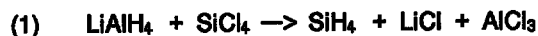


Description

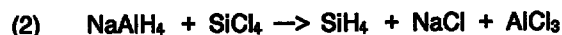
This invention relates to the production of silane from a metal hydride and a silicon halide, particularly to the production of silane and a high purity coproduct. In particular, it relates to a process for the coproduction of silane and a high purity fluoride-containing product from a metal hydride, notably an alkali metal hydride or alkali metal aluminum hydride, and a silicon tetrahalide, notably silicon tetrafluoride.

Applicants are unaware of any prior art that describes the continuous, stoichiometric or virtually stoichiometric process described herein, or that describes application of the method to the production of silane from a silicon halide and a metal hydride.

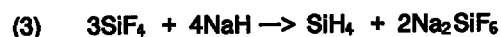
Chemical reactions for the preparation of silane from metal hydrides are known in the art:



Kelly, GB-A 823,496.



Allied, GB-A 851,962.



Ulmer, U.S-A 4,407,783.



Jacubert et al., U.S-A 4,601,798.

(5) Reaction of hydrides such as sodium hydride and lithium hydride with halosilanes, using a zinc catalyst.

DuPont, GB-A 909,950.

(6) Reaction of SiF_4 and LiAlH_4 .

Padma, J. of Fluorine Chemistry 14 (1979) 327-329.

In addition to the reactions disclosed in the literature cited above, E. M. Marlett (U.S.-A 4,632,816), discovered the reaction:



The Marlett patent US-A-4,632,816 and the corresponding earlier EP-A-300 320, disclose a process for the production of silane from a silicon tetrafluoride and a sodium aluminum tetrahydride or potassium aluminum tetrahydride, or mixture thereof. The reaction is carried out in a single reaction vessel, preferably it is suggested, by reacting a stoichiometric excess of the sodium aluminum tetrahydride, or potassium aluminum tetrahydride, with the total silicon tetrafluoride reactant. The stoichiometric excess of the metal hydride is suggested by the Patentee to be employed to eliminate boron impurities to produce a higher purity silane, and suppress the formation of undesirable products. The operation includes the use of a batch, or continuous back-mixed reactor, operated at conditions which causes the reaction to approach completion. This process, albeit a meritorious advancement in the state-of-the-art, leaves something to be desired. For example, the use in the reaction of excess sodium aluminum hydride, besides wasting valuable raw materials, results in the contamination of the sodium aluminum fluoride coproduct, a valuable material for use in the Hall aluminum process. The sodium aluminum fluoride during storage reacts with moisture to produce a hazardous condition. Worse perhaps, during the operation of the process the sodium aluminum hydride decomposes to form metallic aluminum which often creates maintenance problems by plating upon and fouling process equipment. Agitator blades and pumps as a result, e.g., have been damaged. Moreover, the silane product, due to its high solubility in the solvents, has been lost to waste; and flashing off the solvent provides only a partial solution to this loss, as well as resulting in the production of additional metallic aluminum by decomposition of the sodium aluminum hydride.

U. S.-A 4,847,061 (Bossier et al.) discloses a process for the continuous production of silane, and a halogenated coproduct, by the reaction of a silicon halide, notably silicon tetrafluoride, with a metal hydride, notably an alkali metal hydride or alkali metal aluminum hydride. The reaction, which is exothermic, is conducted by transfer of the reactants, in a slurry, between two separate reaction zones, a first generally

relatively large volume reaction zone wherein the metal hydride is reacted with less than a stoichiometric quantity of the silicon halide, and a second generally relatively small volume reaction zone wherein the unreacted metal hydride, or metal hydride remaining in the slurry, is reacted with a quantity of silicon halide in excess of that required to react with the unreacted, remaining metal hydride. In the overall operation, a substantially stoichiometric reaction and high stability are achieved by feeding the same molar amounts of the metal hydride and silicon halide to the two reaction zones while regulating and controlling the flow of reactants between the two reaction zones. In accordance with this control scheme, the difference between the temperature of the reaction medium of the secondary reaction zone and the inlet temperature to the secondary reaction zone is sensed, and the differential temperature is used to regulate and control the flow of silicon halide to the secondary reaction zone.

The stoichiometric, staged reaction sequence has eliminated certain drawbacks of the Marlett process. For example, the chemical raw materials loss has been curtailed, and safety hazards reduced. The aluminum plating problem has been largely eliminated, and there is less contamination of the sodium aluminum fluoride coproduct with sodium aluminum hydride. Albeit however the process of Bossier et al. represents a noteworthy achievement in having advanced the state-of-the-art relating to the production of silane, and a higher purity fluoride salt coproduct, further improvements are desirable. For example, it remains an objective to maintain the very low level of sodium aluminum hydride in the sodium aluminum fluoride coproduct, yet reduce the level of siliceous impurities in the sodium aluminum fluoride. Thus, the sodium aluminum fluoride product is yet often contaminated with silicates, at least one of which has been identified as Na_2SiF_6 , generally analytically reported with other siliceous impurities as SiO_2 . The latter impurity forms as the result of a secondary reaction between the silicon tetrafluoride and the sodium aluminum fluoride coproduct, this differing of course from the primary reaction between the silicon tetrafluoride and the sodium aluminum hydride reactants which forms silane, and the coproduct sodium aluminum fluoride.

This invention relates to improvements in a process which basically comprises a continuous method for the formation of silane by the reaction of a silicon halide with a metal hydride, involving overall a stoichiometric or substantially stoichiometric reaction between the silicon halide and the metal hydride. The method comprises conducting the reaction in a loop system that comprises two reaction zones and a separation zone, a first reaction zone (primary reactor) being preferably larger than the other (secondary reactor), and most of the reaction is preferably conducted in the primary reactor. Preferably, metal hydride is continuously added at a substantially constant rate and in stoichiometric excess to the primary reactor, while in the secondary reactor, silicon halide is continuously added in stoichiometric excess to the hydride present in that reactor. The excess metal hydride in the effluent from the first reactor is contacted with the silicon halide in the second reactor, and thereafter the fluoride containing reaction coproduct is separated. The exposure of the minor amount of metal hydride contained in the effluent from the first reactor, with the large amount of silicon halide introduced in the second reaction zone, helps insure that the solid fluoride-containing coproduct is free, or substantially free, of metal hydride starting material; this being a key feature of the invention since it enhances the purity (and/or the utility) of the coproduct. When the coproduct is separated, it is usually removed along with liquid(s) employed as the reaction medium. The liquid(s) can be separated from the solid coproduct, and if desired, the separated liquid material can be recycled.

The exothermic heat of reaction is used to control the overall process stoichiometry. Since metal hydride is reacted with silicon halide in the secondary reactor heat is produced in the second reaction zone. The difference in temperature (differential temperature) between the primary reactor effluent entering the secondary reactor, and the reaction mass inside the secondary reactor, is used to generate a signal; and that signal is employed to continuously adjust the flow of a reactant to a given reactor, preferably the flow of silicon halide to the secondary reactor. This continuous adjustment results in a stoichiometric or substantially stoichiometric operation.

As stated above, this invention is admirably suited for use with the silane preparation method discovered by E. M. Marlett, (US-A-4,632,816); most preferably with the reaction of NaAlH_4 and SiF_4 depicted by equation (7) above. (Marlett's invention also comprises the reaction of KAlH_4 with SiF_4 . However the sodium analog of KAlH_4 is less expensive, and therefore its use in the instant invention is preferred.)

A key feature of the Marlett process is that it readily forms silane from SiF_4 and NaAlH_4 . Another key feature is the low level of organic impurity in the fluoride-containing, solid coproduct ($\text{Na}_5\text{Al}_3\text{F}_{14} \cdot 2\text{AlF}_3$). (For purposes of this invention, this product can be considered to be NaAlF_4 .) Because the organic content is low, the coproduct can be used as an additive in the Hall aluminum process, i.e., as an additive to the Hall cell to adjust the Na-to-F ratio. If the level of organics in the coproduct was high, utility in the Hall cell would be lessened or made non-existent. This is because Hall cells are operated at high temperatures and

the environment therein is rigorous. Consequently, if the level of organics in an additive is too high, dangerous fires can occur if the additive is added to a Hall cell while the cell is in operation. Therefore, the level of organics must be kept low.

