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(54) **High Yield Silicon Carbide Pre-ceramic Polymers**

(57) Polysilanes which are substituted with  $(\text{CH}_3)_3\text{SiO}$ -groups are useful for the preparation in high yields of fine grained silicon carbide ceramic materials. They consist of 0—60 mole %  $(\text{CH}_3)_2\text{Si}$  units and 100—40 mole %  $\text{CH}_3\text{Si}$  units, all Si valences not

satisfied by  $\text{CH}_3$  groups or Si atoms being directed to groups  $(\text{CH}_3)_3\text{SiO}$ —, which siloxane groups amount to 23—61 weight % of the polysilane. They are prepared by reaction of the corresponding chloro- or bromo-methyl polysilanes with at least the stoichiometric amounts of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  and water in the presence of a strong acid.

GB 2 081 288 A

## SPECIFICATION

**High Yield Silicon Carbide Pre-ceramic Polymers**

This invention relates to high yield silicon carbide pre-ceramic polymers.

The concept of preparing silicon carbide ceramic materials or silicon carbide-containing ceramics from silicon carbide ceramic materials is not new. As applied to the preparation of silicon carbide-containing ceramics from the degradation of polymers, any number of published articles or issued patents have appeared.

Yajima in U.S. Patent 4,052,430, issued October 4, 1977, has described the preparation of polycarbosilanes prepared by pyrolyzing the polysilanes generated by the reaction of sodium or lithium metal with dimethyldichlorosilane. These polycarbosilanes can be heated to yield beta-silicon carbide.

West and Maszdziazni reported in the 22nd AFOSR Chemistry Program Review FY77, R. W. Heffner, ed. March (1978), that a polymer, made by reacting dimethyldichlorosilane with methylphenyldichlorosilane and an alkali metal, could be fired at high temperatures to yield whiskers of beta-silicon carbide.

Verbeek has shown in U.S. Patent No. 3,853,567, the preparation of a mixed ceramic of silicon carbide and silicon nitride by pyrolyzing a polysilazane. In addition, Verbeek has prepared a polycarbosilane suitable for molding by heating organosilicon polymers optionally mixed with silicon dioxide or organic polymers at a temperature between 400° and 1200°C.

Rice *et al.*, in U.S. Patent No. 4,097,794, issued June 27, 1978, have suggested that almost anything containing silicon can be pyrolyzed to give a ceramic material.

Baney, in U.S. Patent application Serial Number 910,247, filed May 30, 1978, now abandoned, and continued as a continuation-in-part, serial number 024,137, filed March 26, 1979, now abandoned and continued as a continuation-in-part of Serial Number 135,567, filed March 31, 1980, disclosed a methylhalopolysilane which can be fired at 1200°C or above to yield fine grain beta-silicon carbide. The yields and handling characteristics of these latter polysilanes were enhanced over the prior materials.

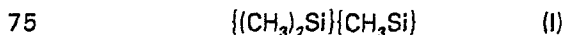
Mention should be made of recent Japanese patent publications 80500/78 and 101099/78 in the name of Takamizawa *et al.* These publications deal with polymers made from

methylchlorosilanes but no mention is made of the yields of ceramic materials generated by the decomposition of the polysilanes. Recent publications by Nakamura (Japanese Kokais 79/114600 and 79/83098) suggest that the preparation of silicon carbide precursor polymers having a silicon carbon (—Si—C—Si—) backbone is effected by heating organosilicon compounds (including  $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{Cl}$ ) in the presence of B, Al, Si, Ge, Sn and Pb compounds

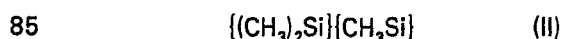
or HI and its salts, at high temperatures.

It has now been determined that high yields of silicon carbide ceramic materials and silicon carbide-containing ceramics can be obtained from the methods and the new materials of the instant invention.

