

Production of solar-grade silicon from silicon dioxide

The invention relates to an overall process for preparing pure silicon which is suitable as solar silicon, comprising the reduction of a purified silicon oxide with one or more pure carbon sources, wherein the purified silicon oxide which has been purified as silicon oxide essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other polyvalent metals, or else metal oxides, of less than or equal to 300 ppm, preferably less than 100 ppm, more preferably less than 50 ppm, according to the invention less than 10 ppm, of the other metals, is advantageously obtained by gel formation under alkaline conditions. The invention further relates to a formulation comprising an activator, and to the use of purified silicon oxide together with an activator for preparing silicon.

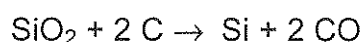
The proportion of photovoltaic cells in global power production has been rising continuously for some years. In order to be able to extend the market share further, it is vital that the production costs of photovoltaic cells are lowered and the efficiency thereof is enhanced.

A significant cost factor in the production of photovoltaic cells is the cost of the high-purity silicon (solar silicon). This is prepared on the industrial scale typically by the Siemens process which was developed more than 50 years ago. In this process, silicon is first reacted with gaseous hydrogen chloride at 300–350°C in a fluidized bed reactor to give trichlorosilane (silicochloroform). After complicated distillation steps, the trichlorosilane is thermally decomposed again at 1000–1200°C over heated ultrapure silicon rods in the presence of hydrogen in a reverse of the above reaction. The elemental silicon grows onto the rods and the hydrogen chloride released is recycled into the circuit. The by-product obtained is silicon tetrachloride, which is either converted to trichlorosilane and recycled into the process or is combusted in an oxygen flame to give fumed silica.

A chlorine-free alternative to the above process is that of the decomposition of monosilane, which can likewise be obtained from the elements and decomposes again

by a purification step over heated surfaces or as it is passed through fluidized bed reactors. Examples thereof can be found in WO 2005/118474 A1.

Another known way of preparing silicon is to reduce silicon dioxide in the presence of carbon according to the following reaction equation (Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 23, pages 721-748, 5th edition, 1993 VCH Weinheim).



In order that this reaction can proceed, very high temperatures are required, preferably above 1700°C, which are attained, for example, in light arc furnaces. In spite of the high temperatures, this reaction begins very slowly and even thereafter proceeds at a slow rate. Owing to the associated long reaction times, the process is energy-intensive and costly.

When the silicon is to be used for solar applications, the silicon prepared must satisfy particularly high demands on its purity. In the field of use specified, even contaminations of the starting compounds in the mg/kg (ppm range), µg/kg (ppb to ppt range), are disruptive.

Owing to their electronic properties, elements of groups III and V of the Periodic Table are particularly disruptive, and so the limits of a contamination in the silicon are particularly low for these elements. For pentavalent phosphorus and arsenic, for example, the doping of the silicon prepared that they cause, as an n-type semiconductor, is problematic. Trivalent boron likewise leads to undesired doping of the silicon prepared, such that a p-type semiconductor is obtained. For example, there is solar grade silicon (Si_{sg}), which has a purity of 99.999% (5 9s) or 99.9999% (6 9s). The silicon suitable for producing semiconductors (electronic grade silicon, Si_{eg}) requires an even higher purity. For these reasons, even the metallurgical silicon from the reaction of silicon oxide with carbon should satisfy high purity demands in order to minimize subsequent complex purification steps by virtue of entrained halogenated compounds, such as boron trichloride, in the halosilanes for preparing silicon (Si_{sg} or Si_{eg}). Particular

difficulties are caused by contamination with boron-containing compounds, because boron in the silicon melt and in the solid phase has a partition coefficient of 0.8 and is therefore virtually impossible to remove from silicon by zone melting (DE 2 546 957 A1).

5 Generally known from the prior art are processes for preparing silicon from silicon oxide. For instance, DE 29 45 141 C2 describes the reduction of porous glass bodies composed of SiO_2 in a light arc. The carbon particles required for reduction may be intercalated into the porous glass bodies. The silicon obtained by means of the process disclosed is suitable, at a boron content of less than 1 ppm, for producing
10 semiconductor components. DE 33 10 828 A1 takes the route via the decomposition of halogenated silanes over solid aluminum. Although this allows the establishment of a low boron content, the content of aluminum in the silicon obtained is increased and the energy demand of the process is considerable owing to the need for electrolytic recycling of the aluminum chloride formed.

15 DE 30 13 319 discloses a process for preparing silicon of a specific purity, proceeding from silicon dioxide and a carbon-containing reducing agent, such as carbon black, with specification of the maximum boron and phosphorus content. The carbon-containing reducing agent was used in the form of tablets with a high-purity binder, such as starch.

20 WO 2007/106860 A1 discloses a process for preparing silicon, in which sodium silicate is passed in the aqueous phase over ion exchangers to remove boron, in order to obtain boron-free purified sodium silicate in the aqueous phase. Subsequently, silicon dioxide is precipitated out of the purified aqueous phase. This process has the disadvantage
25 that primarily only boron and phosphorus impurities are eliminated from the waterglass. This is because, in order to obtain solar silicon in sufficient purity, it is more particularly necessary also to remove metallic impurities. For this purpose, WO 2007/106860 A1 proposes using further ion exchange columns in the process. However, this leads to a very complicated and expensive process with low space-time yield.