Likewise, the NaAlH_4 content (of the Marlett co-product) must also be kept low in order to enhance utility of the coproduct as an additive for aluminum production. If the NaAlH_4 content is too high dangerous fires might occur in the Hall cell, caused by ignition and burning of hydrogen released from the metal hydride. Fortunately, application of the process of the instant invention to the Marlett process produces a coproduct having a very low level of NaAlH_4 contained therein. As stated above, this is a key feature of the instant invention. Sodium aluminum hydride is virtually impossible to separate from the fluoride containing coproduct. Hence, coproduct contaminated with too much NaAlH_4 is not only unsuitable for Hall cell use, but it cannot be economically upgraded for that use, by known means.

A skilled practitioner will recognize that the lithium-fluorine coproduct--that is produced by reaction of silicon tetrafluoride and lithium aluminum hydride--might also be useful in the Hall process if the organic and hydride impurity levels are low enough. This is so because lithium is used with fluorine in the production of aluminum. Experimentation by applicants' co-worker E. M. Marlett has shown that the organic level of the lithium-aluminum-fluoride coproduct is low; although not as low as in the analogous sodium containing coproduct produced under similar conditions. However, in view of the low level of organic impurity, the process of the instant invention will make an attractive lithium-aluminum-fluorine coproduct when applied to the process comprising reaction between SiF_4 and LiAlH_4 . Moreover, the heat of reaction between SiF_4 and LiAlH_4 is high enough for this invention to be used, and thereby improve the process of reacting those two substances.

Generally speaking, the reactions of metal hydrides with halosilanes are characterized by high heats of reaction. Hence, the process of this invention is widely applicable to upgrade such reactions when it is desired to react such materials in a stoichiometric or substantially stoichiometric, continuous procedure to avoid contamination of the solid coproduct with the solid starting material. Hence, for example, the process of this invention can be used to react NaAlH_4 or LiAlH_4 with SiCl_4 or SiF_4 to produce silane and a halogen-containing coproduct.

Figure 1 is a schematic representation of an embodiment of this invention. It shows two reaction zones, one of which is primary and the other secondary. It shows that a stream of sodium aluminum hydride enters the primary reactor, and SiF_4 the other reactor. The drawing has an overall material balance obtained when the system is operating stoichiometrically under a given set of conditions (Example 1).

Figure 2 is a schematic drawing, not to scale, of a reactor loop system that can be used to conduct the process of this invention.

Figure 3 is a schematic representation of an embodiment of this invention illustrated or exemplified by Example 2.

Figure 4 is a schematic representation of a further improved process, as claimed herein.

This invention relates to a process for preparing silane and a coproduct comprising a metal and a halogen. It includes the steps of

- (A) reacting in a first reaction zone and in a liquid reaction medium, a metal hydride selected from alkali metal hydrides and alkali metal aluminum hydrides, with less than a stoichiometric quantity of a silicon halide selected from compounds having the formula SiX_4 , wherein X is fluorine, chlorine, or bromine;
- (B) reacting in a second reaction zone, the metal, hydride remaining in the liquid reaction medium (which also contains liquid/solid reaction product produced by step A), above which is provided a vapor space, with a quantity of SiX_4 reactant in excess of that required to react with said remaining metal hydride;
- (C) separating in a separation zone, a gaseous fraction comprising silane and unreacted silicon halide from solid reaction product suspended in diluting solution and produced in said reaction zones;
- (D) recovering said silane;
- (E) introducing unreacted silicon halide from said second reaction zone into said first reaction zone to react with an additional quantity of metal hydride;
- (F) determining the difference in temperature between the temperature of reaction liquid in said second reaction zone, and the temperature of reactant liquid substantially immediately prior to entry into said second zone; and
- (G) utilizing a signal derived from said difference in temperature to regulate the flow of a reactant to a reaction zone, e.g., the flow of silicon halide to the second reaction zone, to achieve stoichiometric or substantially stoichiometric reaction of the total amounts of silicon halide and metal hydride reacted in both reaction zones, said process comprising the step of
- (H) splitting the SiX_4 reactant introduced to said second reaction zone (B) into two streams, (a) a first SiX_4 stream which is introduced directly into the liquid reaction mixture to better control mass transfer

between the liquid and gaseous phases, and (b) a second SiX_4 stream which is introduced into the separation zone and/or directly into the vapor space above said liquid reaction mixture to suppress the formation of combustible gaseous mixtures.

In preferred embodiments, the liquid reaction mixture of said second reaction zone is also agitated by stirring at agitation levels sufficient to further control the mass transfer characteristics between the liquid and gaseous phases. Additionally, the residence time of the liquid reaction mixture in the second reaction zone is set to control the kinetics of the reaction, e.g. is within the range of 0.5 to 30 minutes, preferably of 5 to 10 minutes.

In highly preferred embodiments, the metal hydride is an alkali metal hydride selected from KH , NaH , and LiH or an alkali metal aluminum hydride selected from LiAlH_4 , NaAlH_4 and KAlH_4 , and the silicon halide is SiF_4 or SiCl_4 . For the purpose of this invention, SiBr_4 is considered as equivalent to the SiF_4 and SiCl_4 reactants which may be employed. Also, mixed silicon halides, wherein at least two halogens are present, are also considered equivalents of the SiX_4 reactants. Such equivalents are illustrated by SiBr_2Cl_2 , SiF_2Cl_2 , SiFCl_2Br , SiF_2/ClBr , and the like.

The process of this invention is conducted in a reaction loop like that disclosed in Bossier et al. Referring to Figure 2, sodium aluminum hydride in a solution is taken from a source thereof (not shown), and introduced via line 10 into reaction vessel 12, the primary reaction vessel. That vessel may be made of carbon steel or other suitable substance. In a preferred embodiment, the NaAlH_4 is admixed with a hydrocarbon such as toluene, and an ether such as diglyme, or monoglyme (dimethoxyethane, DME). Reaction vessel 12 is fitted with a stirrer (not shown), silane exit means 14, and slurry exit means 16. Moreover, vessel 12 is also fitted with fluid entry means 18, through which SiF_4 (from downstream separation zone 28) is introduced.

The streams introduced via lines 10 and 18 are admixed in vessel 12, and the NaAlH_4 and SiF_4 so introduced are caused to react. To enhance mixing the reactants, SiF_4 can be sparged into the liquid containing the NaAlH_4 . By state-of-the-art temperature regulating means (not shown), the reaction temperature is maintained between 10°C and 80°C ; preferably between 30°C and 60°C .

By-product effluent containing metal-aluminum-fluoride coproduct is removed from the reaction vessel via line 16. This effluent contains fluoride-containing by-product ($\text{Na}_5\text{Al}_3\text{F}_{14} + 2\text{AlF}_3$, or NaAlF_4) and liquid reaction medium. It also contains some unreacted NaAlH_4 , since the process is purposely conducted so that less than an equimolar amount of SiF_4 is introduced into vessel 12. Preferably, from 90% to 99% by weight of the NaAlH_4 is reacted in that vessel.

More preferably, from 95 to 99% of the NaAlH_4 is reacted in the primary reaction vessel. In general, it is desirable (a) to react most of the NaAlH_4 in that vessel, with the proviso that (b) enough NaAlH_4 is reacted in the secondary vessel to give a temperature increase in that vessel which will provide (c) a differential temperature high enough to generate a sufficiently sensitive signal to (d) regulate the flow of SiF_4 with enough precision in order to (e) achieve stoichiometric, or substantially stoichiometric reaction.

Continuing the reference to Figure 2, slurry from vessel 12 enters secondary vessel 20 via line 16. Vessel 20 can also be made of carbon steel or other similar substance. The vessel can be considerably smaller in capacity than the primary reaction vessel; for example, if vessel 12 is about 45 gallons (~170 liters) then vessel 20, can be about 10 gallons (~38 liters). In vessel 20, the slurry is contacted at reaction temperature (see above) with SiF_4 introduced into the vessel through line 22. The amount (i.e., the rate) of SiF_4 introduced is controlled in order to be stoichiometrically equal to the amount of NaAlH_4 introduced into reactor 12 via line 10. At any given instant, the reaction system may be somewhat out of stoichiometry, but over time with sufficient iterations about the reaction loop, stoichiometry or near stoichiometry is achieved. As stated above, the differential temperature between the liquid temperature inside vessel 20 and the liquid temperature upstream thereof at a point 24 (inside line 16) is used to generate a signal to regulate SiF_4 flow. The signal can open or close valve means (now shown) in line 22 to increase or decrease the amount of SiF_4 introduced into vessel 20. The temperatures inside and outside the reactor, i.e., in vessel 20 and in line 16 can be determined by any suitable means such as a resistance temperature detector (RTD).