This invention deals with a process for obtaining novel polysilanes, which process consists in a method of preparing a polysilane, having the average formula (I):

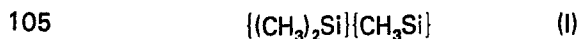


in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole  $\text{CH}_3\text{Si}\equiv$  units, and wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(\text{CH}_3)_3\text{SiO}-$ , based on the weight of the polysilane, which methods consists in (A) reacting a polysilane having the average unit formula (II):



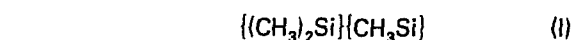
in which there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}\equiv$  units, wherein the remaining bonds on the silicon atoms are attached to either another silicon atom, a chlorine atom or a bromine atom, such that the polysilane contains from 10—43 weight percent, based on the weight of the polysilane, of hydrolyzable chlorine or 21—62 weight percent based on the weight of the polysilane of hydrolyzable bromine, with (i)  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , (ii) a strong acid, and (iii) at least a stoichiometric amount of water, based on the amount of halogen in the polysilane (II), at a temperature of from 25°C to 125°C, for a period of from 1/2 to 24 hours, in a suitable solvent; and (B) thereafter recovering the polysilane (I).

This invention also deals with a composition of matter which is a polysilane having the average formula (I):



in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}-$  radical and wherein there is present in the polysilane 23 or 61 weight percent of  $(\text{CH}_3)_3\text{SiO}-$ , based on the weight of the polysilane. Furthermore, the invention provides shaped articles made from the polysilanes, with or without fillers, and a method by which the shaped articles are obtained.

This invention also consists in a method of preparing a silicon carbide ceramic materials which consists in heating a polysilane having the average unit formula (I):



in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(\text{CH}_3)_3\text{SiO}-$ , based on the weight of the polysilane, in an inert atmosphere or in a vacuum, to an elevated temperature in the range of 1150°C to 1600°C until the polysilane is converted to silicon carbide ceramic material.

The invention described herein represents an improvement over the art in that higher yields of silicon carbide ceramic materials are obtained upon pyrolysis of the polysilanes, and the polysilanes herein are much easier and safer to handle because the replacement of the halogen substituents with  $-\text{OSi}(\text{CH}_3)_3$  radicals limits hydrolysis and thus reduces the quantity of corrosive HCl or HBr gas liberated.

This invention involves replacing halogen atoms on the above-described polyhalosilanes with  $(\text{CH}_3)_3\text{SiO}-$  radicals, the resulting product, upon pyrolysis, giving silicon carbide ceramic materials.

The polyhalosilane starting materials are those set forth and described in the Baney patent application serial number 910,247, filed May 30, 1978, now abandoned, and continued as a continuation-in-part, serial number 024,137, filed March 26, 1979, now abandoned and continued as a continuation-in-part as Serial Number 135,567, filed March 31, 1980, which are hereby incorporated by reference.

The starting materials are those described in the Baney application which consists of 10—43 weight percent, based on the weight of the polysilane, of hydrolyzable chlorine, or 21—62 weight percent, based on the weight of the polysilane, of hydrolyzable bromine.

These polyhalosilane starting materials can be prepared by treating methylhalodisilanes with catalysts such as  $(\text{C}_4\text{H}_9)_4\text{P}^+\text{Cl}^-$ , or they can be prepared by treating an halosilane residue which is derived from the Direct Synthesis of halosilanes. The aforementioned disilane is found in large quantities in the residue (see Eaborn, "Organosilicon Compounds", Butterworths Scientific Publications, 1960, page 1).

The polyhalosilane starting materials are then subjected to a treatment with  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , to yield the polysilane of the invention.

Generally, the process consists in placing a toluene solution of the starting polyhalosilane in a suitably equipped reaction vessel, then adding the  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  and strong acid directly into the reaction vessel as a liquid, and, thereafter, adding water in sufficient quantity to hydrolyze the chlorine atoms. After the initial reaction has taken place, the reaction mass is stirred and sometimes heated to ensure complete reaction. It is then cooled, neutralized and filtered. The resulting products are either solids or liquids depending on the starting materials.

