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(54) **An Improved Method of Preparing Silicon Carbide**

(57) The improved method of preparing silicon carbide comprises forming a desired shape from a polysilane of the average formula:



The polysilane contains from 0 to 60 mole percent  $(\text{CH}_3)_2\text{Si}$ =units and from 40 to 100 mole percent  $\text{CH}_3\text{Si}$ =units.

The remaining bonds on the silicon are attached to another silicon atom or to a halogen atom in such manner that the average ratio of halogen to silicon in the polysilane is from 0.3:1 to 1:1. The polysilane has a melt viscosity at 150°C of from 0.005 to 500 Pa.s and an intrinsic viscosity in toluene of from 0.0001 to 0.1. The shaped polysilane is heated in an inert atmosphere or in a vacuum to an elevated temperature until the polysilane is converted to silicon carbide.

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## SPECIFICATION

**An Improved Method of Preparing Silicon Carbide**

5 This invention relates to an improved method of preparing silicon carbide.

The physical properties of silicon carbide have been known and fully appreciated since it was first discovered and patented in 1891 by Acheson.

10 For example, silicon carbide is known to have chemical inertness, semi-conducting properties, extreme hardness abrasiveness in the powdered form and stability in the face of extremely high temperatures. Silicon carbide therefore finds many uses such as in high temperature electrical heating units, furnace walls, mufflers, abrasives, rocket nozzles automotive engine parts and turbine parts.

15 The early preparation of silicon carbide was a straightforward reaction involving heating high grade silica and coke in a furnace at very high temperatures, of the order of 1975°—2630°C. The crystalline material obtained by this method is crushed and cleaned by washing with acids and alkali. It is used primarily in the crushed or powdered form mainly as a powder bound by resinous matrices. It is also hot pressed and sintered to give fabricated shapes and drawn to yield fibers.

20 Recently, there has been a trend to simplify the procedure for fabricating silicon carbide and silicon carbide containing articles through improvements in the methods of obtaining the silicon carbide itself. Previous methods have suffered from difficulties in handling which in turn led to the high cost normally associated with silicon carbide articles.

25 Late in 1974 and early in 1975, several new approaches to the manufacture of silicon carbide have been reported. Wolfgang Verbeek reported in U.S. Patent No. 3,853,567 that he could form a shaped article, such as a fiber, consisting of a mixture of silicon carbide and a silicon nitride by pyrolysing a silazane at a temperature in the range of from 200°C to 800°C inclusive to form a fusible carbosilazane resin, and then forming a fiber and heating the fiber in an inert atmosphere to the range of 800°C to 2000°C. The silazanes which he found useful were prepared from halosilanes and amines and included monomeric, cyclic and polymeric materials. The silazane compound is converted into a fusible carbosilazane resin by pyrolysis which involves passing the compound through a pipe heated to about 200—800°C which has been filled with a packing such as ceramic saddles. The resin, after devolatizing, is a yellow to red-brown, transparent, brittle, hydrolysis-insensitive product.

30 Other investigators, Seishi Yajima and his associates at the Japanese Research Institute for Iron, Steel and other Metals, Tohoku University, having been working in the field of silicon carbide preparation. They have reported their work quite extensively and for purposes of this

65 discussion, the subject matter of their work will be condensed by relying on their summary disclosure in *Chemistry Letters*, pp. 551—554, 1975, published by the Chemical Society of Japan. It should be noted that the subject matter can also be found in several patent publications, for example, German OLS 2,651,140, German OLS 2,618,150, French Patent No. 2,308,590, Japanese Patent Application Number 76/21365, German OLS 2,628,342, Japanese Patent Publication 77/74000, Japanese Patent Publication 77/73108 and U.S. Patent No. 4,052,430 (issued October 4, 1977).

70 The first synthesis disclosed by Yajima and his co-workers was the use of metallic lithium to dechlorinate dimethyldichlorosilane so as to produce dodecamethylcyclohexasilane. The dodecamethylcyclohexasilane is then purified by means of recrystallization and sublimation. It is then heated at 400°C for 48 hours in an autoclave to produce a product which is polycarbosilane. The polycarbosilane is then treated with solvents to remove low molecular weight fractions and the remaining polycarbosilane is dissolved in benzene or xylene. This product is shown as having a molecular weight of from 1000—2000. The polycarbosilane in benzene or xylene is then spun into fibers by dry spinning.