From vessel 20, material flows through line 26 into separation zone 28. In that zone, silane and unreacted SiF_4 plus other gaseous material(s) (if present) are separated from the solid reaction product ($\text{Na}_5\text{Al}_3\text{F}_{14} + 2\text{AlF}_3$, or NaAlF_4). The solid product is removed via line 30 for further processing. The gaseous material is transported via line 18 into vessel 12 thereby closing the loop.

Reference is now made to Figure 4 which embodies generally the process scheme described by reference to Figure 2, but further includes features which better control the mass transfer of the silicon halide, notably SiF_4 , from the vapor, or bubble phase to the liquid bulk phase of the secondary reactor. The secondary reactor in accordance with this preferred process thus includes means for splitting the flow of SiF_4 into the secondary reactor, and variable speed mixing sufficient to produce substantially complete

reaction between the silicon halide, or SiF_4 , and the metal hydride or metal aluminum hydride in the liquid phase to produce silane and a fluorided salt, notably metal aluminum fluoride, while at the same time minimizing secondary reactions which produce siliceous impurities, SiO_2 . Liquid level control is also provided to maintain consistent liquid residence time, and consequently better control the reaction kinetics.

Sodium aluminum hydride in solution is fed via line 40 into the primary reactor 42 and contacted and reacted with less than a stoichiometric amount of the SiF_4 introduced as a gas into reactor 42 via line 48, while a gaseous silane product is removed from the reactor 42 via line 44. A slurry containing unreacted sodium aluminum hydride is withdrawn from the bottom of reactor 42 via line 46 and introduced into reactor 60, the secondary reactor of the series. Features which distinguish the operation of the secondary reactor 60 over the operation described by reference to Figure 2 are: (1) The SiF_4 introduced into the reactor 60, in this instance via line 52, is split into two streams, a first which is fed via line 52₁ directly into the liquid phase, and a second which is fed via line 52₂ into the vapor space of reactor 60; (2) A variable speed mixer, or agitator 61 employed to stir the liquid of the reactor; and (3) A line 62 which is provided to control the liquid residence time while maintaining a constant liquid level within the reactor. The positive injection of a stream of SiF_4 directly into the vapor space of the reactor 60 more effectively maintains sufficient SiF_4 therein to suppress the build up of flammable gaseous mixtures, and the direct injection of a controlled amount of SiF_4 into the liquid supplies sufficient SiF_4 for rapid reaction between the SiF_4 and the sodium aluminum hydride to produce silane and sodium aluminum fluoride; while at the same time suppressing secondary reactions which produce siliceous impurities, or SiO_2 . As previously discussed, sufficient of the SiF_4 is introduced via line 52 to be stoichiometrically equal to the amount of sodium aluminum hydride introduced via line 40 into the reactor 42, but better control of the mass transfer of SiF_4 into the liquid phase for reaction with the sodium aluminum hydride is provided by feeding just sufficient of the SiF_4 into the liquid phase to react with the sodium aluminum hydride, this being determined by balance between the rate of SiF_4 input into the liquid phase and the amount of agitation provided the liquid. Generally, this balance is provided by feeding from 20 percent to 40 percent, preferably from 23 percent to 30 percent, of the SiF_4 via line 52₁ directly into the liquid phase, while feeding the balance of the SiF_4 via line 52₂ into the vapor phase of the reactor-- viz. from 60 percent to 80 percent, preferably from 70 percent to 77 percent, of the SiF_4 . Expressed in terms of molar ratios, this means that generally from 0.20 to 0.40, preferably from 0.23 to 0.30, of the total amount of SiF_4 introduced into the second reaction zone is introduced directly into the liquid reaction mixture; the balance being introduced directly into the vapor space above the liquid reaction mixture. The variable speed agitator 61 is adjusted to run at a rate of speed sufficient to reduce to the extent possible, consistent with the amount of SiF_4 introduced directly into the liquid, the rate of reaction between the SiF_4 and the by-product sodium aluminum fluoride, and increase to the extent possible, consistent with the amount of SiF_4 introduced directly into the liquid, the reaction between the SiF_4 and the sodium aluminum hydride to form silane. In general, it has been found that the liquid of the reactor 60 should be stirred at a rate ranging from 0.23 to 10.69 W/l (0.0012 to 0.0550 H.P./gal. horsepower/gallon), preferably from 0.64 W/l (0.0033 H.P./gal.) to 1.32 W/l (0.0068 H.P./gal.), for optimizing at these input levels of SiF_4 into the liquid phase the rate of reaction between the SiF_4 and the sodium aluminum hydride, and minimizing the rate of reaction between the SiF_4 and the sodium aluminum fluoride. The adjusted speed of the agitator 61 in concert with the measured amount of SiF_4 injected directly into the liquid phase of the secondary reactor thus regulates and controls the reaction of the SiF_4 and the sodium aluminum hydride to produce silane and sodium aluminum fluoride, while at the same time minimizing secondary reactions which produce siliceous materials other than silane.

The liquid level within the secondary reactor 60 is maintained at a constant level, consistent with the rate of SiF_4 introduced via line 52₁ directly into the liquid and the amount of agitation supplied to the liquid by the agitator 61, to provide a liquid residence time ranging generally from 0.5 minute to 30 minutes, and preferably from 5 minutes to 10 minutes. It is generally preferable to operate on the low side of these ranges to optimize and carry to completion the reaction between the SiF_4 and sodium aluminum hydride, while at the same time minimizing or suppressing the secondary reaction between the SiF_4 and the sodium aluminum fluoride.

In the operation of the unit described by reference to Figure 4, the off gas from the reactor 60 is taken from the gas phase above the liquid level 63 and passed by line 56 directly into the separation column 58. Liquid from the bottom of reactor 60 is fed via a separate line 62 into the separation column 58, the use of separate lines to convey the gas and liquid phases, respectively, to the separation column 58 being preferably to the use of a single line because pluggage problems are greatly minimized. Within the separation column 58 the gases, liquids and solids phases are separated, the gas which is principally SiF_4 being conveyed via line 48 to the primary reactor 42. The liquids and solids are removed from the separation column 58 via line 64. Like the operation described by reference to Figure 2, the overall process

is in stoichiometric balance or at all times near stoichiometric balance and the process controlled by the differential temperature, or temperature difference between the temperature of the reaction mixture within reactor 60 and the temperature of the products from reactor 42 introduced into reactor 60, which is used to regulate and control the amount of SiF_4 introduced via line 52 into the reactor 60, or the amount of sodium aluminum hydride introduced via line 40 into reactor 42, or both.

A skilled practitioner will recognize that pump means are used to move the streams as described; these need not be shown since they are within the art.

One of the features of this invention is that the sodium aluminum hydride employed in the embodiment being described need not be pure. It can be used in the mixture produced by reacting aluminum and sodium (or sodium hydride) with hydrogen under pressure and in the presence of an aluminum alkyl catalyst and a hydrocarbon medium such as toluene. Thus, NaAlH_4 starting material can be made in general accordance with one or the other methods of Ashby; U.S. 4,045,545, U.S. 4,081,524. Other methods are known: for example, U.S. 4,528,176, and 4,529,580.

The following non-limiting examples are illustratively typical of considerable operating experience gained while developing this invention. Reference is first made to Example 1. The reaction vessels had about the dimensions given above (170 and 38 liters). They were equipped in general accordance with the embodiment illustrated by Figure 2. The sodium aluminum hydride feed stream is 14% sodium aluminum hydride, but it is diluted to 11% for conducting the reaction.

20 Example 1

(I) Bases:

(1) Feed rate of SiF_4 to secondary reaction vessel is 70 pounds per hour (31.8 kg per hour).

(2) Analysis of sodium aluminum hydride solution used as starting materials:

14% sodium aluminum hydride

0.85% $\text{NaAl}(\text{C}_2\text{H}_5)_2\text{H}_2$ (OMH-1)

0.60% Na_3AlH_6

0.20% aluminum metal

(3) 98.5% of NaAlH_4 reacts in primary reactor; balance in secondary reactor.

(4) All OMH-1 reacts in secondary reactor.

(5) 1 mole of SiF_4 reacts with 2 moles of OMH-1.

(6) SiH_4 Product contains 1.5 mole % H_2 ,

13,000 ppm $\text{C}_2\text{H}_5\text{SiH}_3$ (mole basis),

10,000 ppm C_2H_6 (mole basis).

(7) Neglect any DME decomposition and DME leaving entrained with SiH_4 .

(8) 70 pounds per hour (31.8 kg/hr) SiF_4 feed rate.