30 In order to provide silicon for production in a quality suitable for solar cells, it is generally necessary to use silicon dioxide with purity of at least 99.99% by weight. The

concentration of impurities, such as boron, phosphorus, should not exceed 1 ppm. Although it is possible to use natural resources, such as high-quality quartz, as the silicon dioxide starting material with high purity, the natural limits thereon cause them to be available for industrial mass production only to a limited degree. In addition,
5 procurement is too expensive from economic aspects. A common factor in the above-described processes is that they are very complicated and/or energy-intensive, and so there is a high demand for less expensive and more effective processes for preparing solar silicon.

10 There is thus a need to prepare high-purity silicon dioxide from readily available, cheap silicates. There are known processes in which a flux is added to a silicon-containing material, such as silicon dioxide sand or feldspar, and the mixture is melted. A fibrous silicate glass is drawn from the melt and leached with an acid to form pulverulent porous silicon dioxide (SiO_2) (DE 31 23 009). To prepare high-purity silicon dioxide by leaching,
15 the glass material is restricted to one which can be leached readily, and aluminum oxide and alkaline earth metal salts have to be added additionally to the silicon dioxide as glass components. A serious disadvantage is the subsequent need to remove the metals with the exception of the silicon dioxide.

20 There is also a known process in which a silicon dioxide gel is obtained by reacting an alkali metal silicate (which is generally referred to as waterglass or soluble silicate) with an acid (cf., for example, J.G. Vail, "Soluble Silicates" (ACS monograph series), Reinhold, New York, 1952, Vol. 2, p. 549). This silica gel generally leads to SiO_2 with a purity of about 99.5% by weight; in each case, the content of impurities, such as boron,
25 phosphorus, iron and/or aluminum, is much too high for use of this silicon dioxide to prepare solar silicon.

It was an object of the invention to provide an overall process for preparing solar silicon which is economically viable on the industrial scale and can be performed
30 advantageously using customary, unrepurified silicates or silicon dioxides as starting materials; and to prepare purified silicon dioxide. Further objects are evident from the overall context of the description.

It has been found that, surprisingly, an economically viable process for preparing pure silicon which is suitable as solar silicon or is suitable for preparing solar silicon can be provided by reducing purified silicon dioxide with one or more pure carbon sources, the
5 purified silicon dioxide having been purified as silicon dioxide essentially dissolved in the aqueous phase and, based on the silicon oxide, having a content of other polyvalent metals of less than 300 ppm, preferably less than 100 ppm, more preferably of less than 50 ppm, most preferably of less than 10 ppm. A silicon carbide was preferably added to the reduction to silicon, especially in the amounts defined below.

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The object is achieved by the overall process for preparing pure silicon defined in the description which follows, the examples, drawings and claims, and by the process component steps described in detail therein.

15 The invention therefore provides a process for preparing pure silicon, comprising the reduction of purified silicon oxide which has been purified as silicon oxide essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other polyvalent metals of preferably of less than 100 ppm, more preferably of less than 50 ppm and most preferably of less than 10 ppm, with one or more pure carbon
20 sources.

A further embodiment comprises the above-described process wherein the aqueous purification of the silicon oxide comprises at least one process step in which the aqueous silicon oxide solution is contacted with an ion exchanger. In a preferred
25 embodiment, the aqueous silicon oxide solution is contacted at least by means of an anion and/or cation exchanger.

The present invention further provides a process wherein the purified silicon oxide is obtained from the silicon oxide solution, which has been purified as silicon dioxide
30 essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other polyvalent metals preferably of less than 100 ppm, more preferably of less than 50 ppm and most preferably of less than 10 ppm, by means of gel formation or

spray drying or by concentrating the silicon oxide solution to a concentration greater than or equal to 10% by weight of SiO_2 with subsequent contacting with an acidifying agent. In a variant of this embodiment, the purified silicon oxide is prepared or obtainable by gel formation, more particularly with addition of ammonia and optional
5 subsequent calcination at temperatures up to 1500°C , especially around 1400°C .

The invention likewise provides a process for preparing pure silicon, comprising the reduction of purified silicon oxide which has been purified as silicon oxide essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other
10 metals, especially in the form of polyvalent metal oxides, of less than 300 ppm, preferably less than 100 ppm, more preferably of less than 50 ppm, most preferably of less than 10 ppm, in relation to the metal, with one or more pure carbon sources, the silicon oxide dissolved in the aqueous phase, especially silicate such as alkali metal silicate with a content of from 2 to 6% by weight of silicon dioxide, being passed over a
15 strongly acidic cation exchanger and being obtained with a pH of from 0 to 4, and the purified silicon oxide being obtained by gel formation and/or spray-drying. For all process steps, preference is given to working under an inert gas atmosphere in order to minimize additional contamination. Preference is given to performing the process or component steps thereof under an argon atmosphere. When the gel is formed by
20 adding ammonia, preference is given to a downstream calcination step.

The present invention provides the processes defined in the above-described embodiments, which are performed in such a way that solar silicon or silicon suitable for production of solar silicon is obtained.
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The present invention further provides a process according to the embodiments defined above, in which the reduction of the purified silicon oxide, especially of the purified silicon dioxide, is carried out with one or more pure carbon sources and with addition of silicon carbide which as an activator and/or carbon source.
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The present invention additionally provides formulations comprising silicon carbide as an activator, preferably a binder, and purified silicon oxide and/or at least one pure

carbon source, and also a process for preparing pure silicon wherein the formulation is added separately in the reduction step.

