
(12) **UK Patent Application** (19) **GB** (11) **2 024 789** **A**

(21) Application No **7917110**
(22) Date of filing **16 May 1979**
(23) Claims filed **16 May 1979**
(30) Priority data
(31) **910247**
24137U
(32) **30 May 1978**
26 Mar 1979
(33) **United States of America**
(US)
(43) Application published
16 Jan 1980
(51) **INT CL³**
C01B 31/36
(52) Domestic classification
C1A 512 514 517 E2K1
PB5
(56) Documents cited
None
(58) Field of search
C1A
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(54) **An improved method for
preparing silicon carbide**

(57) A desired shape is formed from a polysilane having the average formula $\{(\text{CH}_3)_2\text{Si}\}_x\{\text{CH}_3\text{Si}\}_y$ and the shape is heated in an inert atmosphere or under vacuum to 1150 - 1600°C until the polysilane is converted to silicon carbide. The polysilane contains from 0 to 60 mole percent of $(\text{CH}_3)_2\text{Si} =$ units and from 40 to 100 mole percent of $\text{CH}_3\text{Si} \equiv$ units. The remaining bonds on silicon are attached to another silicon atom or to a chlorine or bromine atom, such that the polysilane contains from 10 to 43 weight percent of hydrolyzable chlorine or from 21 to 63 weight percent of hydrolyzable bromine.

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SPECIFICATION

An improved method for preparing silicon carbide

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

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

10 For example, silicon carbide is known to have chemical inertness, semiconducting properties, extreme hardness, abrasiveness in the powdered form and it is stable to extremely high temperatures.

15 It therefore finds many uses such as in high temperature electrical heating units, furnace walls, mufflers, abrasives, rocket nozzles, automotive engine parts and turbine parts.

20 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 give fibres.

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

40 Late in 1974, and early in 1975, several new approaches to the manufacture of silicon carbide were reported. Wolfgang Verbeek in U.S. Patent No. 3,853,567 reported that he could form a shaped article, such as a fibre, consisting of a mixture of silicon carbide and a silicon nitride by pyrolyzing a silazane at about 200° to 800°C to form a fusible carbosilazane resin and then forming a fibre and heating the fibre in an inert atmosphere to about 800 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 by 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 devolatilizing, is a yellow to red-brown, transparent, brittle, hydrolysis-insensitive product.

55 Other investigators, Seishi Yajima and his associates at the Japanese Research Institute for Iron, Steel and other Metals, Tohoku University, have been working in the field of silicon carbide preparation.

60 They have reported their work quite extensively and, for the purpose of this discussion, the subject matter of their work will be condensed by relying on their summary disclosure in Chemistry Letters, pp.

65 551-554, 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 No. 2,651,140, German OLS No. 2,618,150, French Patent No. 2,308,590, Japanese Application No. 76/21365, German OLS No. 70 2,628,342, Japanese Patent Publication No. 77/74000, Japanese Patent Publication No. 77/73108 and U.S. Patent No. 4,052,430 issued October 4, 1977.

75 The first synthesis disclosed by Yajima and co-workers was the use of metallic lithium to dechlorinate dimethyldichlorosilane 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 80 1000-2000. The polycarbosilane in benzene or xylene is then spun into fibres by dry spinning.

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

90 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 of the use of a mixture of silane and metallic sodium in a flask, which mixture was covered by a stream of argon gas. The starting material dimethyldichlorosilane 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*-hexane solution, filtered again and 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.

115 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 pyrolyzed to a ceramic material, but, apart from two brief exam-

ples, the disclosure does not teach those skilled in the art the specific ways and means to the ceramic material. Rice essentially teaches that one can take a silicon-containing polymer and heat it to high temperatures and produce 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 forth. Throughout the disclosure, Rice speculates on what may happen and his statement are filled with auxiliaries such as would, should and could. It can be said, therefore, that Rice fails to set forth with particularity what one skilled in the art needs to know to carry out the methods of the present invention.

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.

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

The invention provides a method of preparing silicon carbide which comprises (A) forming a desired shape from a polysilane having the average formula



in which polysilane there is from 0 to 60 mole percent of $(CH_3)_2Si=$ units and from 40 to 100 mole percent of $CH_3Si\equiv$ units, wherein the remaining bonds on silicon 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 from 21-63 weight percent, based on the weight of the polysilane, of hydrolyzable bromine, wherein the polysilane preferably has a melt viscosity at 150°C of from .005-500 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 in the range of from 1150°C to 1600°C until the polysilane is converted to silicon carbide.

The amount of chlorine or bromine in the polysilane can also be defined in terms of the ratio of halogen atoms to silicon atoms. Thus, a ratio of 0.10:1 to 1:1 is essentially equivalent to 10 to 43 weight percent of chlorine or 21 to 63 weight percent of bromine in the polysilane. Either representation of the amount of halogen is satisfactory.