(9) molecular weights:

Silane 32

SiF_4 104

NaAlH_4 54

$\text{NaAl}(\text{C}_2\text{H}_5)_2\text{H}_2$ 110

$\text{C}_2\text{H}_5\text{SiH}_3$ 60

45 (II) Calculation of hydrides reacted per hour

Let x = pounds per hour SiF_4 react with NaAlH_4

Let y = pounds per hour SiF_4 react with OMH-1

$$\text{NaAlH}_4 = \frac{54 (x)}{104} = 0.5192x.$$

$$\text{OMH-1} = \frac{2 \times 110(y)}{104} = 2.1154y$$

$$\frac{\text{NaAlH}_4}{\text{OMH-1}} = \frac{0.5192x}{2.1154y} = \frac{14}{0.85}$$

$$x = 67.1069$$

Y

$$x + y = 70$$

$$= \frac{70 \text{ pounds SiF}_4 \text{ per hour}}{31.8 \text{ kg per hour}} \quad \text{or}$$

$$67.1069y + y = 70$$

$$68.1069y = 70$$

$$y = \frac{1.02 \text{ pounds per hour}}{\text{or } 0.46 \text{ kg/hour}}$$

$$x = 70.0 - 1.02 = \frac{68.98 \text{ pounds per hour}}{31.4 \text{ kg/hour}} \quad \text{or}$$

(III) Calculation of amount of solution to be utilized per hour at 11% dilution

$$\text{NaAlH}_4 \text{ solution} = (0.5192) (68.98)$$

$$0.11$$

$$= 325.6 \text{ lbs per hour, or}$$

$$148 \text{ kg per hour}$$

$$\text{NaAlH}_4 = (0.5192) (68.98)$$

$$= 35.8 \text{ lbs per hour, or}$$

$$16.3 \text{ kg per hour}$$

$$\text{NaAlH}_4 \text{ feed solution} = (0.5192) (68.98)$$

$$0.14$$

$$= 255.8 \text{ pounds per hour or } 116.3 \text{ kg/hour}$$

(IV) calculation of amount of diluent required per hour

Diluting solution required = 325.6 - 255.8

= 69.8 lbs per hour

= 31.7 kg per hour

(V) Sum of Materials Added	pounds/hour	kg/hour
SiF ₄	70	31.8
NaAlH ₄ solution	255.8	116.3
Diluting Solution	69.8	31.7
	<u>395.6</u>	<u>179.8</u>

(VI) Solvent in NaAlH₄ feed

$$255.8 \times [1.00 - (0.14 + 0.0085 + 0.006 + 0.002)]$$

$$= \underline{\underline{215.8 \text{ lbs/hr or } 98.1 \text{ kg/hr}}}$$

10 (VII) Gaseous Products

$$\underline{\text{Amount of SiH}_4 \text{ produced}} = \frac{(0.5192) (68.98) \times 32}{54}$$

$$= \underline{\underline{21.2 \text{ lbs per hour or}}}$$

$$9.6 \text{ kg per hour}$$

$$\text{C}_2\text{H}_5\text{SiH}_3 \text{ produced} = 60 \times \frac{21.2}{32} \times \frac{13,000}{10^6} \times \frac{1}{0.962}$$

$$= \underline{\underline{0.54 \text{ lbs/hr or } 0.24 \text{ kg/hr}}}$$

[The factor (1/0.962) takes into account the molar purity of SiH₄ relative to H₂, C₂H₆, and ethyl silane.]

$$\text{C}_2\text{H}_6 \text{ produced} = 30 \times \frac{21.2}{32} \times \frac{10,000}{10^6} \times \frac{1}{0.962}$$

$$= \underline{\underline{0.21 \text{ lbs/hr or } 0.08 \text{ kg/hr}}}$$

$$\text{H}_2 \text{ produced} = 2 \times \frac{21.2}{32} \times \frac{15,000}{10^6} \times \frac{1}{0.962}$$

$$= \underline{\underline{0.02 \text{ lbs/hr or } 0.01 \text{ kg/hr}}}$$

EP 0 377 900 B1

Sum of Gaseous Products produced	lbs/hour	kg/hour
silane	21.2	9.6
hydrogen	0.02	0.01
$C_2H_5SiH_3$	0.54	0.24
C_2H_6	0.21	0.09
	<u>22.0</u>	<u>10 kg</u>

5

10

15

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25

30

35

40

45

50

55

(VIII) Amount of Slurry Produced (by difference)

materials in - gases out = slurry produced

$$395.6 - 22 = \underline{373.6} \text{ pounds per hour or}$$

$$169.8 \text{ kg/hr}$$

(IX) NaAlH₄ and SiF₄ ReactantsAmount of NaAlH₄ reacting in primary reactor

$$35.8 \times 0.985 = \underline{35.3} \text{ lbs/hr or}$$

$$16.0 \text{ kg/hr}$$

Amount of NaAlH₄ reacting in secondary reactor

$$35.8 - 35.3 = \underline{0.5} \text{ lbs/hr or}$$

$$0.22 \text{ kg/hr}$$

Amount of SiF₄ reacting in secondary reactor

OMH-1 (see II above)	1.0 lbs/hr	0.45 kg/hr
NaAlH ₄ = 68.98 x 0.015	<u>1.0 lbs/hr</u>	<u>0.45 kg/hr</u>
	<u>2.0 lbs/hr</u>	<u>0.9 kg/hr</u>

(X) Amount of SiF₄ to primary reactor

$$69.3 - 2.04 = \underline{68} \text{ lbs/hr or}$$

$$30.9 \text{ kg/hr}$$

(XI) Amount of (NaAlF₄) produced from NaAlH₄

$$35.8 \times \frac{126}{54} = \underline{83.5} \text{ lbs/hr or}$$

$$38.0 \text{ kg/hr}$$

(XII) Solvents leaving primary reactor

$$215.8 + 69.8 = 285.6 \text{ lbs/hr or}$$

$$129.8 \text{ kg/hr}$$

The above calculations, which are summarized in Figure 1, illustrate the process of this invention applied to an embodiment of the Marlett invention, i.e., the reaction summarized by equation (7) above. In this example, the sodium aluminum hydride employed was not pure; rather, it was contained in a mixture which comprised toluene, aluminum, OMH-1 and Na_3AlH_6 . This mixture was formed by reacting sodium, aluminum, and hydrogen under high pressure and in the presence of toluene as a reaction medium and triethyl aluminum as a catalyst. The slurry also contained dimethoxyethane which is used to solubilize the reactants NaAlH_4 and SiF_4 . The process of the example can encompass use of reactants that contain extraneous materials. For example, the SiF_4 need not be pure but can contain about 1% HCl. Of course, purer reactants than those used in the example may be employed if desired. Likewise the process need not contain NaAlH_4 in toluene. Thus, for example, the NaAlH_4 can be admixed with one or more of the other hydrocarbons disclosed in the Ashby patents, *supra*. As appreciated by a skilled practitioner it is good practice to keep the NaAlH_4 under an inert liquid such as a hydrocarbon since the hydride is reactive to air and moisture. For the process of the example, the 14% mixture of NaAlH_4 used as a stock solution was diluted prior to entry into the reaction zone by mixing with additional DME/toluene mixture in order to bring the reaction mixture to a concentration of 11%.

It was found that in the equipment used to conduct the process of the invention, that operation at an NaAlH_4 concentration of 8 to 12 percent helped alleviate some pluggage problems in the lines. Obviously, the concentration of the reactants is an important, but not critical factor of the invention. For example, it is possible to run at an NaAlH_4 concentration of 4 to 6%.

The primary and secondary reactors had a capacity of about 170 to 37,85 l (45 and 10 gallons), respectively. This relative size is not critical. Both reactors are stirred; vigorous stirring helps diminish plugging problems.

The reaction was conducted so that 98.5% of the NaAlH_4 reacted in the first reactor. It is not necessary to use this fractional amount; more or less NaAlH_4 can be reacted as desired, so long as the heat of reaction in the secondary reactor is high enough to produce a differential temperature sufficient to generate a signal that can accurately govern the flow of SiF_4 . Under the conditions in the example about 92,31 kJ (87,500) BTU were generated per hour. Of this heat, about 2,32 kJ (2200 BTU) were generated in the secondary reactor. This was sufficient to allow use of the RTDs employed to determine the relative temperatures in the reactor and upstream thereof and to generate means to vary the flow of SiF_4 to the secondary reactor. The application of the use of the differential temperature to adjust SiF_4 flow is within the skill of the art.