5 The invention also provides a process which comprises at least one step in which a carbohydrate is pyrolysed in the presence of silicon oxide, preferably high-purity silicon dioxide, as a defoamer, and in this way at least some of the carbon required as a carbon source is obtained. Preference is given here to purifying the carbohydrate, more preferably an aqueous solution of a carbohydrate, before the pyrolysis by contacting with at least one ion exchanger. Likewise preferably, the carbohydrate, preferably an
10 aqueous solution of a carbohydrate, and the silicon oxide, preferably the high-purity silicon oxide, is subjected to a shaping process before the pyrolysis, such that the corresponding moldings, for example briquettes, are pyrolyzed.

Definitions

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Pure or purified or high-purity silicon is understood to mean silicon having a contamination profile as follows:

- 20 a. aluminum less than or equal to 5 ppm or in the range from 5 ppm to 0.0001 ppt, especially in the range from 3 ppm to 0.0001 ppt, preferably in the range from 0.8 ppm to 0.0001 ppt, more preferably in the range from 0.6 ppm to 0.0001 ppt, even better in the range from 0.1 ppm to 0.0001 ppt, most preferably in the range from 0.01 ppm to 0.0001 ppt, even greater preference being given to from 1 ppb to 0.0001 ppt,
- 25 b. boron from less than 10 ppm to 0.0001 ppt, especially in the range from 5 ppm to 0.0001 ppt, preferably in the range from 3 ppm to 0.0001 ppt or more preferably in the range from 10 ppb to 0.0001 ppt, even more preferably in the range from 1 ppb to 0.0001 ppt,
- 30 c. calcium less than or equal to 2 ppm, preferably in the range from 2 ppm to 0.0001 ppt, especially in the range from 0.3 ppm to 0.0001 ppt, preferably in the range from 0.01 ppm to 0.0001 ppt, more preferably in the range from 1 ppb to 0.0001 ppt,

- d. iron less than or equal to 20 ppm, preferably in the range from 10 ppm to 0.0001 ppt, especially in the range from 0.6 ppm to 0.0001 ppt, preferably in the range from 0.05 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably from 1 ppb to 0.0001 ppt;
- 5 e. nickel less than or equal to 10 ppm, preferably in the range from 5 ppm to 0.0001 ppt, especially in the range from 0.5 ppm to 0.0001 ppt, preferably in the range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt
- f. phosphorus from less than 10 ppm to 0.0001 ppt, preferably in the range from 10
10 5 ppm to 0.0001 ppt, especially from less than 3 ppm to 0.0001 ppt, preferably in the range from 10 ppb to 0.0001 ppt and most preferably in the range from 1 ppb to 0.0001 ppt;
- g. titanium less than or equal to 2 ppm, preferably from less than or equal to 1 ppm to 0.0001 ppt, especially in the range from 0.6 ppm to 0.0001 ppt,
15 preferably in the range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt;
- h. zinc less than or equal to 3 ppm, preferably from less than or equal to 1 ppm to 0.0001 ppt, especially in the range from 0.3 ppm to 0.0001 ppt, preferably in the
20 range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt,

the aim being a purity in the region of limit of detection for each element. The total contamination with the aforementioned elements should be less than 100 ppm by
25 weight, preferably less than 10 ppm by weight, more preferably less than 5 ppm by weight in total in the silicon as the direct process product of the melt.

The resulting pure silicon is more preferably suitable as solar silicon. Appropriately, the reduction may be followed by a controlled solidification of the resulting silicon, especially
30 in order to obtain pure silicon.

Purified or high-purity silicon oxide, especially silicon dioxide, is characterized in that its content of:

- 5 a. aluminum is less than or equal to 5 ppm or in the range from 5 ppm to 0.0001 ppt, especially in the range from 3 ppm to 0.0001 ppt, preferably in the range from 0.8 ppm to 0.0001 ppt, more preferably in the range from 0.6 ppm to 0.0001 ppt, even better in the range from 0.1 ppm to 0.0001 ppt, most preferably in the range from 0.01 ppm to 0.0001 ppt, even greater preference being given to from 1 ppb to 0.0001 ppt,
- 10 b. boron is from less than 10 ppm to 0.0001 ppt, especially in the range from 5 ppm to 0.0001 ppt, preferably in the range from 3 ppm to 0.0001 ppt or more preferably in the range from 10 ppb to 0.0001 ppt, even more preferably in the range from 1 ppb to 0.0001 ppt,
- 15 c. calcium is less than or equal to 2 ppm, preferably in the range from 2 ppm to 0.0001 ppt, especially in the range from 0.3 ppm to 0.0001 ppt, preferably in the range from 0.01 ppm to 0.0001 ppt, more preferably in the range from 1 ppb to 0.0001 ppt,
- 20 d. iron is less than or equal to 20 ppm, preferably in the range from 10 ppm to 0.0001 ppt, especially in the range from 0.6 ppm to 0.0001 ppt, preferably in the range from 0.05 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably from 1 ppb to 0.0001 ppt;
- 25 e. nickel is less than or equal to 10 ppm, preferably in the range from 5 ppm to 0.0001 ppt, especially in the range from 0.5 ppm to 0.0001 ppt, preferably in the range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt
- f. phosphorus is from less than 10 ppm to 0.0001 ppt, preferably in the range from 5 ppm to 0.0001 ppt, especially from less than 3 ppm to 0.0001 ppt, preferably in the range from 10 ppb to 0.0001 ppt and most preferably in the range from 1 ppb to 0.0001 ppt;
- 30 g. titanium is less than or equal to 2 ppm, preferably from less than or equal to 1 ppm to 0.0001 ppt, especially in the range from 0.6 ppm to 0.0001 ppt, preferably in the

range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt;

h. zinc is less than or equal to 3 ppm, preferably from less than or equal to 1 ppm to 0.0001 ppt, especially in the range from 0.3 ppm to 0.0001 ppt, preferably in the range from 0.1 ppm to 0.0001 ppt, more preferably in the range from 0.01 ppm to 0.0001 ppt, and most preferably in the range from 1 ppb to 0.0001 ppt,

and in that the sum of the abovementioned impurities plus sodium and potassium is less than 5 ppm, preferably less than 4 ppm, more preferably less than 3 ppm, even more preferably from 0.5 to 3 ppm and especially preferably from 1 ppm to 3 ppm, more particularly is less than 10 ppm combined with sodium and potassium.