80 As admitted by Yajima therein, this method was technically difficult owing to the expensive and time consuming specific chemical reaction, the use of lithium metal, of an autoclave, of acetone fractionation and of dry spinning.

85 As a solution to the difficulties encountered in Yajima's original synthesis, he and his co-workers reported on a second improved synthesis for silicon carbide. The method consisted in the use of a mixture of silane and metallic sodium in a flask which mixture was covered by a stream of gaseous argon. The dimethyldichlorosilane starting material was set up in a dropping funnel and the flask was heated to reflux, thereby melting the sodium. With stirring, the dimethyldichlorosilane was added dropwise and the molten sodium dechlorinated the silane to give a precipitate of polydimethylsilanes. The resulting product, in the illustrative example, had an average molecular weight of approximately 3200. The polycarbosilane was thereafter removed using filtration and the metallic sodium remaining with the product was decomposed with methyl alcohol. It was then washed with water twice, dried and placed in a reaction vessel whereupon it was converted to a liquid by heating to 320°C. Thereafter, it was refluxed for 5 hours up to a temperature of 470°C to remove volatiles. The resulting viscous substance was taken up in *n*-hexan solution, filtered again, concentrated at reduced pressure and again heated to remove low molecular weight components. The average molecular weight of the final product was about 948, i.e. lower than the polysilane at 3200, indicating that the precipitated polysilane is chopped up and rearranged to give lower

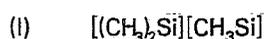
molecular weight polycarbosilane.

Finally, note should be made of some work being done by Roy Rice which has been described in a U.S. Department of Commerce, National Technical Information Service Bulletin AD-D003-165 which is based on a U.S. Patent Application Serial Number 716,729. Rice makes the broad statement that almost any polymer containing silicon can be pyrolysed to a ceramic material but, aside from two brief examples, the disclosure does not teach those skilled in the art the specific ways and means to obtain the ceramic material. Rice essentially teaches that one can take a silicon-containing polymer and heat it to high temperatures and realize a silicon-based ceramic material. No explanation in the Rice disclosure gives the necessary detail set forth in Verbeek and Yajima *et al.*, on how one handles the materials, or what starting materials to use or whether volatiles are involved or how they are to be handled. Rice only sets forth commonly known techniques such as the rate of heating, the use of an inert atmosphere and so on.

The invention disclosed herein overcomes the difficulties of the Yajima methods and sets forth a succinct method, easily followed by those skilled in the art, to prepare silicon carbide.

The invention herein is a practical, inexpensive, safe method for preparing silicon carbide. The details of why the method is practical, inexpensive and safe are set forth below during the detailed discussion.

This invention is a method of preparing silicon carbide comprising (A) forming a desired shape from a polysilane having the average formula:



in which polysilane there is from 0 to 60 mole percent  $(CH_3)_2Si$  units and 40 to 100 mole percent  $CH_3Si$  units, wherein the remaining bonds on the silicon are attached either to another silicon atom or to a halogen atom in such manner that the average ratio of halogen to silicon in the polysilane is from 0.3:1 to 1:1, wherein the polysilane has a melt viscosity at 150°C of from 0.005 to 500 Pa.s and an intrinsic viscosity in toluene of from 0.0001 to 0.1; and (B) heating the shape in an inert atmosphere or in a vacuum to an elevated temperature until the polysilane is converted to silicon carbide.

The polysilane used in step (A) of this method can be prepared by the methods of Alfred R. Gilbert and Glenn D. Cooper set forth in U.S. Patent No. 2,842,580.

The latter U.S. Patent discloses the use of quaternary halides as catalysts for cleaving organohalogenpolysilanes to obtain low molecular weight monosilanes. At column 2, lines 51 to 70, the U.S. Patent describes a "high boiling residue" and how it is obtained. For the most part, that "high boiling residue" is analogous to the starting material found in step (A) of this invention. In fact, the polysilane useful in this invention can be obtained from any source

provided the starting material contains the disilane:



where  $x$  is a whole number equal to from 0 to 3 and  $y$  is a whole number equal to from 0 to 3 and the sum of  $x+y$  is equal to at least one and generally between 2 and 4 as set forth in the aforementioned U.S. Patent.