The reaction of SiF_4 with OMH-1 is slower than with NaAlH_4 , and for this example it appears that practically all of the OMH-1 reacts in the secondary reactor. Under the conditions employed, where 98.5% of the NaAlH_4 reacts in the primary reactor, the OMH-1 is exposed to a relatively great deal of SiF_4 in the secondary reactor. It appears that these operating conditions cause all or about all of the OMH-1 to react to yield products other than SiF_4 . Evidence indicates that if the relative SiF_4 concentration is reduced, say by reacting more NaAlH_4 in the secondary reactor, the amount of SiH_4 produced from OMH-1 may increase. The amount of Na_3AlH_6 present in the reaction mixture is low enough that the gaseous products produced therefrom can be ignored, if the process is conducted as in the example.

The process of the above example can be modified by using one or more of the following as a replacement for SiF_4 : H_3SiF , H_2SiF_2 , HSiF_3 , H_3SiCl , H_3SiBr , H_2SiCl_2 , SiCl_2F_2 , SiClF_3 , and SiBrF_3 .

The slurry product produced by the invention can be dried to remove solvent (toluene plus DME). After removal of the solvent by any suitable technique known in the art, the product can be ground or compacted to a desired size. The product contains little or no NaAlH_4 and the amount of solvent complexed with the product (and therefore not readily removed by heating the wet product) is low. Consequently the product is in a form suitable for use in Hall electrolytic cells.

The process of this invention can be used to prepare silane suitable for use as a source of electronic grade silicon. For this purpose, the silane produced by the method of this invention can be subjected to further purification. Silane can be purified by many known techniques, for example cryogenic distillation, pressure distillation, selective absorption, large scale gas chromatography and similar techniques; confer U.S. 3,019,087; 3,041,141; 3,491,517; 4,554,141 and 4,537,759.

To aid contacting the reactants, the SiF_4 is preferably sparged into an agitated solution of the NaAlH_4 using vigorous stirring to aid disposal of SiF_4 into the body of the liquid. Preferably, the liquid contains sufficient ether such as DME to assist the solubilization of the NaAlH_4 to the extent necessary for the reaction to take place under the conditions employed.

In the above example, the relative amount of dimethoxyethane and toluene in the mixture employed was 3.6 to 1. It is not necessary to use that relative concentration. For example, toluene can be wholly absent. When it is employed, the relative concentration is not critical but for physical limitations is kept below about 30%. The toluene arises from its use in the preparation of the NaAlH_4 and need not be separated from the reaction mixture thereby produced. The amount of DME used is enough to appropriately dissolve the NaAlH_4 .

The ether reaction medium can be selected from those named and described in E. M. Mariett, *supra*.

Thus the liquid media include the polyethers such as the dimethyl ether of diethylene glycol (diglyme), the dimethyl ether of ethylene glycol (monoglyme), the dimethyl ether of triethylene glycol (triglyme), the dimethyl ether of tetraethylene glycol (tetraglyme), 1,4-dioxane, and 1,3-dioxolanes, and tetrahydrofuran (THF).

Preferred liquid reaction media are the polyethers. These include 1,4-dioxane, 1,3-dioxolane, the diethyl ether of ethylene glycol, the dimethyl ether of ethylene glycol, the dimethyl ether of propylene glycol and the dimethyl ether of diethylene glycol.

A more preferred class of liquid reaction media are the di-loweralkyl ethers of alkylene glycols. These include the diethyl ether of ethylene glycol, the dimethyl ether of propylene glycol and the dimethyl ether of diethylene glycol.

Still more preferred are the di-loweralkyl ethers of ethylene glycols. These include the dimethyl ether of ethylene glycol and the dimethyl ether of triethylene glycol. The diethyl ether of ethylene glycol is an advantageous reaction medium because the normal ether cleavage attributable to solvent attack does not produce methane. The dimethyl ether of ethylene glycol is the most preferred inert liquid reaction medium. Dimethoxypropane and the dimethyl ether of propylene glycol also work well.

The preferred solvents of the invention are those which provide reasonable solubility for hydride reactant such as sodium aluminum tetrahydride or potassium aluminum tetrahydride. Reaction media other than ethers can be used; other useful media include tertiary amines such as triethylamine, tributylamine, N-methyl-pyrrolidine and mixtures of such liquids.

Liquid reaction media outside the preferred class of polyethers are also generally somewhat water-miscible. Hydrocarbons can be used, but when used alone they will provide low to moderate yields of silane unless very strong agitation is used.

Of types of ethers that are mentioned, ethers that have the requisite solvent power and that are relatively low boiling materials are preferred. This is because hydrides such as NaAlH_4 are very reactive substances, and must be handled with care. In order to promote safety, it is better if the ether solvent be low boiling so that it can be readily separated from the reaction mixture to avoid dangerous conditions in case of a process upset.

As indicated above, dimethoxyethane (DME) has been shown to have the requisite solvent power, and it has a sufficiently low boiling point. For these reasons and because it is commercially available at an acceptable price, it offers promise as a reaction solvent. However, its use is not without some drawbacks. However, an important feature of this invention is that it provides means for substantially overcoming some of the drawbacks and allows DME to be used. For example, NaAlH_4 and DME mixtures can explode if the temperature gets too high and furthermore NaAlF_4 or other similar products can lower the decomposition temperature of this mixture. Moreover, silane and DME mixtures containing 30 to 70% silane are very flammable. In the process of this invention the $\text{Na}_5\text{Al}_3\text{F}_{14} \cdot \text{AlF}_3$ coproduct is continually removed. This lowers the hazard inherent with its presence in NaAlH_4 mixtures. Secondly, the addition of the large excess of SiF_4 in the secondary reactor provides SiF_4 in the vapor space in the separation zone and eliminates the vapor explosion hazard with DME/silane mixtures. These are important features.

There are additional, important significant features of this invention. As stated above, NaAlH_4 is virtually impossible to separate from NaAlF_4 and consequently its content therein should be minimized or more preferably, substantially eliminated. This invention provides means for keeping the NaAlH_4 concentration in the coproduct below unacceptable levels. Without the control mechanism provided by the invention, the NaAlH_4 would have to be very precisely added to the reaction vessel and this would require more costly means of addition, storage, and much more analytical support personnel time. Thus, this invention eliminates significant investment and operating expense. Moreover, as appreciated by a skilled practitioner, time consuming sampling and analytical procedures would be required if this invention were not used. As a result, analysis would be completed after a substantial time had elapsed. Since the results would not be

received in real time, they would not necessarily depict current operation. Therefore, the process of this invention provides a greater degree of reaction control than would otherwise be available. It should also be appreciated by a skilled practitioner that the iterative, loop process provided by this invention also provides a greater degree of stoichiometric control than could be afforded by any simple, single back-mix reactor of economically feasible size.

This invention provides means for making silane from NaAlH_4 on a scale heretofore unknown. It also provides commercially acceptable SiH_4 and coproduct of high quality, under conditions of adequate safety. As indicated above, it also provides means for producing silane on a stoichiometric or substantially stoichiometric basis that thereby conserves materials, eliminates costly separation techniques, and significantly reduces required chemical analysis, manpower and investment. In this invention, the preparative process itself is used as an analytical tool to control the input and usage of SiF_4 and NaAlH_4 .

Furthermore, this invention allows the NaAlH_4 starting material to be used in the reaction mixture in which it is produced. Thus, the NaAlH_4 can be produced in toluene and then mixed with a DME/toluene mixture rich in DME before feeding to the reactor in which silane is produced. In short, this invention not only overcomes a set of very difficult technical hurdles, but it does so in a manner that provides many highly desirable advantages.

The reaction of NaAlH_4 and SiF_4 , and similar reactions, carried out as illustrated by Example 1 can be conducted over a broad range of temperatures. A suitable range extends up to where cleavage of the liquid reaction medium, or other extraneous, undesirable side reaction occurs. Temperatures up to 160°C may be used. For reaction mixtures comprising ethers, a preferred range is 0 to 80°C . A more preferred range for ether solvents is 10 to 65°C , and a highly preferred range is 20 to 45°C . Operation should not be conducted above 65°C when using DME to avoid decomposition problems. Operation below 10°C may cause gelling problems.

The process may be conducted at, above, or below atmospheric pressure. An operable pressure range is from one-half to 100 atmospheres (25 to 10,000 kPa). Atmospheric pressure is a convenient reaction pressure to use. Not much benefit is gained by using other reaction pressures since for example, the reaction of SiF_4 with alkali metal aluminum hydrides is not very pressure dependent.

The process is preferably carried out with agitation. Vigorous agitation improves contacting the reactants, favors the intended reaction, and diminishes side reactions which can complicate the process. Some side reactions might cause deleterious effects such as plugging, coproduct purity problems, and the like.

Since the process is exothermic, evolved heat may be removed if desired by circulating the mixture through an external heat exchanger or by using an internal cooling coil or condensing a boiling solvent. Such expedients are more preferably used in conjunction with the primary, rather than secondary reactor.