For each element, the aim may be a purity in the range of the detection limit.

According to the invention, the **active silica** present in the aqueous phase is essentially protonated, i.e. it is essentially free of metallic compounds such as other metal cations.

The **silicon oxide, especially silicon dioxide**, dissolved in the aqueous phase is, in accordance with the invention, an aqueous silicate solution, especially an alkali metal silicate solution.

The aqueous silicate solution is a waterglass and can be purchased commercially, prepared from silicon dioxide and sodium carbonate or, for example, prepared via hydrothermal processes directly from silicon dioxide and sodium hydroxide and water at elevated temperature. The hydrothermal process may be preferred over the soda process because it can lead to cleaner precipitated silicon dioxides. One disadvantage of the hydrothermal process is the limited range of obtainable moduli; for example, the modulus of SiO_2 to N_2O is up to 2, preferred moduli being from 3 to 4; in addition, the waterglasses, after the hydrothermal process, generally have to be concentrated before a precipitation. Generally, a person skilled in the art is aware of the preparation of waterglass as such.

In one alternative, an alkali metal waterglass, especially sodium waterglass, is optionally filtered and, thereafter, concentrated or diluted if necessary. The filtration of the

waterglass or of the aqueous solution of dissolved silicates to remove solid, undissolved constituents can be effected by processes known to those skilled in the art and with apparatus known to those skilled in the art.

- 5 It is obvious that any water used is demineralized; it has preferably been treated several times to remove metallic compounds. Before being contacted with an immobilized compound which complexes boron or boron compounds, the waterglass preferably has a silicon dioxide content of from about 1 to 30% by weight, preferably from 1 to 20% by weight, more preferably from 2 to 10% by weight and most preferably from 2 to 6% by
10 weight.

In the process according to the invention, the **pure carbon source** used is one or more pure carbon sources, optionally in a mixture, an organic compound of natural origin, a carbohydrate, graphite (activated carbon), coke, coal, carbon black, thermal black,
15 pyrolyzed carbohydrate, especially pyrolyzed sugars. The carbon sources, especially in pellet form, can be purified, for example, by treatment with hot hydrochloric acid solution. In addition, an activator can be added to the process according to the invention. The activator may fulfill the purpose of a reaction initiator, reaction accelerant, or else the purpose of the carbon source. An activator is pure silicon carbide, silicon-
20 infiltrated silicon carbide, or else a pure silicon carbide with a carbon and/or silicon oxide matrix, for example silicon carbide containing carbon fibers.

According to the invention, the pure carbon source, optionally containing at least one carbohydrate, or a mixture of carbon sources, has the following contamination profile: boron below 2 [$\mu\text{g/g}$], phosphorus below 0.5 [$\mu\text{g/g}$] and aluminum below 2 [$\mu\text{g/g}$],
25 preferably less than or equal to 1 [$\mu\text{g/g}$], especially iron below 60 [$\mu\text{g/g}$], the content of iron preferably being below 10 [$\mu\text{g/g}$], more preferably below 5 [$\mu\text{g/g}$]. Overall, the aim in accordance with the invention is to use a pure carbon source in which the content of impurities, such as boron, phosphorus, aluminum and/or arsenic, is below the technically possible detection limit in each case.

30 The pure or further carbon source optionally comprising at least one carbohydrate, or the mixture of carbon sources, preferably has the following contamination profile of boron, phosphorus and aluminum and possibly of iron, sodium, potassium, nickel and/or

chromium: the contamination with boron (B) is especially in the range from 5 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from 2 to 0.00001 µg/g, according to the invention from below 2 to 0.00001 µg/g. The contamination with phosphorus (P) is especially in the range from 5 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from 1 to 0.00001 µg/g, according to the invention from below 0.5 to 0.00001 µg/g. The contamination with iron (Fe) is in the range from 100 to 0.000001 µg/g, especially in the range from 55 to 0.00001 µg/g, preferably from 2 to 0.00001 µg/g, more preferably from below 1 to 0.00001 µg/g, according to the invention from below 0.5 to 0.00001 µg/g. The contamination with sodium (Na) is especially in the range from 20 to 0.000001 µg/g, preferably from 15 to 0.00001 µg/g, more preferably from 12 to 0.00001 µg/g, according to the invention from below 10 to 0.00001 µg/g. The contamination with potassium (K) is especially in the range from 30 to 0.000001 µg/g, preferably from 25 to 0.00001 µg/g, more preferably from below 20 to 0.00001 µg/g, according to the invention from below 16 to 0.00001 µg/g.

