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(71) Applicant: ETHYL CORPORATION [US/US]; 451 Florida Boulevard, Baton Rouge, LA 70801 (US).

(72) Inventor: MARLETT, Everett, Michael ; 9355 Greenbriar Drive, Baton Rouge, LA 70815 (US).

(74) Agents: HANDELMAN, Joseph, H. et al.; Ladas & Parry, 26 West 61 Street, New York, NY 10023 (US).

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(54) Title: PROCESS FOR PRODUCTION OF SILANE

(57) Abstract

A process for the production of high purity silane by reacting silicon tetrafluoride exclusively with sodium aluminum tetrahydride, potassium aluminum tetrahydride, or a mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride, preferably in a polyether liquid reaction medium. The inventive process is a highly advantageous and economical route to silane and is preferably carried out on a continous basis in diglyme.

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PROCESS FOR PRODUCTION OF SILANE

This invention relates to the production of silane gas (SiH_4) and more specifically to a highly advantageous, commercially attractive process for production of silane.

The production of pure silane is an important step in the ultimate production of ultrahigh purity silicon for semiconductor materials and other purposes.

In the past, the art has taught several schemes to synthesize silane from silicon tetrachloride ($SiCl_4$) but these have not proven commercially feasible. Rather, industry has selected various other routes for commercial silane production. For example, one foreign producer reportedly reacts magnesium silicide (Mg_2Si) with ammonium chloride (NH_4Cl) in liquid ammonia. Another domestic producer reacts silicon tetrachloride with the relatively expensive lithium aluminum tetrahydride ($LiAlH_4$). Another producer obtains various chlorosilanes by hydrochlorination of metallurgical grade silicon and then disproportionates the chlorosilanes in a catalyst bed to silane and silicon tetrachloride. Still other producers avoid silane altogether, instead depositing silicon from chlorosilanes. Thus, there exists a need to provide pure silane by an economical synthesis from readily available starting materials.

The present invention is directed to the provision of pure silane gas by an economically feasible route from readily available starting materials.

The present invention is a process for the production of silane wherein silicon tetrafluoride is reacted exclusively with sodium aluminum tetrahydride, potassium aluminum tetrahydride, or a mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride.

The present invention is also a process wherein the silicon tetrafluoride is introduced into the reaction zone in non-solid form.

The present invention is also a process wherein silicon tetrafluoride is reacted with a specified tetrahydride on a continuous basis in an inert liquid reaction mixture whereby throughout substantially the entire reaction period the reaction mixture comprises a non-viscous slurry of by-product solids in said medium.

The present invention is also the mentioned continuous process wherein the molar ratio of by-product solids to reactant tetrahydride is at least one.

The present invention also involves a process for the production of silane wherein gaseous silicon tetrafluoride is introduced into an inert liquid reaction medium containing sodium aluminum tetrahydride and the reaction medium is maintained at a temperature in the range of from 30 to 80 degrees Centigrade.

In a further embodiment, this invention provides a process for the production of silane which comprises introducing gaseous silicon tetrafluoride into an agitated, inert liquid polyether reaction medium containing sodium aluminum tetrahydride, the reaction mixture being maintained (i) at a temperature in the range of from 30 to 80 degrees Centigrade, (ii) at a pressure in the range of from atmospheric pressure up to 100 atmospheres, and (iii) under an atmosphere of hydrogen, silane or both.

A still further embodiment of this invention involves a process for the economical production of high purity silane gas, said process comprising the steps of:

(a) introducing gaseous silicon tetrafluoride into an inert liquid reaction medium containing sodium aluminum tetrahydride for reaction at a temperature in the range of 0 to 150^{o}C to produce high purity silane gas and by-product solids, said liquid reaction medium being further characterized in that said by-product solids are insoluble therein and said by-product solids do not form a stable complex therewith;

(b) recovering high purity silane gas product;

(c) separating said by-product solids from said liquid reaction medium; and

(d) separately recovering said liquid reaction medium and said by-product solids.

In another embodiment of this invention, the foregoing process for the economical production of silane gas is further characterized by being conducted on a continuous basis whereby at least periodically, and preferably continuously, (a) gaseous silicon tetrafluoride and (b) sodium aluminum tetrahydride dissolved in fresh inert liquid reaction medium are separately introduced into the inert liquid reaction medium in the reaction zone, and at least periodically, and preferably continuously, (c) silane gas product and (d) liquid reaction medium containing said by-product solids are withdrawn from the reaction zone.