The polysilane preferably contains a filler, e.g. powdered silicon carbide, before step (B) is carried out.

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

In that patent, there is disclosed the use of quaternary halides as catalysts for cleaving

organohalogenpolysilanes to obtain low molecular weight monosilanes. At column 2, lines 51 to line 70, the 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 as long as the starting material contains the disilane, $(CH_3)_xZ_{3-x}SiSiZ_{3-y}(CH_3)_y$, where Z is chlorine or bromine, X is 0, 1, 2 or 3 and y is 0, 1, 2 or 3 and the sum of $x + y$ is equal to at least 1 and generally between 2 and 4 as set forth in the aforementioned 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, cf. Eaborn, "Organosilicon Compounds", Butterworths Scientific Publications, 1960, page 1. The disilane, $CH_3Cl_2SiSi(CH_3)_2Cl$ 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.* patent. 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 present invention. One difference between the method disclosed in the Gilbert *et al.* patent and the present invention is the fact that the reaction of the present invention is not forced, as is shown in the Gilbert *et al.* patent, that is, the reaction is carried out until a handleable polysilane is obtained, while in the Gilbert *et al.* 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 $(CH_3)_2Si=$ and $CH_3Si\equiv$ units. The remaining valences on these silane units are satisfied by another silicon atom or a halogen atom. Thus, contemplated within the scope of this invention are polysilanes having an average of 0.1 or more halogens per silicon atom. For example, other units can be (where Hal is halogen), $(Hal)_2Si=$, $CH_3HalSi=$, $CH_3(Hal)_2Si-$, $(CH_3)_2HalSi-$, $(Hal)_3Si-$ or $(CH_3)_3Si-$, provided the halogen to silicon ratio of 0.1:1 to 1:1 is maintained. Materials having the required halogen to silicon ratio generally have melt viscosities in the range of from .005 to 500 Pa.s.

Halogen, for the purposes of this invention, is

chlorine or bromine, and preferably chlorine. The other halogens, i.e. iodine and fluorine, undergo undesirable side reactions and are difficult to handle so they are not useful in this invention. It is preferred, for the purposes of this invention, that all the halogen groups in the disilane are the same halogen but it is also within the scope of this invention to have both chlorine and bromine groups on the disilane.

10 The polysilane useful in this invention is not easily analyzed 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, generally have an intrinsic
15 viscosity in toluene in the range of from 0.0001 to 0.1. It is conceivable that higher and lower materials could be useful but, for the purposes of this invention, the above range is preferred.

The catalyst 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.

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 can range from 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 when the disilane and catalyst are mixed. Generally, this can be done by
35 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 atmosphere, the use of nitrogen can serve a dual purpose. It is within the scope of this invention
40 to utilize vacuum rather than an inert gas.

Other significant aspects are the low 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
45 out at 70° to 300°C for 4 to 24 hours. Higher or lower temperatures may be used 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
50 temperatures are a waste of energy and often lead to undesirable side products such as carbosilanes and to loss of control of the reaction.

After the polysilane is prepared, it can be utilized as a melt to spin fibres and form shapes. It should be
55 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 fibres.

The polymer melt, i.e. the pre-silicon carbide polymer in whatever form is desired, is then pyrolyzed 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, generally for 0.1 to 4 hours.

65 In summary, 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 mixture is heated and the volatile silanes are formed and are
70 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. This material, as a melt, can be formed at
75 this point and then pyrolyzed 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
80 stirred with a paddle stirrer. The silanes can be removed through the use of simple distillation 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 $(Cl_2CH_3Si)_2$

A 250 millilitre, 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
90 nitrogen was started. Tetrabutylphosphonium chloride, 2.5 grams, was added to the flask and was subjected to dry nitrogen for 1 hour, a vacuum was drawn on the flask and then nitrogen flow was started with a rate of one bubble of nitrogen/15 sec-
100 ond.

50 grams of the $(Cl_2CH_3Si)_2$ were added to the flask via a syringe. The mixture was heated to reflux and it had a slight aqua coloured tint. It appeared to precipitate slightly and the pot temperature rose to
105 90°C, 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.
110 The residue in the flask was very viscous and fibres 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 colour.