The contamination with aluminum (Al) is especially in the range from 4 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from below 2 to 0.00001 µg/g, according to the invention from below 1.5 to 0.00001 µg/g. The contamination with nickel (Ni) is especially in the range from 4 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from below 2 to 0.00001 µg/g, according to the invention from below 1.5 to 0.00001 µg/g. The contamination with chromium (Cr) is especially in the range from 4 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from below 2 to 0.00001 µg/g, according to the invention from below 1 to 0.00001 µg/g. Preference is given to a minimal contamination with the particular elements, more preferably below 10 ppb or below 1 ppb.

Alternatively, the pure carbon source consists of the activator, i.e. the sole carbon source used in the process according to the invention is the activator. This measure allows the charge composition to be denser, because one molar equivalent of carbon monoxide gas is saved in this process step, the reduction to the silicon. The activator can thus be used in the process in catalytic amounts up to equimolar amounts in relation to the silicon oxide.

According to further alternatives, the activator can be used in a weight ratio of from 1000:1 to 1:1000 relative to the pure carbon source, such as graphite, carbon black, carbohydrate, carbon. Preference is given to using the carbon source in a weight ratio of from 1:100 to 100:1, more preferably from 1:100 to 1:9.

Pure or high-purity silicon carbide is interpreted as a silicon carbide which, as well as silicon carbide, may also comprise carbon and silicon oxide such as Si_yO_z where $y =$ from 1.0 to 20 and $z =$ from 0.1 to 2.0, especially as a carbon matrix and/or SiO_2 matrix or Si_yO_z matrix where $y =$ from 1.0 to 20 and $z =$ from 0.1 to 2.0, and possibly small amounts of silicon. High-purity silicon carbide is preferably interpreted as a corresponding silicon carbide with a passivation layer comprising silicon dioxide. Equally, high-purity silicon carbide is considered to be a high-purity composition which contains silicon carbide, carbon, silicon oxide and possibly small amounts of silicon, or consists thereof, and the high-purity silicon carbide or the high-purity composition especially comprises a contamination profile of boron and phosphorus of below 100 ppm of boron, especially in the range from 10 ppm to 0.001 ppt, and below 200 ppm of phosphorus, especially in the range from 20 ppm to 0.001 ppt of phosphorus; more particularly, it has an overall contamination profile of boron, phosphorus, arsenic, aluminum, iron, sodium, potassium, nickel, chromium of below 100 ppm by weight, preferably of below 10 ppm by weight, more preferably below 5 ppm by weight, in relation to the high-purity overall composition or the high-purity silicon carbide.

The contamination profile of the pure, preferably high-purity silicon carbide with boron, phosphorus, arsenic, aluminum, iron, sodium, potassium, nickel, chromium is, for each element, preferably from below 5 ppm to 0.01 ppt (by weight), and for high-purity silicon carbide especially from below 2.5 ppm to 0.1 ppt. The silicon carbide obtained by the process according to the invention, with or without carbon and/or Si_yO_z matrices, more preferably has a content as follows:
boron below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or

phosphorus below 200 ppm, preferably in the range from 20 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or sodium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 1 ppm to 0.001 ppt and/or

5 aluminum below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 1 ppm to 0.001 ppt and/or iron below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or chromium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more

10 preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or nickel below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or potassium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or

15 sulfur below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 2 ppm to 0.001 ppt and/or barium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 3 ppm to 0.001 ppt and/or zinc below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably

20 from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or zirconium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or titanium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and/or

25 calcium below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably from 5 ppm to 0.001 ppt or from below 0.5 ppm to 0.001 ppt and especially magnesium at below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably in the range from 11 ppm to 0.001 ppt and/or copper below 100 ppm, preferably in the range from 10 ppm to 0.001 ppt, more preferably in the

30 range from 2 ppm to 0.001 ppt, and/or cobalt below 100 ppm, especially in the range from 10 ppm to 0.001 ppt, more preferably in the range from 2 ppm to 0.001 ppt, and/or vanadium below 100 ppm, especially in the range from 10 ppm to 0.001 ppt, preferably

in the range from 2 ppm to 0.001 ppt, and/or manganese below 100 ppm, especially in the range from 10 ppm to 0.001 ppt, preferably in the range from 2 ppm to 0.001 ppt, and/or lead below 100 ppm, especially in the range from 20 ppm to 0.001 ppt, preferably in the range from 10 ppm to 0.001 ppt, more preferably in the range from
5 5 ppm to 0.001 ppt.

A particularly preferred pure to high-purity silicon carbide or a high-purity composition contains or consists of silicon carbide, carbon, silicon oxide and possibly small amounts of silicon, the high-purity silicon carbide or the high-purity composition having especially
10 a contamination profile of boron, phosphorus, arsenic, aluminum, iron, sodium, potassium, nickel, chromium, sulfur, barium, zirconium, zinc, titanium, calcium, magnesium, copper, chromium, cobalt, zinc, vanadium, manganese and/or lead of below 100 ppm for pure silicon carbide, preferably from below 20 ppm to 0.001 ppt for high-purity silicon carbide, more preferably in the range from 10 ppm to 0.001 ppt in
15 relation to the high-purity overall composition or the high-purity silicon carbide.

Description of the overall process

According to the invention, a process for preparing pure silicon, comprising the
20 reduction of purified silicon oxide, preferably silicon dioxide, which has been purified, especially to free it of other metals, as silicon oxide essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other polyvalent metals of less than or equal to 300 ppm, preferably less than 100 ppm, more preferably less than 50 ppm, most preferably less than 10 ppm in relation to the metal, with one or more pure
25 carbon sources.