In accordance with the present invention, pure silane gas is produced from the reaction of silicon tetrafluoride (SiF_4)with sodium aluminum tetrahydride ($NaAlH_4$), potassium aluminum tetrahydride ($KAlH_4$), or a mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride. The preferred reaction is silicon tetrafluoride with sodium aluminum tetrahydride.

Silicon tetrafluoride is readily produced as a gas from fluosilicic acid (H_2SiF_6), a by-product of the phosphate fertilizer industry and also available from other sources. Silicon tetrafluoride offers several advantages over silicon tetrachloride. For example, the fluoride by-products obtained from reaction with sodium aluminum tetrahydride or potassium aluminum tetrahydride do not complex with the preferred polyether reaction mediums and are therefore more easily separated from the medium. By comparison, the counterpart chloride by-products are soluble in the preferred polyether medium and form stable complexes from which solvent recovery is difficult making the overall reaction less economical and less practical. While the fluorides sometimes form a viscous slurry, they are, nevertheless, ordinarily filterable for solvent recovery. The solubility of sodium aluminum tetrafluoride, for example, has been measured at 0.55 weight percent in diglyme at room temperature, whereas the solubility of sodium aluminum tetrachloride has been measured at about 30 percent in diglyme at room temperature.

The invention uses complex metal hydrides for reaction with silicon tetrafluoride. The complex metal hydrides of the invention include sodium aluminum tetrahydride and potassium aluminum tetrahydride. Alkaline earth metal aluminum tetrahydrides, such as magnesium aluminum tetrahydride $Mg(AlH_4)_2$ and calcium aluminum tetrahydride $Ca(AlH_4)_2$ are excluded from the invention. The sodium aluminum tetrahydride is preferred for the invention since it is more easily prepared and handled, is relatively stable, and forms by-products which are generally insoluble in favored liquid reaction mediums.

The process of the invention is preferably carried out in a liquid reaction medium. The liquid mediums of the invention 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), the dialkoxyl,4-dioxane, and 1,3-dioxolanes, tetrahydrofuran (THF), hydrocarbons including toluene and xylene; simple aliphatic and aromatic ethers including diethyl ether and diphenyl ether, and tertiary amines including triethylamine, tributylamine, and N-methylpyrrolidine.

Liquid reaction mediums outside the preferred class of polyethers are also generally somewhat water-miscible. The hydrocarbon mediums provide low to moderate yields of silane unless strong agitation, such as a ball mill reactor, is used.

The preferred liquid reaction mediums 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, the dimethyl ether of diethylene glycol, and the like.

A more preferred class of liquid reaction mediums are the diloweralkyl ethers of alkylene glycols. These include the diethyl ether of ethylene glycol, the dimethyl ether of propylene glycol, the dimethylene ether of diethylene glycol, and the like.

Still more preferred are the diloweralkyl ethers of ethylene glycols. These include the dimethyl ether of ethylene glycol, the dimethyl ether of diethylene glycol, the dimethyl ether of triethylene glycol, the diethyl ether of diethylene glycol, and the like.

The most preferred medium is the dimethyl ether of diethylene glycol (diglyme). The preferred solvents of the invention are those which provide reasonable solubility for reactant sodium aluminum tetrahydride or potassium aluminum tetrahydride.

It is preferable to carry out the reaction with a stoichiometric excess of the tetrahydrides of the invention, preferably an excess of sodium aluminum tetrahydride. The reactant silicon tetrafluoride often contains boron impurities which detract from the value of the silane when used for the production of ultrapure silicon. The excess tetrahydride reactant ties up the boron contaminants within the liquid reaction medium.

The concentration of tetrahydride in liquid reaction medium is preferably at least about two percent by weight of the liquid reaction medium in a batch process. Lower concentrations are uneconomical and contribute to problems in the recovery of by-products and reaction medium. Concentrations as low as one percent by weight tetrahydride of reaction medium are commercially impractical in a batch process. Also, too large an amount of reaction medium requires unnessarily high agitation power requirements.