The disilane can be prepared from the appropriate silanes or the disilane can be utilized as it is found as a component of the process residue from the direct synthesis of organochlorosilanes. The direct synthesis of organochlorosilanes involves passing the vapour of an organic chloride over heated silicon and a catalyst. (see: Eaborn, "Organosilicon Compounds", Butterworth's Scientific Publications, 1960, page 1). The disilane,



is found in large quantities in the residue from the reaction and, therefore, this Direct Process Residue (DPR) is a good starting material for obtaining the polysilane used in this invention.

In practice, the DPR is treated with a catalyst and heated as illustrated by the Gilbert *et al.* U.S. Patent No. 2,842,580. If DPR is used rather than the pure disilane, the presence of other organosilicon compounds in the DPR does not significantly affect the inventive method or the end result because, upon treatment of the DPR with catalyst, a rearrangement takes place which forms volatile useful silanes and the pre-silicon carbide polymer, the polymer as shown by the formula in step (A). The silanes are distilled from the reaction mixture as they are formed. It will be observed that removal of the volatile silanes enhances the rate of the reaction. These silanes are utilized commercially in other areas, and, therefore, their value offsets some of the cost of operating under the instant invention. One difference between the method disclosed in the Gilbert *et al.* U.S. Patent and the instant invention is the fact that the reaction of the instant invention is not forced as is shown in the Gilbert *et al.* U.S. Patent, that is, the reaction is carried out until a handleable polysilane is obtained while, in the Gilbert *et al.* U.S. Patent, the reaction was forced in order to produce all the silane monomers that were possible from the reactants and the residue was not always a material that could be easily handled.

For the purposes of this invention, the polysilane consists principally of  $(CH_3)_2Si$  units and  $CH_3Si$ . The remaining valences on these silane units are satisfied by other silicon atoms or halogen atoms. Thus, contemplated within the scope of this invention are polysilanes having an average of 0.3 or more halogen atoms per silicon atom. For example, other units present may be  $(Hal)_2Si$ ,  $CH_3HalSi$ ,  $CH_3(Hal)_2Si$ ,  $(CH_3)_2HalSi$  or  $(Hal)_3Si$  (where Hal is halogen)

or  $(\text{CH}_3)_3\text{Si}$ — provided a halogen to silicon ratio of 0.3:1 to 1:1 is maintained. Materials having the required halogen to silicon ratio generally have melt viscosities in the range of .005 to 500 Pa . s.

5 The halogen, for the purposes of this invention, is chlorine or bromine and preferably chlorine. The other halogen atoms, i.e. iodine, fluorine and  
10 astatine, undergo undesirable side-reactions and are difficult to handle so they are not generally useful in this invention. It is preferred, for the purposes of this invention, that all the halogen atoms on the disilane be the same halogen but it is also within the scope of this invention to have both chlorine and bromine atoms on the disilane.  
15 The polysilane useful in this invention is not easily analysed because of the nature of the material. The molecular weight of the polysilane can only be estimated but it is known that useful polysilanes having good handling properties  
20 generally have an intrinsic viscosity in toluene in the range of from 0.0001 to 0.1, inclusive it is conceivable that higher and lower materials could be useful but, for the purposes of this invention, the above range is preferred.

25 The catalysts that are useful are rearranging catalysts and examples of such catalysts are ammonium halides, tertiary organic amines, quaternary ammonium halides, phosphonium halides and silver cyanide.

30 Preferred are the phosphonium halides and the quaternary ammonium halides. Most preferred are the phosphonium halides, for example, tetrabutylphosphonium chloride.

The amount of catalyst utilized may range from  
35 0.001 to 10 weight percent based on the weight of the starting disilane. The catalysts and starting materials require anhydrous conditions and, therefore, one must take care to ensure that moisture is excluded from the reaction system  
40 when the disilane and catalyst are mixed. Generally, this can be done by using a stream of dry nitrogen as a cover over the reaction mixture. Generally, since the pyrolysis of the pre-silicon carbide polymer is carried out in an inert  
45 atmosphere, the use of nitrogen can serve a dual purpose. It is however within the scope of this invention to utilize vacuum rather than an inert gas.

Other significant aspects are the low  
50 temperature at which this reaction can be run and the fact that pressure is not required. The reaction to form the polysilane and the volatile silanes is usually carried out at 70° to 300°C for 4 to 24 hours. Higher or lower temperatures may be used  
55 but are not required as the desired reaction products can be obtained within the heating range set forth above, the lower temperatures tend to slow down the reaction and higher temperatures are a waste of energy and often lead to undesirable side-products such as  
60 carbosilanes and to loss of control of the reaction.