According to the invention, the purification of the silicon oxide essentially dissolved in the aqueous phase preferably comprises the following steps a), b), c), d) and e):
a) providing silicates dissolved in the aqueous phase, especially an aqueous alkali
30 metal silicate and/or alkaline earth metal silicate solution or a mixture thereof, especially an aqueous phase having a content of from 1 to 30% by weight, preferably from 1 to

20% by weight, more preferably from 2 to 10% by weight and most preferably from 2 to 6% by weight of SiO₂;

optionally adding soluble alkaline earth metal and/or transition metal salts, especially calcium, magnesium and/or transition metal salts, to precipitate phosphorus or

5 phosphorus compounds,

and then optionally filtering the aqueous phase to remove sparingly soluble alkaline earth metal and/or transition metal salts or other sparingly soluble impurities; this may optionally be followed by contacting of the aqueous phase with an immobilized compound which complexes boron or boron compounds. Compounds which complex

10 boron or boron compounds include electron donors, for example amines, which can be used immobilized on a resin in a column, preference being given to N-methylglucamines immobilized on a resin, for example Amberlite® IRA-743-A, and then

b) optionally adjusting the aqueous phase to a content of from 2 to 6% by weight of
15 SiO₂, which additionally comprises other polyvalent metals, especially metal oxides, than silicon dioxide, and

c) contacting with a strongly acidic cation exchange resin, especially of the hydrogen type, in a column, according to the invention with Amberlite® IR-120, in an amount
20 which is sufficient for the ion exchange of essentially all other metal ions in the aqueous phase, the temperature of the aqueous phase being in the range from 0°C to 60°C, preferably in the range from 5 to 50°C,

d) obtaining the aqueous phase of an active silica with an SiO₂ concentration of from 2 to 6% by weight and a pH of from 0 to 4 and, more particularly,

25 e) obtaining purified silicon oxide, especially by means of

a.2) Concentration of the aqueous phase from step d) to a concentration greater than or equal to 10% by weight of SiO₂ by contacting with an acidifying agent.

30 Alternatively, the contacting in step e) can be effected by the addition of an acidifying agent to the silicate solution or else the addition of the concentrated silicate solution to an acidifying agent.

b.2) Performance of a gel formation, optionally followed by a thermal aftertreatment and/or spray drying.

- 5 gel formation, preferably by adding ammonia, or spray-drying, or, according to an alternative, by concentrating the aqueous phase from step d) to a concentration greater than or equal to 10% by weight of SiO₂ by contacting with an acidifying agent. The gel formation can preferably be effected by addition of an amine, more preferably by addition of ammonia.

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c.2) spray drying the aqueous phase or

According to the invention, after performance of the above steps, especially after thermal treatment for drying or calcination, a purified silicon oxide is obtained. The
15 purification of the silicon oxide, especially of the silicate solution, preferably consists of the aforementioned steps.

If the purity is still insufficient, a further treatment may immediately follow step d) according to step d.2). The further treatment according to step d.2) is preferably
20 effected as follows:

d.2) further treatment by, in a first step 1), adding a strong aqueous acid to the aqueous phase composed of active silica from step d), such that the pH is from 0 to 2.0, and keeping the aqueous phase thus obtained at from 0°C to 100°C for from 0.5 to 120
25 hours; by, in a second step 2), contacting the resulting aqueous phase with a strongly acidic cation exchange resin of the hydrogen type, especially as an ion exchange column, preferably Amberlite® IR 120, in an amount which is sufficient for the ion exchange of essentially all other metal ions in the aqueous phase, the temperature of the aqueous phase being in the range from 0 to 60°C, preferably from 5 to 50°C, then,
30 in the third step 3), contacting the aqueous phase with a strongly basic anion exchange resin of the hydroxyl type (Amberlite® 440 OH, or Amberlite(R) IRA 440) in an amount which is sufficient for the ion exchange of essentially all anions in the aqueous phase,

the temperature of the aqueous phase being from 0 to 60°C, especially in the range from 5 to 50°C and more particularly in the interior of the column, then, in the fourth step 4), obtaining the aqueous phase of the resulting active silica, which is essentially free of other dissolved substances than the active silica, and has a concentration of SiO₂ of
5 from 2 to 6% by weight and a pH of from 2 to 5.

In process step d.2) step 1), the strong acid used is an inorganic acid such as hydrochloric acid, nitric acid or sulfuric acid. This addition is effected to eliminate aluminum and iron compounds. The strong acid is added to the active silica-containing
10 aqueous solution, as obtained after step d), before the aqueous phase decomposes. According to the invention, the addition is therefore effected immediately after it is obtained. The amount of strong acid is guided by the fact that the pH of the resulting phase is in the range from 0 to 2, preferably in the range from 0.5 to 1.8. The phase is then aged at from 0 to 120°C for a period of from 0.5 to 120 hours.

15 The particular space velocities in the course of passage or contacting with an ion exchanger are guided entirely by the columns used; in each case, the velocity is adjusted such that essentially all ions have been correspondingly exchanged when the phase leaves the column again.