These materials are then shaped (if desired),

filled with ceramic type fillers (if desired) and then fired to temperatures of 1150°C or above, *in vacuo* or in an inert atmosphere, to yield silicon carbide ceramic materials or silicon carbide ceramic material-containing ceramic articles.

Thus, this invention contemplates the preparation of a filled ceramic article prepared from the silicon carbide ceramic materials of this invention. The method consists in (A) mixing a polysilane with at least one conventional ceramic filler which polysilane has the average formula (I):



in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(\text{CH}_3)_3\text{SiO}-$ , based on the weight of the polysilane; (B) forming an article of the desired shape from the mixture of polysilane and fillers; and (C) heating the article formed in (B), in an inert atmosphere or in a vacuum, to an elevated temperature in the range of 1150°C to 1600°C, until the polysilane is converted to a silicon carbide-containing ceramic.

It is also contemplated with the scope of this invention to prepare articles which are coated with the silicon carbide ceramic materials of this invention and which are then pyrolyzed to yield articles coated with silicon carbide-containing ceramics. Thus, the method of preparing such an article coated with ceramic consists in (A) mixing a polysilane with at least one conventional ceramic filler which polysilane has the average unit formula (II):



in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}-$  radical, and wherein there is present in the polysilane 23 to 61 weight percent of  $(\text{CH}_3)_3\text{SiO}-$  based on the weight of the polysilane; (B) coating a substrate with the mixture of polysilane and fillers; and (C) heating the coated substrate, in an inert atmosphere or in a vacuum, to an elevated temperature in the range of 1150°C to 1600°C, until the coating is converted to a silicon carbide ceramic material, whereby a silicon carbide-containing ceramic coated article is obtained.

The acids useful herein are those acids which are known to those skilled in the art for the rearrangement of siloxane bonds, for example,  $\text{F}_3\text{CSO}_3\text{H}$  and sulfuric acid. The acid;  $\text{F}_3\text{CSO}_3\text{H}$  is preferred for this invention.

Generally, the  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  is used in a stoichiometric excess to ensure that the reaction is enhanced. Excess  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  as well as any solvents, water and byproducts can be

stripped or strip distilled at the end of the reaction.

Solvents for the starting polyhalosilanes can be any organic solvent in which the material is soluble and which does not react with the material except in the desired manner. Examples of useful solvents include toluene, xylene, benzene, tetrahydrofuran and ethers. Specifically, toluene is preferred.

Generally, the order of addition of the components is not critical, but it has been found preferable to add the  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  and acid to the polyhalosilane in a solvent solution, such as toluene. The water is then added. The addition and reaction are carried out while the materials are stirred or otherwise agitated.

The reaction can be run at temperatures of  $25^\circ\text{C}$  to  $125^\circ\text{C}$  but, preferably, the reaction is run at room temperature or slightly above room temperature to prevent or to decrease undesirable side-reactions. When the addition of the  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , acid and water is complete, the reaction mixture is stirred for a time, with or without heating, to ensure the completion of the reaction.

The reaction mixture is cooled to room temperature, if necessary, and then filtered by conventional means, and the solvents and other volatile materials are then removed by stripping under vacuum, with the addition of heat if necessary. The resulting polysilanes are liquids or solids, depending on the polyhalosilane starting material and the reaction conditions used.

The resulting materials are then formed into shapes such as by melt spinning and fired at elevated temperatures to yield silicon carbide ceramic materials.

Filled silicon carbide ceramic materials can be made by adding fillers and adjuvants to the polysilane before firing.

For example, fine silicon carbide, silicon nitrides, oxides such as silica, alumina, glasses and silicates may be used as fillers in the polysilanes of this invention, and, when the mixture is fired, high strength ceramic articles result. We prefer powdered silicon carbide and silicon nitrides.

Fillers and adjuvants may be milled on 3-roll mills by simply mixing the polysilanes of this invention with the fillers and making several passes on the mill. The mixture is then shaped to the desired form and is fired to prepare the silicon carbide ceramic article.