The preferred reactant, sodium aluminum tetrahydride, is preferably introduced as a solution in a polyether reaction medium and gaseous silicon tetrafluoride is added thereto for synthesis of silane.

The inventive process may be carried out over a broad range of temperatures. For example, silicon tetrafluoride may be metered as a gas and condensed into a reaction zone where it is frozen to a solid. Thereafter, as the temperature of the system is raised, the silicon tetrafluoride begins to react with reactant sodium aluminum tetrahydride, potassium aluminum tetrahydride, or mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride. The silicon tetrafluoride may be frozen with liquid nitrogen at about -196°C.

A suitable reaction temperature range extends up to the temperature where cleavage of the liquid reaction medium occurs and other reactions may then interfere with the invention. An applicable reaction temperature range extends up to about 160°C. A preferred range for ether reaction mediums is 0 to 80°C. A more preferred range, especially for those reactions of the invention using ether-type liquid reaction mediums is 40 to 70°C. The most preferred reaction temperature range is 50-60°C.

The process of the invention may be conducted at, above, or below atmospheric pressure, but pressure does not strongly affect the reactivity of silicon tetrafluoride with sodium aluminum tetrahydride, potassium aluminum tetrahydride, or a mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride. A suitable range of reaction pressures is one to one hundred atmospheres. A preferred range is about one to forty atmospheres. Notably, the solubility of silicon tetrafluoride is about 0.75 percent in dyglyme at atmospheric pressure and is about five percent in diglyme at 500 psig.

The reaction may be carried out under an inert atmosphere. Conveniently, a silane atmosphere, optionally with a hydrogen sweep, is maintained as the product is evolved above a reaction zone, preferably in a liquid reaction medium. Argon, helium, nitrogen, and other inert gases may also be used.

The inventive process is preferably carried out with mechanical or other agitation. Agitation is improved above 50^{o}C in diglyme where the slurry viscosity decreases markedly.

The reaction is almost instantaneous at most reaction conditions. Where silicon tetrafluoride gas is bubbled into a liquid reaction medium, pure silane gas is readily evolved.

The reaction may be carried out without a liquid reaction mixture where silicon tetrafluoride is provided to the tetrahydride in an agitated reaction vessel such as a ball mill reactor. The ball mill reactor and similar apparatus are also preferred for certain reaction mediums such as hydrocarbons. A high shear agitation effects better reaction when such mediums are used.

Since the reaction is somewhat exothermic, evolved heat may be removed by circulating the reactants/reaction slurry through an external heat exchanger or using an internal cooling coil.

A preferred embodiment of the invention is the continuous feed of silicon tetrafluoride gas and sodium aluminum tetrahydride dissolved in diglyme. This embodiment includes operation of the reaction in a continuous back-mixed reactor, operated at conditions approaching completion of the reaction. Once the molar concentration of the by-product solids in the slurry of the reaction zone exceeds the molar amount of tetrahydride reactant, the consistency of the slurry goes from a high viscosity (thick) to a moderate viscosity (thin). This is favorable to mass transfer of the gaseous silicon tetrafluoride to the liquid slurry and therefore, a more complete and rapid reaction results.

Contrary to the batch process of the invention, the concentration of tetrahydride in the liquid reaction medium may well, and preferably does, fall below two percent by weight of the reaction medium in a continuous process. The advantages of the continuous process override any problems mentioned above with respect to the batch process.

The following examples further serve to illustrate the invention.

EXAMPLE 1

To a 50 mL three-necked, round bottom reaction flask was added 10 millimoles of sodium aluminum tetrahydride ($NaAlH_4$) as a 4% solution in diglyme. The flask was connected to a gas collection train and purged with prepurified hydrogen. A one-eighth inch diameter polytetrafluoroethylene tube was connected to a reservoir of silicon tetrafluoride gas with one end extending into the flask below the surface of the sodium aluminum tetrahydride/diglyme solution. A condenser following the reactor was cooled with a mixture of dry ice and acetone and a product trap was chilled in liquid nitrogen. Magnetic stirring was started and silicon tetrafluoride was bled in beneath the surface of the solution at a feed rate of 10 millimoles over a thirty minute period. The temperature of the diglyme solution of sodium aluminum tetrahydride was 50°C when the silicon tetrafluoride feed was started and gradually rose to a final temperature of 60°C. After the addition of about 10 millimoles silicon tetrafluoride, the reactor and collection system were swept with hydrogen for an additional 30 minutes. The valve between the condenser and the product trap was blocked and the trap and collection system were evacuated. The calibrated section was isolated and the condensed product was permitted to vaporize into it. The amount of gaseous product was calculated by means of the ideal gas law based upon observed initial and final pressures. A sample was analyzed by mass spectrometry and the yield of silane was 99 percent based on sodium aluminum tetrahydride charged.