Example 2

The process of this Example comprises the reaction of LiAlH_4 and SiF_4 to produce silane and a fluoride salt coproduct containing lithium and aluminum. The process results are illustrated by Figure 3. It is conducted similarly to the process of Example 1 using the same size reactors as mentioned above. The solvent is DME, and the reaction temperature is similar to that used in the first example. Calculations that further illustrate the process are as follows:

(I) Bases

SiF_4 feed rate and purity same as in Example 1.

LiAlH_4 100% pure and introduced as a 14% solution reacted at 11% concentration.

98.5% of LiAlH_4 reacts in primary reactor, remainder reacts in secondary reactor.

Neglect dimethoxyethane (DME) decomposition and DME leaving with SiH_4 .

Molecular weight:

$\text{LiAlH}_4 = 38$

$\text{LiAlF}_4 = 110$

$\text{SiF}_4 = \sim 104$

$\text{SiH}_4 = \sim 32$

(II) Calculations of Amount of LiAlH₄ reacted

$$\begin{aligned}
 & \frac{38}{104} \times 70 = 25.6 \\
 & = \frac{25.6 \text{ lbs per hour or}}{11.6 \text{ kg/hr}}
 \end{aligned}$$

In primary reactor; 25.6×0.985

$$\begin{aligned}
 & = \frac{25.2 \text{ lbs per hour or}}{11.5 \text{ kg/hr}}
 \end{aligned}$$

In secondary reactor; $25.6 - 25.2 = 0.4$

$$= \frac{0.4 \text{ lbs per hour or } 0.2 \text{ kg/hr}}{}$$

$$\begin{aligned}
 & \frac{25.6}{0.14} = \frac{182.9 \text{ lbs per hour}}{\text{or } 83.1 \text{ kg/hr}} \\
 \text{As 14\% solution}
 \end{aligned}$$

$$\begin{aligned}
 & \frac{25.6}{0.11} = \frac{232.7 \text{ lbs per hour}}{\text{or } 105.8 \text{ kg/hr}} \\
 \text{As 11\% solution}
 \end{aligned}$$

Solvent present in 11% solution $232.7 - 25.6$

$$= \frac{207.1 \text{ lbs per hour or } 94.1 \text{ kg/hr}}{}$$

(III) Amount of Diluent solution required

$$\begin{aligned}
 & 232.7 - 182.9 = \frac{49.8 \text{ lbs per hour or}}{22.6 \text{ kg/hr}}
 \end{aligned}$$

(IV) Amounts of products produced

32

$$\text{Amount of SiH}_4 = 104 \times 70.1 = 21.5 \text{ lbs per hour}$$

or

$$\underline{\underline{9.8 \text{ kg/hr}}}$$

110

$$\text{Amount of LiAlF}_4 = 104 \times 70$$

$$= 74.0 \text{ lbs per hour or}$$

$$\underline{\underline{33.7 \text{ kg/hr}}}$$

$$\text{From primary reactor, } 74 \times 0.985$$

$$= 72.9 \text{ lbs per hour or}$$

$$\underline{\underline{33.1 \text{ kg/hr}}}$$

(V) Amount of SiF₄ from Secondary reactor

$$70.0 \times 0.985 = 69.0 \text{ lbs per hour or}$$

$$\underline{\underline{31.3 \text{ kg/hr}}}$$

The process of this Example is also conducted (as the process of Example 1) using RTDs to measure the temperature inside the secondary reactor and upstream therefrom. The noted differential temperature is used to generate a signal to govern the flow of SiF₄ to the secondary reactor. For this purpose a metal (platinum) film RTD is preferred over more simple constructions such as the "bird-cage" element commonly used in the laboratory. As well known by skilled practitioners, the film RTD has increased resistance per given size, and since the device is relatively small, it can respond more quickly to changes in temperature. For better temperature measurement, the RTDs are used with a Wheatstone bridge, or preferably a 4-wire ohm measurement system to increase the accuracy of the temperature measurement. RTDs are more linear than thermocouples, but still require some curve fitting, as recognized by a skilled practitioner. The Callendar-Van Dusen equation can be used for curve fitting. Alternatively the 20th order polynomial can be used to provide a more accurate curve fit, as known in the art.

Example 3

A series of runs were made each over discrete period of time to illustrate the advantages in using split feed of silicon halide to the secondary reactor of a series of two reactors. A first portion of the silicon halide feed was fed directly into the liquid phase of said secondary reactor to control, with liquid agitation by a variable speed stirrer, the mass transfer characteristics of the reaction, while a second portion of the silicon halide was fed in runs 3 to 7 to a separation column, and in runs 8 to 9 directly into the vapor space above the liquid to suppress any accumulation of combustible gases within the vapor space above the liquid. In runs 8 and 9a liquid level control constituted of a pump, and liquid level regulator for controlling the operation of the pump was provided for setting the liquid residence time to aid in controlling reaction kinetics. The results of operations of this type, depicted by reference to Figure 4 and described as Runs 3 to 9 Table 1, are compared to an operation conducted as described by reference to Figure 2, these latter

being described as Runs 1 to 2 in the Table.

These runs were each conducted over a period of several days with a temperature of 35°C in the first reactor of the series, with the differential temperature between the two reactors ranging from 17 to 22°C (Centigrade degrees). In conducting these runs, SiF₄ was fed into the secondary reactor, the total amount of SiF₄ fed in the secondary reactor during Run 1 having been 408,24 kg/h (900 pounds/hour) and, during Runs 2 through 9, 453,6 kg/h (1000 pounds/hour). Sodium aluminum hydride was introduced into the first reactor of the series, with SiF₄ in amount less than required to completely react with the sodium aluminum hydride, during the several runs, the amount of the hydride after dilution with DME and toluene in Run 1 having been 0.07 percent, and in all of Runs 2 to 9, respectively, 0.08 percent, based on weight. In the secondary reactor during Runs 1 and 2, 0.05 and 0.07 percent of sodium aluminum hydride, respectively, based on the amount of sodium aluminum hydride in the feed to the initial reactor of the series, was converted; and in each of Runs 3 to 9, 0.08 percent of the sodium aluminum hydride was converted. Essentially complete conversion of the sodium aluminum hydride took place in each run within the two reactors of the series, with the major amount of the conversion of silane, and a coproduct sodium aluminum fluoride, having been obtained in the first reactor of the series. The pressure in the secondary reactor, in bar (pounds per square inch gauge (psig)), during each of the several runs was as follows to wit: In Run 1 2,94 bar (28 psig); In Runs 2 to 4 2,46 bar (21 psig); In Runs 5 to 7 2,11 bar (16 psig); and in Runs 8 to 9 1,42 bar (6 psig). SiF₄ was introduced into the secondary reactor in total amount in excess of that required to react with the unreacted sodium aluminum hydride passed from the first reactor to the second reactor of the series. Table 1 lists in separate columns for each of the runs (a) the ratio of the amount of SiF₄ introduced via a dipleg directly into the liquid relative to the total amount of SiF₄ introduced into the secondary reactor (Column 3), this being referred to in the Table as "SiF₄ split"; (b) the residence time (in minutes) of the liquid within the secondary reactor (Column 4); and (c) the amount of agitation in W/l (HP/gallon) applied to the liquid of the secondary reactor during the reaction (Column 5). The first column of Table 1 gives the Run Number, and Column 2 the analytical results for the total SiO₂ found in the sodium aluminum fluoride product for each of the several runs.

Table 1

Run No.	SiO ₂ In Sodium Aluminum Fluoride	SiF ₄ Split	Residence Time, Minutes	Agitation HP/gal (W/l)
1	2.74	1.00	14.95	0.0549 (10,67)
2	1.99	1.00	7.58	0.0549 (10,67)
3	1.03	0.20	7.58	0.0549 (10,67)
4	1.61	0.30	7.58	0.0549 (10,67)
5	0.66	0.35	5.46	0.0068 (1,32)
6	0.66	0.35	5.46	0.0046 (0,89)
7	0.43	0.30	5.46	0.0040 (0,78)
8	0.54	0.30	7.58	0.0033 (0,64)
9	0.34	0.27	7.58	0.0033 (0,64)

These data clearly illustrate, inter alia, the advantages of reducing the amount of SiF₄ fed directly into the liquid phase of the secondary reactor, and the amount of agitation applied to the liquid contents of the secondary reactor during the reaction to control mass transfer. It also clearly shows the advantages, at these conditions, of reducing the residence time of the liquid within the secondary reactor during the reaction to control the kinetics of the reaction.