Usually, the materials of this invention, whether filled or unfilled, are heated to  $1150^\circ\text{C}$  and above to ceramify them. Generally,  $1600^\circ\text{C}$  is the hottest temperature required to convert the polysilanes to silicon carbide. Thus, heating the polysilanes from  $1150^\circ\text{C}$  to  $1600^\circ\text{C}$  will suffice to give optimum physical properties in the final ceramic product.

The following examples are given for the purposes of illustration and are not intended to limit the scope of this invention.

Titration of chloride ion in these examples was

carried out in a solution of toluene and isopropanol (essentially non-aqueous), using an 0.1% solution of tetrabromophenolphthalein ethyl ester in methanol/toluene. Titration was carried out using 0.5N KOH in ethanol.

#### Example 1

##### Preparation of the Polychlorosilane

Four hundred and eighty-one and one-tenth grams of tetramethyldichlorodisilane were treated with 1.4 grams (0.3 weight percent) of tetrabutyl phosphonium chloride in a 500 ml., 3-necked, round-bottomed glass flask under an argon blanket. The initial addition caused the reaction mixture to clear momentarily and, at about  $53^\circ\text{C}$ , the reaction mass turned cloudy white. At  $84^\circ\text{C}$ , the color turned from white to yellow. Distillation of by-produced chlorosilane monomers began at  $117.5^\circ\text{C}$  and the reaction mixture cleared. The flask was heated to  $145^\circ\text{C}$ , held a short period and then allowed to cool overnight with stirring while the argon blanket was continued. In the morning, the temperature was raised to  $250^\circ\text{C}$  and held for 1 hour and the product was then cooled to yield a yellowish white solid. A sample of the yellowish white solid contained 18.25 weight percent hydrolyzable chlorine.

#### Example 2

##### Preparation of the Polysilane of the Invention

Fifty grams of the polychlorosilane prepared in Example 1 were mixed with 150 grams of hexamethyldisiloxane and 100 grams of toluene to form a clear yellow solution. Approximately 1.0 ml of  $\text{F}_3\text{CSO}_3\text{H}$  was then added. Twice the stoichiometric amount of water to hydrolyze the chlorine (9 grams) was then added, and a phase separation occurred. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then subjected to vacuum for 2 hours, and refluxed for three hours under argon. The yellowish organic layer was decanted from the water layer and dried over  $\text{MgSO}_4$ . After filtering,  $\text{NaHCO}_3$  was added (10 grams) and the slurry was allowed to stand overnight. The slurry was filtered and the filtrate was stripped of solvent to yield a yellow foamy material. The residual chlorine content was 1.1 weight percent.

Thermal Gravimetric Analysis (TGA) of a sample of the yellow foamy material showed a 24% weight loss at  $155\text{--}850^\circ\text{C}$ , and an additional 8.4% weight loss at  $850$  to  $1555^\circ\text{C}$ . The resulting fine-grained material was identified by X-rays as being mostly beta-silicon carbide having an average grain size of  $30 \text{ \AA} \pm 10 \text{ \AA}$ .

A second programmed TGA gave the following results

temperature	% yield
room temperature	100.0
$1200^\circ\text{C}$	40.1
$1600^\circ\text{C}$	31.6

The material when fired to  $2000^\circ\text{C}$  was light green in color and was fine-grained.

A polymeric polycarbosilane material prepared by Yajima *et al.* was reported to yield about 24% of silicon carbide at 1330°C (Nature, Vol. 261, No. 5562, pages 683—685 (1976)).

### 5 Claims

1. A method of preparing a polysilane having the average formula (I):



10 in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(CH_3)_3SiO-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(CH_3)_3SiO-$ , based on the weight of the polysilane, which method consists in: (A) reacting

15 (A) reacting a polysilane having the average unit formula (II):



20 in which there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein the remaining bonds on the silicon atoms are attached to either another silicon atom, a chlorine atom or a bromine atom,

25 such that the polysilane contains from 10—43 weight percent, based on the weight of the polysilane, of hydrolyzable chlorine, or 21—62 weight percent, based on the weight of the polysilane, of hydrolyzable bromine, with:

30 (i)  $(CH_3)_3SiOSi(CH_3)_3$ ;  
(ii) a strong acid; and  
(iii) at least a stoichiometric amount of water, based on the amount of halogen in the polysilane (II), at a temperature of from 25°C

35 to 125°C for a period of from 1/2 to 24 hours, in a suitable solvent; and  
(B) thereafter recovering the polysilane (I).