EXAMPLE 2

The general procedure of Example 1 was followed except that the reaction was conducted at 60-70°C.

The silane yield on sodium aluminum tetrahydride was 90 percent.

EXAMPLE 3

The general procedure of Example 1 was followed except that the reaction was conducted at 55°C and 30 psig pressure. Also, a slight stoichiometric excess (1.0:0.97) of silicon tetrafluoride was used. The yield after one hour was 96 percent and the product silane contained some silicon tetrafluoride gas.

EXAMPLE 4

The same general procedure of Example 1 was followed except that the reaction was conducted at 50°C and 60 psig. The yield was 80 percent and the product silane contained some silicon tetrafluoride.

EXAMPLE 5

The same general procedure of Example 1 was followed except that the reaction was conducted at 50°C and 53 psig. Also, a stoichiometric excess (1.0:1.2) of sodium aluminum tetrahydride was used. The yield was 96 percent silane, free of silicon tetrafluoride.

EXAMPLE 6

The same general procedure of Example 1 was followed. However, the sodium aluminum tetrahydride was supplied as a six percent solution in diglyme and the reaction was conducted at 50°C and 60 psig. Also, a stoichiometric excess (1.0:1.2) of sodium aluminum tetrahydride was again employed. After two hours, the 97 percent yield of silane was again free of silicon tetrafluoride.

EXAMPLE 7

The general procedure of Example 1 was followed. However, the sodium aluminum tetrahydride was supplied as a five percent solution and the silicon tetrafluoride was fed above the surface of the liquid reaction medium. A stoichiometric excess (1.0:0.91) of silicon tetrafluoride was reacted at 50°C and atmospheric pressure. The yield of silane after two hours was 98 percent.

EXAMPLE 8

The same general procedure was followed as in Example 1 except that the liquid reaction medium also contained some tetrahydrofuran and the reaction was conducted at 25-50°C. The yield of silane was 86 percent.

EXAMPLE 9

The same general procedure of Example 1 was followed except that the sodium aluminum tetrahydride was recrystallized prior to use. The reaction at 55°C and 33 psig provided a silane yield of 86 percent after one hour.

EXAMPLE 10

The same general procedure of Example 1 was followed. A stoichiometric excess (1.0:1.3) of recrystallized sodium aluminum tetrahydride was employed in a 4.5

percent solution of dimethoxyethane at 23°C and atmospheric pressure. The silane yield after one hour was 84 percent.

It is possible to conduct the inventive process with the introduction of seed materials into the reaction zone. The seed materials include MgO, Na_2SiF_6, $CaCO_3$, KF, and others. Also, some runs were made under similar conditions to those in the examples above with similarly good results.

Examples 11 and 12 demonstrate the addition of seed materials to the reaction mixture.

EXAMPLE 11

The same general procedure of Example 1 was followed except that about 20 millimoles MgO was also put into the reaction mixture with the sodium aluminnum tetrahydride. The silane yield was high and the by-product slurry was more quickly filtered than the slurry from the Examples above.

EXAMPLE 12

The same general procedure of Example 1 was followed except that 4 millimoles sodium fluosilicate (Na_2SiF_6) were added to the reaction mixture. The yield of silane was 94 percent and the nature of the by-product solids was changed.

Some experiments with methyl *tert*-butyl ether, diphenyl ether, and toluene reaction mediums provided low yields (less than 10%, 5%, and less than 1%, respectively) of silane, but use of high shear agitation apparatus with reaction mixtures employing these liquid mediums would increase the yield.

CLAIMS:

1. A process for the production of silane characterized in that silicon tetrafluoride is reacted exclusively with sodium aluminum tetrahydride, potassium aluminum tetrahydride, or a mixture of sodium aluminum tetrahydride and potassium aluminum tetrahydride.