20 If the active silica obtained in step 4) has the desired purity, it is possible to process it further by steps a.3), b.3) or c.3); more particularly, the aqueous phase obtained in the fourth step 4) in process step d.2) is alternatively treated further by one of the following steps a.3), b.3) or c.3):

25 a.3) concentrating the aqueous phase from the fourth step 4) of process step d.2) to a concentration of SiO₂ greater than or equal to 10% by weight and adding to an acidifying agent or adding an acidifying agent, or concentrating to completion by adding an acidifying agent or adding to an acidifying agent. The acidifying agents are preferably
30 strong acids.

b.3) performing a gel formation, optionally followed by a thermal aftertreatment and/or spray-drying; the gel formation can preferably be effected by adding ammonia or else an amine; a thermal aftertreatment preferably comprises a calcination at about 1400°C, or

5

c.3) spray-drying the aqueous phase.

When the active silica obtained from process step 4) does not have the desired purity, it is treated further as follows:

10

d.3) further treatment in a fifth step 5), by adding an aqueous sodium hydroxide and/or potassium hydroxide phase, especially with a concentration of from 2 to 20% by weight of KOH or NaOH in the aqueous phase, where the purity of the KOH or NaOH used should be greater than 95% by weight, preferably 99.9% by weight, to the aqueous

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phase of the active silica, where the molar ratio of $\text{SiO}_2/\text{M}_2\text{O}$ is from 60 to 200, and M is independently sodium or potassium and originates from the hydroxide added, and the SiO_2 originates from the aqueous phase of the active silica, and the temperature of the resulting aqueous phase is also kept at from 0 to 60°C and a stabilized aqueous phase of an active silica with an SiO_2 concentration of from 2 to 6% by weight and a pH of

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from 7 to 9 is maintained, in a sixth step 6) the stabilized aqueous phase of the active silica is partly or fully added to a vessel as a stock solution and the stock solution is kept at from 70 to 100°C, the vessel can be kept under standard pressure or under reduced pressure, more particularly the water removed is metered in by supplying further stabilized aqueous phase of the active silica from the preceding component step d.3)

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step 5) essentially to the degree in which water is removed, to form a stable aqueous silica sol with an SiO_2 concentration of from 30 to 50% by weight and a particle size of the colloidal silicon dioxide of from 10 to 30 nm; in a seventh step 7), the stable aqueous silica sol is contacted with a strongly acidic cation exchange resin of the hydrogen type, especially Amberlite® IR 120 (acidic cation exchanger with sulfonic acid

30

groups), at from 0 to 60°C in such an amount that essentially all metal ions present in the sol are exchanged, the resulting aqueous phase is subsequently contacted with a strongly basic anion exchanger of the hydroxyl type (Amberlite® 440 OH or Amberlite®

IRA 440) at from 0 to 60°C in such an amount that an aqueous acidic silica sol which is essentially free of other polyvalent metals, especially metal oxides, than silicon oxide is obtained in the eighth step 8) and performing a gel formation.

- 5 The vessel for step 6) is made of an acid-resistant and alkali-resistant material and does not itself contribute to the contamination of the aqueous phases present therein. The vessel is preferably suitable for operation under reduced pressure. In step 6), the stabilized phase is transferred partly or fully to the vessel; when a portion of the phase is transferred into the vessel, this may preferably be from one quarter to one thirtieth of
- 10 the phase which is obtained continuously or batchwise from step 5) and is used as the stock solution. In the case of partial use of the phase from step 5), the remaining portion of the stock solution can be supplied continuously or batchwise. Preference is given to removing water from the stock solution, especially by distillation, and to adding further stabilized aqueous phase from step 5) to the degree to which water is removed from the
- 15 system. The temperature, the distillation of the water and the addition of further stabilized aqueous phase from step 5) are preferably adjusted such that this step can be ended after from 5 to 200 hours. Preference is given to continuously removing water and continuously adding aqueous phase from step 5).
- 20 All cation exchangers used and also the anion exchangers may be customary ion exchangers and may be used in each component step of the process, though different ion exchangers can equally be used in the particular component steps.

For all steps in which gel formation is intended, especially in steps b.2) or b.3) or after

25 step d.3) step 8), the gel formation is preferably initiated or accelerated by adding ammonia or another compound which is free of alkali metal cations, is sufficiently clean and is familiar to those skilled in the art. Further conceivable compounds are organic amines which are soluble in the aqueous phase. According to the invention, the gel formation is effected at a temperature in the range from 0 to 120°C, preferably in the

30 range from 0 to 100°C, and especially at a pH in the range from 0 to 7, preferably in the range from pH 3 to 7.

The sol formation is effected preferably at a pH of from 7 to 10.5, more preferably from 7.5 to 10. In this way, a stable sol can be formed. The formation of a stable sol may be followed by spray-drying with optional subsequent calcination; alternatively, the stable sol can be calcined directly, but the sol is preferably mixed with a pure carbon,
5 especially containing a carbohydrate, and further purified SiO₂ is optionally added in solid form, more particularly formulated together, and pyrolyzed and/or calcined.

More preferably, the purified silicon oxide, especially the purified silicon dioxide, can be obtained in step e) by, before drying the aqueous SiO₂-containing phase, adding a pure
10 carbohydrate to it, especially containing a carbohydrate and/or more preferably an activator, such as silicon carbide. This measure allows the resulting formulation, optionally with addition of a binder, for example of the siloxanes, silanols, alkoxysilanes below, to be shaped and dried or pyrolyzed and/or calcined.

15 More preferably, the gel formation is likewise followed by a thermal aftertreatment, especially a calcination at temperatures in the range from 900 to 2000°C, in which case the calcination may optionally be preceded by spray-drying.

20 The purified silicon oxide, preferably silicon dioxide, can be supplied completely to the reduction step, i.e. converted with at least one carbon source to silicon. Alternatively, however, it is also possible to use portions of the purified silicon oxide in component processes which are likewise inventive as a defoamer in the production of the high-purity carbon. The carbon thus obtained can be used in the reduction step. Details of
25 this optional component process are explained below.