2. A method of preparing a polysilane as claimed in claim 1, wherein there is present 0.1 to

40 10 weight percent, based on the weight of the polysilane, of a strong acid and a stoichiometric quantity of  $(CH_3)_3SiOSi(CH_3)_3$ , based on the amount of halogen in the polysilane (II).

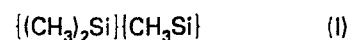
3. A composition of matter consisting

45 essentially of a polysilane having the average unit formula (I):



50 in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(CH_3)_3SiO-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(CH_3)_3SiO-$  based on the weight of the polysilane.

55 4. A method of preparing silicon carbide ceramic material which consists of heating a polysilane having the average unit formula (I):



60 in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(CH_3)_3SiO-$  radical, and wherein there is present in the polysilane 23 to 61 weight percent of  $(CH_3)_3SiO-$ , based on the weight of the polysilane, in an inert atmosphere or in a vacuum, to an elevated temperature in the range of

70 1150°C to 1600°C, until the polysilane is converted to silicon carbide ceramic material.

5. Silicon carbide ceramic material prepared by the method claimed in claim 4.

6. A method of preparing a silicon carbide-containing ceramic article which consists in:

75 (A) forming an article of the desired shape from a polysilane having the average formula (I):



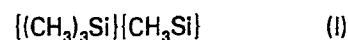
in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(CH_3)_3SiO-$  radical and wherein there is present in the polysilane 23 to 61 weight percent of  $(CH_3)_3SiO-$  based on the weight of the polysilane and

85 (B) heating the article formed in (A), in an inert atmosphere or in a vacuum, to an elevated temperature in the range of 1150°C to 1600°C, until the polysilane is converted to silicon carbide-containing ceramic.

90 7. The article prepared by the method of claim 6.

8. A method of preparing a filled ceramic article which consists in:

95 (A) mixing a polysilane with at least one conventional ceramic filler which polysilane has the average formula (I):



100 in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si=$  units and 40 to 100 mole percent  $CH_3Si\equiv$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(CH_3)_3SiO-$  radical, and wherein there is present in the polysilane 23 to 61 weight percent of  $(CH_3)_3SiO-$  based on the weight of the polysilane,

105 (B) forming an article of the desired shape from the mixture of polysilane and fillers; and  
(C) heating the article formed in (B) in an inert atmosphere or in a vacuum, to an elevated temperature in the range of 1150°C to 1600°C, until the polysilane is converted to a silicon carbide-containing ceramic.

110 9. An article prepared by the method of claim 8.

115 10. A method of preparing an article coated with ceramic, which consists in:

- (A) mixing a polysilane with at least one conventional ceramic filler, which polysilane has the average unit formula (I):
- $$\{(\text{CH}_3)_2\text{Si}\}\{\text{CH}_3\text{Si}\} \quad (I)$$
- 5 in which polysilane there is from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}$  units, wherein there is also bonded to the silicon atoms other silicon atoms and the  $(\text{CH}_3)_3\text{SiO}$  radical, and where there is present in the polysilane 23 to 61 weight percent
- 10 of  $(\text{CH}_3)_3\text{SiO}$ — based on the weight of the polysilane;
- (B) coating a substrate with the mixture of polysilane and fillers; and
- 15 (C) heating the coated substrate in an inert atmosphere or in a vacuum to an elevated temperature in the range of 1150°C to 1600°C until the coating is converted to a silicon carbide ceramic material, whereby a silicon carbide-containing ceramic coated article is obtained.
- 20 11. An article prepared by the method of claim 10.