After the polysilane (I) is prepared, it can be utilized as a melt to spin fibers and to form  
65 shapes. It should be noted that the polymers so formed are clear and highly viscous. They do not

require dilution with solvents in order to lower the viscosity for spinning or drawing fibers.

The polymer melt, i.e. the pre-silicon carbide polymer in whatever form is desired, is then  
70 pyrolysed in an inert atmosphere or vacuum to obtain the silicon carbide. Such pyrolysis procedures are carried out at temperatures in the range of from 1150°C to 1600°C for 0.1 to 4 hours.

75 In summary then, the method is carried out by placing a disilane, or DPR containing the disilane, in a reaction vessel filled with nitrogen and adding thereto the proper amount of catalyst. The reaction is heated and the volatile silanes are formed and continuously removed. When the proper viscosity of the residue in the reaction vessel is reached, the reaction is terminated by lowering the temperature. The residue remaining in the reaction vessel is the polysilane (I). This  
80 material, as a melt, can be formed at this point and then pyrolysed to give the silicon carbide.

It should be noted that no special procedure is required for mixing the disilane and catalyst. The catalyst and disilane can be mixed all at once and stirred with a paddle stirrer. The silanes can be removed through the use of simple distillation  
90 apparatus.

Now, so that those skilled in the art can better understand and appreciate this invention, the following examples are given.

#### Example 1

Preparation of polysilane from  $(\text{Cl}_2\text{CH}_2\text{Si})_2$ .

A 250 milliliter, 3-necked glass flask was equipped with a nitrogen inlet tube, thermometer and condenser affixed to a toluene bubbler trap. The trap was equipped with a bleed line to a vented hood. A vacuum was drawn on the flask and then the flask was flushed with dry nitrogen for a few hours. Vacuum was again drawn on the flask and a flow of dry nitrogen was started.  
100 Tetrabutylphosphonium chloride (2.5 grams) was added to the flask and subjected to dry nitrogen for 1 hour. A vacuum was drawn on the flask and nitrogen flow was then started at a rate of one bubble of nitrogen/15 seconds.

Employing a syringe, 50 grams of the disilane were added to the flask. The mixture was heated to reflux and had a slight aquacoloured tint. It appeared to precipitate slightly and the pot  
115 temperature rose to 90°C and then fell to 81°C within one hour. An acid gas was evolved and the slight precipitate disappeared. After 3 hours, the temperature dropped to 73°C and after 4 hours the temperature dropped to 71°C. The reaction, except for nitrogen flow, was shut down. The residue in the flask was very viscous and fibers could be drawn with a glass rod by immersing the glass rod in the material and quickly withdrawing it. The material was clear with a light yellow  
120 colour.

#### Example 2

The apparatus was essentially the same as in Example 1 and 2.5 grams of  $(\text{Butyl})_4\text{PCl}$  and 66.7

grams of  $(\text{Cl}_2\text{CH}_3\text{Si})_2$  were added to the flask. The flask and contents had previously been dried and treated with nitrogen as in Example 1. The mixture was clear. After stirring at room temperature for about 16 hours, the mixture was heated and the temperature of the mixture rose to about  $70^\circ\text{C}$  all the while the mixture becoming more viscous. The mixture at this point was slightly cloudy and had some lumpiness. The temperature went up to  $94^\circ\text{C}$  and remained at  $90\text{--}98^\circ\text{C}$  most of an additional 8 hour period. The mixture turned a clear, pale yellow colour and had a very high viscosity. Fibers were pulled from the melt before cooling down. The material was soluble in toluene and also in acetone but not in isopropanol.

### Example 3

Preparation of polysilane from DPR.

