium oxide into a closed system generating deuterium oxide vapor at a constant rate in said system, reacting said deuterium oxide vapor and a reducing agent in a first reaction zone at a temperature sufficient to reduce the deuterium oxide vapor to gaseous deuterium, dehumidifying the deuterium and then reacting the deuterium with uranium in said system.

5. The process of obtaining uranium deuteride which comprises introducing deuterium oxide in a closed system generating deuterium oxide vapor at a constant rate in said system, reducing said deuterium oxide vapor to gaseous deuterium at a constant rate and passing the gaseous deuterium into contact with uranium at a temperature between 150° C. and 400° C. in said system.

6. The process of preparing uranium deuteride which comprises generating gaseous deuterium in a closed system, reacting the deuterium substantially as rapidly as formed with uranium in said system, and visually indicating the gas pressure within the system whereby an increase in said pressure indicates the completion of the reaction between the deuterium and the uranium.

7. A method of preparing uranium deuteride which comprises introducing a composition in which the preponderant liquid aqueous component is deuterium oxide into a closed system having three zones communicating in series, introducing a reducing metal into the second zone and uranium metal into the third zone, heating the deuterium oxide whereby deuterium oxide vapor is generated and forced into the second zone, heating the second zone to cause interaction of the reducing metal with the vapor and generate deuterium gas which is forced by the incoming vapor into the third zone and heating the third zone to react the deuterium with the uranium.

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