Example 4

In an additional run the secondary reactor of the unit, as employed in conducting Runs 3-7 described in Example 3, was controlled to provide an SiF₄ split of 0.35 and a total liquid residence time of 5.46 minutes, while the amount of liquid agitation was varied over a range of values. The first column of Table 2 lists the amount of agitation in W/l (HP/gallon) applied to the liquid, and the second column thereof the amount of SiO₂ found by analysis in the sodium aluminum fluoride product produced at the different levels of agitation.

Table 2

Agitation HP/gallon (W/l)	% SiO ₂ In Sodium aluminum fluoride
0.0763 (14,83)	1.50
0.0763 (14,83)	1.29
0.0646 (12,55)	1.07
0.0611 (11,87)	0.86
0.0451 (8,76)	0.64
0.0322 (6,26)	0.56
0.0220 (4,27)	0.47
0.0129 (2,51)	0.47
0.0084 (1,63)	0.77
0.0076 (1,48)	0.86
0.0068 (1,32)	0.99
0.0060 (1,17)	0.49
0.0060 (1,17)	0.36
0.0060 (1,17)	0.41
0.0046 (0,89)	0.34
0.0046 (0,89)	0.36
0.0046 (0,89)	0.34
0.0046 (0,89)	0.34
0.0046 (0,89)	0.39
0.0046 (0,89)	0.41
0.0046 (0,89)	0.36

These results, it is clear, show a definite advantage in controlling at low levels the amount of agitation applied to the liquid during the reaction.

Following the procedure of the above examples, KAlH_4 , NaH , KH or LiH can be reacted with SiF_4 or SiCl_4 . Also, LiAlH_4 and NaAlH_4 can be reacted with SiCl_4 . Mixtures such as NaH and NaAlH_4 can also be used.

These reactions can be conducted using an ether reaction medium such as discussed above, and by reacting from 90 to 99% of the metal hydride in the primary reactor and the remainder in the secondary reactor.

The process temperature is within the range of from 10 to 65°C and the processes are preferably conducted at atmospheric pressure. When SiCl_4 is used as a liquid, the temperature is maintained below 59°C.

The RTDs used are exemplified by 100 ohm platinum RTOS, 60,96 cm (24 inches) long, 0,64 cm (1/4") O.D. 316 stainless steel sheath, 3 wire, 1 foot extension supplied by Child's Instruments. The silane product can be separated from the other materials by its difference in boiling point.

Claims

1. Continuous process for preparing silane and a coproduct comprising a metal and a halogen, wherein are included the steps of
 - (A) reacting in a first reaction zone and in a liquid reaction medium, a metal hydride reactant selected from alkali metal hydrides and alkali metal aluminum hydrides, with less than a stoichiometric quantity of a silicon halide selected from compounds having the formula SiX_4 , wherein X is fluorine, chlorine, or bromine;
 - (B) reacting in a second reaction zone, the metal hydride remaining in the liquid reaction medium, above which a vapor space is provided, with a quantity of SiX_4 reactant in excess of that required to react with said remaining metal hydride;
 - (C) separating in a separation zone, a gaseous fraction comprising silane and unreacted silicon halide from solid reaction product suspended in a diluting solution and produced in said reaction zones;
 - (D) recovering said silane;



Table 2

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0.0451 (8,76)	0.64
0.0322 (6,26)	0.56
0.0220 (4,27)	0.47
0.0129 (2,51)	0.47
0.0084 (1,63)	0.77
0.0076 (1,48)	0.86
0.0068 (1,32)	0.99
0.0060 (1,17)	0.49
0.0060 (1,17)	0.36
0.0060 (1,17)	0.41
0.0046 (0,89)	0.34
0.0046 (0,89)	0.36
0.0046 (0,89)	0.34
0.0046 (0,89)	0.34
0.0046 (0,89)	0.39
0.0046 (0,89)	0.41
0.0046 (0,89)	0.36

These results, it is clear, show a definite advantage in controlling at low levels the amount of agitation applied to the liquid during the reaction.

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The process temperature is within the range of from 10 to 65°C and the processes are preferably conducted at atmospheric pressure. When SiCl_4 is used as a liquid, the temperature is maintained below 59°C.

The RTDs used are exemplified by 100 ohm platinum RTOS, 60,96 cm (24 inches) long, 0,64 cm (1/4") O.D. 316 stainless steel sheath, 3 wire, 1 foot extension supplied by Child's Instruments. The silane product can be separated from the other materials by its difference in boiling point.

Claims

1. Continuous process for preparing silane and a coproduct comprising a metal and a halogen, wherein are included the steps of
 - (A) reacting in a first reaction zone and in a liquid reaction medium, a metal hydride reactant selected from alkali metal hydrides and alkali metal aluminum hydrides, with less than a stoichiometric quantity of a silicon halide selected from compounds having the formula SiX_4 , wherein X is fluorine, chlorine, or bromine;
 - (B) reacting in a second reaction zone, the metal hydride remaining in the liquid reaction medium, above which a vapor space is provided, with a quantity of SiX_4 reactant in excess of that required to react with said remaining metal hydride;
 - (C) separating in a separation zone, a gaseous fraction comprising silane and unreacted silicon halide from solid reaction product suspended in a diluting solution and produced in said reaction zones;
 - (D) recovering said silane;



(E) introducing unreacted silicon halide from said second reaction zone into said first reaction zone to react with an additional quantity of metal hydride;

(F) determining the difference in temperature between the temperature of reaction liquid in said second reaction zone, and the temperature of reactant liquid substantially immediately prior to entry into said second zone; and

(G) utilizing a signal derived from said difference in temperature to regulate the flow of a reactant to a reaction zone to achieve substantially stoichiometric reaction of the total amounts of silicon halide and metal hydride reacted in both reaction zones, said process comprising the step

(H) splitting the SiX_4 reactant introduced to said second reaction zone (B) into two streams, (a) a first SiX_4 stream which is introduced directly into the liquid reaction mixture to improve mass transfer between the liquid and gaseous phases, and (b) a second SiX_4 stream which is introduced into the separation zone and/or directly into the vapor space above said liquid reaction mixture to suppress the formation of combustible gaseous mixtures.

2. The process of Claim 1 wherein said metal hydride is an alkali metal hydride wherein the alkali metal is selected from lithium, sodium, and potassium.

3. The process of Claim 1 wherein said metal hydride is an alkali metal aluminum hydride wherein said alkali metal is selected from lithium, sodium, and potassium.

4. The process of Claim 1 wherein said silicon halide is selected from SiF_4 and SiCl_4 .

5. The process of Claim 1 wherein the ratio of the SiX_4 introduced directly into the liquid reaction mixture of said second reaction zone, relative to the total amount of SiX_4 introduced into said second reaction zone, as described in step (H), ranges from 0.20 to 0.40.

6. The process of Claim 5 wherein the ratio of the SiX_4 introduced directly into the liquid reaction mixture relative to the total amount of SiX_4 introduced into said second reaction zones ranges from 0.23 to 0.30.

7. The process of Claim 1 wherein the liquid reaction mixture of said second reaction zone is stirred at agitation levels sufficient to further control mass transfer between the liquid and gaseous phases.

8. The process of Claim 7 wherein the liquid reaction mixture of said second reaction zone is stirred at agitation levels ranging from 0,64 W/l (0.0033 HP/gal) to 1,32 W/l (0.0068 HP/gal) of energy input.

9. The process of Claim 1 wherein the residence time of the liquid reaction mixture in said second reaction zone ranges from 0.5 minute to 30 minutes.

10. The process of Claim 9 wherein the residence time of the liquid reaction mixture in said second reaction zone ranges from 5 minutes to 10 minutes.