2. The process as claimed in Claim 1 in which the silicon tetrafluoride is introduced into the reaction zone in gaseous form.

3. The process as claimed in Claim 1 in which the reaction is conducted in an inert liquid reaction medium.

4. The process of as claimed in Claim 3 in which said polyether is a diloweralkyl ether of an alkylene glycol.

5. The process as claimed in Claim 3 in which said polyether is the dimethyl ether of diethylene glycol.

6. The process as claimed in Claim 3 in which said polyether is the dimethyl ether of ethylene glycol.

7. The process as claimed in Claim 1 in which the reaction is conducted with agitation in an inert liquid reaction medium under an atmosphere of hydrogen or silane, or both.

8. The process as claimed in Claim 1 in which silicon tetrafluoride is reacted exclusively with sodium aluminum tetrahydride.

9. The process as claimed in Claim 8 in which gaseous silicon tetrafluoride is introduced into an inert liquid reaction medium containing sodium aluminum tetrahydride and the reaction medium is maintained at a temperature in the range of from 30 to 80 degrees Centigrade.

10. The process as claimed in Claim 9 in which the silicon tetrafluoride and the sodium aluminum tetrahydride are proportioned such that throughout substantially the entire reaction period the amount of the sodium aluminum tetrahydride is in excess of the stoichiometric amount of the silicon tetrafluoride employed.

11. The process as claimed in Claim 9 in which said reaction is carried out at a temperature in the range of 50 to 60 degrees Centigrade and a pressure in the range of from one to 100 atmospheres.

12. The process as claimed in Claim 9 in which said gaseous silicon tetrafluoride is introduced into an agitated, inert liquid polyether reaction medium containing sodium aluminum tetrahydride, the reaction mixture being maintained (i) at a temperature in the range of from 30 to 80 degrees Centigrade, (ii) at a

pressure in the range of from atmospheric pressure up to 100 atmospheres, and (iii) under an atmosphere of hydrogen, silane or both.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/01975

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. CL^3 C01B33/04
US CL. 423/347

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	423/347

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	GB, A 823,496, (Kelly) 11 November 1959	1-12
Y	N, Journal of Fluorine Chemistry, 14 issued 1979, Padma et al Silicon Tetrafluoride: Preparation and Reduction with Lithium Aluminum Hydride, pp. 327-329	1-12 1-12
X	GB, A 851,962, (Allied Chem. Corp.) 19 October 1960	1-12
Y	GB, A 909,950, (W, E.1. Du pont De Nemours Co.) 07 November 1962	1-12
A	GB, A 832,333, (Radley et al) 06 April 1960	1
A	EP, A1 52,808, (Lefrancois) 02 June 1982	1
Y	N, Journal of the Electrochemical Society, 12 issued 1961, Lewis et al Preparation of High-Purity Silicon from Silane pp. 1114-1118	1-12

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 07 March 1984	Date of Mailing of this International Search Report [3] 14 MAR 1984
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] J. Cooper

Form PCT/ISA/210 (second sheet) (October 1981)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	N, Journal of the Electrochemical Society, 12 issued 1975, Yusa et al Ultrahigh Purification of Silane for Semiconductor Silicon pp. 1700-1705	1
A	N, Chemical Abstracts, Vol. 53 issued 1959 Vit et al Manufacturing Monosilane from Silicon Tetrachloride and Metal Hydride, Abstract No. 39392Z	1

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

International Application No. PCT/US83/01975

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	N, Chemical Abstracts, Vol. 59 issued 1963 de Pape Reduction of Silicon Tetrachloride and Boron Trifluoride by Calcium Hydride, Abstract No. 6023g	1
Y	Kelly et al, The Preparation of Transistor Grade Silicon from Silane or Analogous Compounds Metal Hydrides Incorporated, Beverly, Massachusetts, Final Report under Air Force Contract No. AF19(604)-1928, issued 1957	1-12
Y	Lewis et al, The Preparation of Transistor Grade Silicon from Silane or Analogous Compounds, Metal Hydrides Incorporated, Beverly, Massachusetts, Final Report under Air Force Contract No. AF19(604)-3464 issued 1959	1-12
Y	N, Journal of the American Chemical Society, Vol 69, issued 1947 Finholt et al, Hydrides of Fourth Group Elements and Their Organic Derivatives pp 2692-2969	1-12