An analysis of DPR from chlorosilane

production units showed that it contained the following:

Compound	Weight Percent
Lower boilers	0.9
Higher boilers	1.1
$(\text{CH}_3)_2\text{SiCl}_2$	2.7
$(\text{CH}_3)_4\text{Si}_2\text{Cl}_2$	4.9
$(\text{CH}_3)_3\text{Si}_2\text{Cl}_3$	40.3
$(\text{CH}_3)_2\text{Si}_2\text{Cl}_4$	50.1

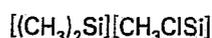
A 250 ml flask was equipped as in Example 1. The system was purged with dry nitrogen and then shut down while 2.5 gms of tetrabutylphosphonium chloride were added. A vacuum was then drawn on the flask for about one hour. It was re-purged with dry nitrogen and 66.7 gms of the above-identified DPR were added to the flask. The mixture was heated up to  $74^\circ\text{C}$  and it refluxed between  $70\text{--}80^\circ\text{C}$  during the removal of the low boilers and the  $(\text{CH}_3)_2\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$ . The solution initially had a bluish or aquacoloured tint and the colour disappeared while the mixture turned slightly cloudy. After about 5 hours heating, the solution had cleared. After an additional heating time of 8 hours, the viscosity started to rise and the material was cloudy yellow in appearance and, after two more hours, the material was clear, yellow in colour and viscous enough to pull fibers.

The material was analysed with the following results:

	Calculated %	Found
Si—Si	33.3	33.4
—SiCH <sub>2</sub> Si—	0	0

The yield of SiC upon pyrolysis was 47 percent and it was calculated to be 48 percent.

The data are consistent with a polymer of the structure



where the mole percent of  $(\text{CH}_3)_2\text{Si}=\text{}$  is 28 and the ratio of chlorine to silicon is 0.72:1. The percentage of hydrolysable chlorine was found to be about 38 weight percent. The intrinsic viscosity in toluene at  $25^\circ\text{C}$  was  $2 \times 10^{-2}$ . Polymer fibers were taken from the melt and heated in a thermogravimetric apparatus (TGA) in an argon atmosphere at  $5^\circ\text{C}/\text{min}$  to  $1200^\circ\text{C}$ . As indicated above, it lost 53% of its weight. X-ray powder analysis revealed the residue to be extremely fine grain  $\beta\text{-SiC}$  ( $\sim 70\text{\AA}$ ). Numerous other runs were made and fired in the TGA, producing the same results. About 0.5 gm of one batch of the polymer was heated in a tube furnace in a helium atmosphere for four hours to produce the same ultra-fine grain  $\beta\text{-SiC}$ .

### Example 4

In a manner similar to Example 3, an apparatus was set up and a nitrogen flow was started after 0.5 gm of  $(\text{Butyl})_4\text{PCI}$  was added to the flask and heated to melting. DPR (400 gms) was slowly added to the flask after the initial addition of 30—50 milliliters of DPR. After 10 minutes, distillate was seen to collect in the receiving flask. The flask temperature was about  $105^\circ\text{C}$  at this time. The DPR was slowly added over the next three hours and the temperature rose to  $150^\circ\text{C}$ . During the course of the next five hours, the temperature remained the same and the distillate temperature never exceeded  $65^\circ\text{C}$ . The reaction was shut down but the nitrogen flow was maintained. After sitting overnight (approximately 16 hours), the flask was heated again to  $250\text{--}270^\circ\text{C}$ . After eight hours of collecting distillate at less than  $80^\circ\text{C}$  head temperature, the heating was stopped. There remained in the flask a viscous, yellow fluid that cooled to a yellow wax-like solid. The material when reheated began melting at approximately  $100^\circ\text{C}$ . When cooled, a portion of the material was chipped from the flask and it was soluble in toluene.

### 100 Claims

1. A method of preparing silicon carbide which consists of

(A) Forming a desired shape from a polysilane having the average formula:



in which polysilane there is from 0 to 60 mole percent of  $(\text{CH}_3)_2\text{Si}=\text{}$  units and 40 to 100 mole percent  $\text{CH}_3\text{Si}=\text{}$  units, the remaining bonds on the silicon being attached either to another silicon atom or to a halogen atom, in such manner that the average ratio of halogen to silicon in the polysilane is in the range of from 0.3:1 to 1:1, and the polysilane having a melt viscosity at  $150^\circ\text{C}$  of from .005—500 Pa . s and an intrinsic viscosity in toluene of from 0.0001 to 0.1; and

115 (B) heating the shape in an inert atmosphere or in a vacuum to an elevated temperature until the polysilane is converted to silicon carbide.

2. A method as claimed in Claim 1 wherein the halogen is chlorine.
3. A method according to Claim 1 substantially as herein described with reference to any of the specific examples.

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