Patentansprüche

1. Kontinuierliches Verfahren zur Herstellung von Silan und eines ein Metall und ein Halogen umfassenden Nebenprodukts, welches folgende Schritte umfaßt:

(A) Umsetzen eines aus Alkalimetallhydrid und Alkalimetallaluminiumhydriden ausgewählten Metallhydridreaktanten mit weniger als der stöchiometrischen Menge eines aus Verbindungen mit der Formel SiX_4 , in der X Fluor, Chlor oder Brom ist, ausgewählten Siliciumhalogenids in einer ersten Reaktionszone und in einem flüssigen Reaktionsmedium;

(B) Umsetzen des in dem flüssigen Reaktionsmedium, über dem ein Dampfraum zur Verfügung gestellt wird, verbleibenden Metallhydrids mit einer Menge des SiX_4 -Reaktanten, die größer ist als die für die Reaktion mit dem verbleibenden Metallhydrid erforderliche Menge, in einer zweiten Reaktionszone;

(C) Abscheiden einer Silan und nicht umgesetztes Siliciumhalogenid umfassenden gasförmigen Fraktion von dem festen Reaktionsprodukt, das in einer Verdünnungslösung suspendiert ist und in den Reaktionszonen hergestellt wurde, in einer Abscheidungszone;

(D) Entnahme des Silans;



(E) Einleitung des nicht umgesetzten Siliciumhalogenids aus der zweiten Reaktionszone in die erste Reaktionszone zur Umsetzung mit einer zusätzlichen Menge Metallhydrid;

(F) Ermittlung des Temperaturunterschieds zwischen der Temperatur der Reaktionsflüssigkeit in der zweiten Reaktionszone und der Temperatur der Reaktantenflüssigkeit im wesentlichen unmittelbar vor dem Eintritt in die zweite Reaktionszone sowie

(G) Nutzung eines aus dieser Temperaturdifferenz abgeleiteten Signals zur Regulierung des Flusses eines Reaktanten in eine Reaktionszone, um die im wesentlichen stöchiometrische Reaktion der in beiden Reaktionszonen umgesetzten Gesamtmengen von Siliciumhalogenid und Metallhydrid zu bewirken, wobei das Verfahren folgende Schritte umfaßt:

(H) Aufteilung des in die zweite Reaktionszone (B) eingeleiteten SiX_4 -Reaktanten in zwei Ströme, (a) einen ersten SiX_4 -Strom, der direkt in das flüssige Reaktionsgemisch eingeleitet wird, um den Stoffübergang zwischen der flüssigen und der gasförmigen Phase zu verbessern, und (b) einen zweiten SiX_4 -Strom, der in die Abscheidungszone und/oder direkt in den Dampfraum oberhalb des flüssigen Reaktionsgemischs eingeleitet wird, um die Bildung von brennbaren Gasgemischen zu unterdrücken.

2. Verfahren nach Anspruch 1, bei dem das Metallhydrid ein Alkalimetallhydrid ist, wobei das Alkalimetall aus Lithium, Natrium und Kalium ausgewählt ist.

3. Verfahren nach Anspruch 1, bei dem das Metallhydrid ein Alkalimetallaluminiumhydrid ist, wobei das Alkalimetall aus Lithium, Natrium und Kalium ausgewählt ist.

4. Verfahren nach Anspruch 1, bei dem das Siliciumhalogenid aus SiF_4 und SiCl_4 ausgewählt ist.

5. Verfahren nach Anspruch 1, bei dem das Verhältnis von direkt in das flüssige Reaktionsgemisch der zweiten Reaktionszone eingeleitetem SiX_4 bezogen auf die gesamte in die zweite Reaktionszone eingeleiteten SiX_4 -Menge wie in Schritt (H) beschrieben im Bereich von 0,20 bis 0,40 liegt.

6. Verfahren nach Anspruch 5, bei dem das Verhältnis von direkt in das flüssige Reaktionsgemisch eingeleitetem SiX_4 bezogen auf die gesamte in die zweite Reaktionszone eingeleiteten SiX_4 -Menge im Bereich von 0,23 bis 0,30 liegt.

7. Verfahren nach Anspruch 1, bei dem das flüssige Reaktionsgemisch der zweiten Reaktionszone auf einem Bewegungsniveau gerührt wird, das ausreicht, um den Stoffübergang zwischen der flüssigen und der gasförmigen Phase zu steuern.

8. Verfahren nach Anspruch 7, bei dem das flüssige Reaktionsgemisch der zweiten Reaktionszone auf einem Bewegungsniveau im Bereich von 0,64 w/l (0,0033 HP/gal) bis 1,32 w/l (0,0068 HP/gal) Energiezufuhr liegt.

9. Verfahren nach Anspruch 1, bei dem die Verweildauer des flüssigen Reaktionsgemischs in der zweiten Reaktionszone im Bereich von 0,5 bis 30 Minuten liegt.

10. Verfahren nach Anspruch 9, bei dem die Verweildauer des flüssigen Reaktionsgemischs in der zweiten Reaktionszone im Bereich von 5 bis 10 Minuten liegt.

Revendications

1. Procédé continu de préparation d'un silane et d'un coproduit comprenant un métal et un halogène, dans lequel sont mises en oeuvre les étapes consistant

(A) à faire réagir dans une première zone de réaction et dans un milieu réactionnel liquide un corps réactionnel du type hydrure métallique choisi entre des hydrures de métaux alcalins et des hydrures de métaux alcalins et d'aluminium avec une quantité inférieure à une quantité stoechiométrique d'un halogénure de silicium choisi entre des composés répondant à la formule SiX_4 , dans laquelle X représente le fluor, le chlore ou le brome ;

(B) à faire réagir dans une seconde zone de réaction l'hydrure métallique restant dans le milieu réactionnel liquide, au-dessus duquel se trouve un espace rempli de vapeur, avec une quantité de corps réactionnel SiX_4 supérieure à la quantité requise pour la réaction avec ledit hydrure métallique



restant ;

(C) à séparer dans une zone de séparation une fraction gazeuse, comprenant un silane et l'halogénure de silicium n'ayant pas réagi, du produit solide de réaction mis en suspension dans une solution de dilution et formé dans lesdites zones de réaction ;

(D) à séparer ledit silane ;

(E) à introduire l'halogénure de silicium n'ayant pas réagi, provenant de la seconde zone de réaction, dans ladite première zone de réaction pour sa réaction avec une quantité supplémentaire d'hydruure métallique ;

(F) à déterminer la différence de température entre la température du liquide réactionnel dans ladite seconde zone de réaction et la température du liquide réactionnel pratiquement immédiatement avant la pénétration dans ladite seconde zone ; et

(G) à utiliser un signal dérivé de ladite différence de température pour la régulation du débit d'un corps réactionnel dans une zone de réaction pour parvenir à une réaction pratiquement stoechiométrique des quantités totales d'halogénure de silicium et d'hydruure métallique ayant réagi dans les deux zones de réaction, ledit procédé comprenant l'étape consistant

(H) à diviser le corps réactionnel SiX_4 introduit dans ladite seconde zone de réaction (B) en deux courants, (a) un premier courant de SiX_4 qui est introduit directement dans le mélange réactionnel liquide pour améliorer le transfert de masse entre les phases liquide et gazeuse, et (b) un second courant de SiX_4 qui est introduit dans la zone de séparation et/ou directement dans l'espace de vapeur au-dessus dudit mélange réactionnel liquide pour supprimer la formation de mélanges gazeux combustibles.

2. Procédé selon la revendication 1, dans lequel l'hydruure métallique est un hydruure de métal alcalin dans lequel le métal alcalin est choisi entre le lithium, le sodium et le potassium.

3. Procédé suivant la revendication 1, dans lequel l'hydruure métallique est un hydruure de métal alcalin et d'aluminium dans lequel ledit métal alcalin est choisi entre le lithium, le sodium et le potassium.

4. Procédé suivant la revendication 1, dans lequel l'halogénure de silicium est choisi entre SiF_4 et SiCl_4 .

5. Procédé suivant la revendication 1, dans lequel le rapport du SiX_4 introduit directement dans le mélange réactionnel liquide de la seconde zone de réaction à la quantité totale de SiX_4 introduite dans ladite zone de réaction, de la manière décrite dans l'étape H, est compris dans l'intervalle de 0,20 à 0,40.

6. Procédé suivant la revendication 5, dans lequel le rapport du SiX_4 introduit directement dans le mélange réactionnel liquide à la quantité totale de SiX_4 introduite dans la seconde zone de réaction est compris dans l'intervalle de 0,23 à 0,30.

7. Procédé suivant la revendication 1, dans lequel le mélange réactionnel liquide de la seconde zone de réaction est agité à des intensités d'agitation suffisantes pour ajuster de nouveau le transfert de masse entre les phases liquide et gazeuse.

8. Procédé suivant la revendication 7, dans lequel le mélange réactionnel liquide de la seconde zone de réaction est agité à des intensités d'agitation correspondant à un apport d'énergie de 0,64 W/l (0,0033 HP/gal) à 1,32 W/l (0,0068 HP/gal).

9. Procédé suivant la revendication 1, dans lequel le temps de séjour du mélange réactionnel liquide dans la seconde zone de réaction est compris dans l'intervalle de 0,5 à 30 minutes.

10. Procédé suivant la revendication 9, dans lequel le temps de séjour du mélange réactionnel liquide dans la seconde zone de réaction est compris dans l'intervalle de 5 minutes à 10 minutes.