Example 2

115 The apparatus was essentially the same as in Example 1 and to the flask was added 2.5 grams of $(Butyl)_4P$ and 66.7 grams of $(CH_3SiCl_2)_2$. The flask and contents had previously been dried and treated with nitrogen as in Example 1. The mixture was
120 clear. After stirring at room temperature for about 16 hours, the temperature rose to about 70°C and all the while the mixture became more viscous. The mixture at this point was slightly cloudy and had some lumpiness. The temperature went up to 94°C and
125 remained at 90-98°C for most of an additional 8 hour period. The mixture turned a clear, pale yellow colour and had a very high viscosity. Fibres were pulled from the melt before cooling down. The material was soluble in toluene and also in acetone but not in
130 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
5 Lower boilers	0.9
Higher boilers	1.1
(CH ₃) ₂ SiCl ₂	2.7
(CH ₃) ₄ Si ₂ Cl ₂	4.9
(CH ₃) ₃ Si ₂ Cl ₃	40.3
10 (CH ₃) ₂ Si ₂ 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°C and it refluxed between 70°-80°C during the removal of the low boilers and the (CH₃)₂SiCl₂ and CH₃SiCl₃. The solution initially had a bluish or aqua coloured tint and the colour disappeared while the mixture turned slightly cloudy. After about 5 hours heating, the solution has 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 fibres.

The material was analyzed with the following results:

	Calculated %	Found
Si-Si	33.3	33.4
-SiCH ₂ Si-	0	0

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

The data is consistent with a polymer of the structure $\{(\text{CH}_3)_2\text{Si}\} \{ \text{CH}_3\text{ClSi} \}$ where the mole percent of (CH₃)₂Si= is 28 and the ratio of chlorine to silicon is 0.72:1. The percent hydrolyzable chlorine was found to be about 38 weight percent. The intrinsic viscosity in toluene at 25°C was 2×10^{-2} . Polymer fibres were taken from the melt and heated in a TGA in an argon atmosphere at 5°C/min. to 1200°C. As indicated above, it lost 53% of its weight. X-ray powder analysis revealed the residue to be extremely fine grain β-SiC (~70Å). Numerous other runs were made and fired in the TGA, producing the same results. About 0.5 gms 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 β-SiC.

Example 4

In a manner similar to Example 3, an apparatus was set up and a nitrogen flow was started after 0.5 gms. of (Butyl)₄PCl 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 millilitres. After 10 minutes, distillate was seen to collect in the receiving flask. The flask temperature was about 105°C. at this time. The DPR was slowly added over the next three hours and the temperature rose to 150°C. During the course of the next five hours the temperature remained the same and the distillate

temperature never exceeded 65°C. The reaction was shut down but the nitrogen flow was maintained. After setting overnight (approximately 16 hours), the flask was heated again to 250°C-270°C. After eight hours of collecting distillate at less than 80°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°C.

When cooled, a portion of the material was chipped from the flask and it was soluble in toluene.

Example 5

654.5 gms of DPR and 7.7 gms of (C₄H₉)₄P+Cl⁻ were placed in a round-bottomed flask which was fitted with a thermometer, condensers, heating apparatus and a distillation apparatus and slowly heated. Silanes were distilled over up to a temperature of 340°C. The residue upon analysis had 11.0 weight percent of hydrolyzable chlorine. The chlorine ion was titrated in a non-aqueous solution of toluene and isopropanol using a 0.1% solution of tetrabromophenolphthalein ethyl ester in methanol/toluene solution and 0.5N KOH in ethanol. The higher the temperature is raised, the more halide is removed from the polysilane. Removal of too much halide results in a non-handleable material. In this example, the appearance of solids indicated that the polysilane was on the verge of crosslinking to an unhandleable material at 340°C or approximately 10 to 11.0 weight percent of chlorine.

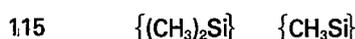
Additional runs were made at temperatures of 300°C and 325°C. A summary of all the runs can be found below.

100	T°C	Avg % Cl from two titrations
	300	12.0
	325	11.9
	340	11.0

Additional heating to give approximately 10 weight percent of chlorine gives a polysilane with a significant amount of solid material in it.

CLAIMS

1. A method of preparing silicon carbide which comprises
(A) forming a desired shape from a polysilane having the average formula



in which polysilane there is from 0 to 60 mole percent of (CH₃)₂Si= units and from 40 to 100 mole percent of CH₃Si≡ units, wherein the remaining bonds on silicon 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 from 21-63 weight percent, based on the weight of the polysilane, of hydrolyzable bromine, and
(B) heating the shape in an inert atmosphere or in a vacuum to an elevated temperature in the range of from 1150°C to 1600°C until the polysilane is converted to silicon carbide.

2. A method as claimed in Claim 1, wherein the polysilane has a melt viscosity at 150°C of from 0.005 to 500 Pa.s.
3. A method as claimed in claim 1 or 2, wherein the polysilane has an intrinsic viscosity in toluene of from 0.001 to 0.1.
4. A method as claimed in any one of claims 1 to 3, wherein the polysilane contains a filler before step (B) is carried out.
5. A method as claimed in claim 4, wherein the filler is powdered silicon carbide.
6. A method as claimed in Claim 1, substantially as hereinbefore described with reference to any of the Examples.
7. Silicon carbide when prepared by a method as claimed in any one of claims 1 to 6.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd.,
Berwick-upon-Tweed, 1979.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.