It is likewise possible that portions of the purified silicon oxide are used in component processes which are likewise inventive for preparation of silicon carbide. This silicon carbide can in turn be reacted in the reduction step with high-purity silicon oxide, or
30 added as an activator in the reduction step. Details of this optional component process are explained later in the description.

Preferably, in overall processes for preparing pure silicon, the purified silicon oxide is formulated and converted together with at least one pure carbon source, for example in the reduction step or in one of the optional component processes.

- 5 For example, the still-moist silicon oxide can be formulated, extruded, pelletized, granulated or briqueted together with a pure carbohydrate. This formulation can be dried and sent to a reduction step to prepare pure silicon, or first be used in a preceding process component step with the aid of a pyrolysis to prepare high-purity carbon or, in an alternative process component, be sent to a pyrolysis and/or calcination to prepare
10 pure silicon carbide.

Silicon carbide, especially high-purity silicon carbide, optionally comprising or containing a carbon matrix or else a silicon oxide matrix, and/or optionally infiltrated with silicon, are added to the process according to the invention preferably as an activator, or as an
15 activator and simultaneously as a pure carbon source or only as a pure carbon source.

Silicon carbide can thus be added in accordance with the invention to the process for preparing pure silicon by reducing purified silicon oxide as an activator as defined above, or as pure or high-purity silicon carbide; the silicon carbide may equally also be
20 added as a pure carbon source.

In one alternative variant, the process step of reduction to prepare pure silicon consists of the reaction of the purified silicon oxide, especially of the silicon dioxide, with a pure or high-purity silicon carbide, as defined above or below.
25

In a further alternative variant, the process step of reduction to prepare pure silicon consists of the reaction of the purified silicon oxide, especially of the silicon dioxide, with one or more pure carbon sources with addition of pure or high-purity silicon carbide, as defined above or below, the silicon carbide being added individually or preferably in an
30 inventive formulation. The use of added silicon carbide has the advantage that the reduction proceeds more rapidly, since silicon carbide acts as a reaction initiator, reaction accelerant, and, especially when it is added in relatively large amounts,

significantly reduces the gas loading in the reduction step. The activator is preferably in a weight ratio of 1000:1 to 1:1000 relative to the pure carbon source, the carbon source being calculated without SiC therein, more preferably from 1:100 to 100:1, most preferably from 1:100 to 1:9.

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According to the invention, in the process for preparing pure silicon, comprising the reduction of purified silicon oxide with one or more pure carbon sources, the purified silicon oxide is used together with at least one pure carbon source and preferably with a silicon carbide and optionally silicon, where the silicon carbide may comprise a carbon
10 matrix and/or a silicon oxide matrix, and may be infiltrated with silicon, especially in a formulation, where the formulation alternatively comprises

a) the purified silicon oxide and at least one pure carbon source and optionally silicon carbide and optionally silicon and/or

b) the purified silicon oxide and optionally silicon carbide and optionally silicon and/or

15 c) at least one pure carbon source and optionally silicon carbide and optionally silicon, the particular formulation optionally containing binder and where the pure carbon source may also comprise an activated carbon.

Purified silicon oxide, especially purified silicon dioxide, such as silica, pure carbon, especially activated carbon, and/or silicon carbide may be added to the process a) in
20 pulverulent, particulate and/or piece form and/or b) in a formulation, for example in a porous glass, especially quartz glass, in an extrudate and/or pressing, such as pellet or briquet, optionally together with further additives, especially as binders and/or as a second and further carbon source. Activated carbon is understood to mean a carbon
25 source with graphite fractions or a graphite. The graphite fraction in the carbon source is preferably in the range from 30 to 99% by weight in relation to the carbon source; the graphite fraction is preferably from 40 to 99% by weight, more preferably from 50 to 99% by weight.

30 Processes suitable for shaping the formulation, especially briquetting, such as extrusion, pressing, tableting, pelletization, granulation and further processes known per se, are sufficiently well known to those skilled in the art.

Further additives may be silicon oxides or a second carbon source, especially cleaned rice husks, for example after washing and/or boiling with HCl, or mixtures of further pure carbon sources, such as sugar, graphite, carbon fibers, and/or the binders and the second and further carbon and/or silicon sources may be natural or synthetic resins, such as phenol resin, functional silanes or siloxanes, industrial alkylcelluloses, such as methylcellulose, polyethylene glycols, polyacrylates and polymethacrylates, or mixtures of at least two of the aforementioned compounds. Functional silanes and siloxanes include, for example – but not exclusively: tetraalkoxysilanes, trialkoxysilanes, alkyl silicates, alkylalkoxysilanes, methacryloxyalkylalkoxysilanes, glycidyoxyalkylalkoxysilanes, polyetheralkylalkoxysilanes and corresponding hydrolyzates or condensates, or cocondensates of at least two of the aforementioned compounds, where “alkoxy” represents especially methoxy, ethoxy, propoxy or butoxy and “alkyl” represents a mono- or bivalent alkyl group having from 1 to 18 carbon atoms, such as methyl, ethyl, n-propyl, butyl, isobutyl, pentyl, hexyl, heptyl, n-/i-octyl, etc.; examples thus include tetraethoxysilane, silanol, ethyl silicate, trimethoxysilane, methyltrimethoxysilane, dimethyldiethoxysilane, trimethylpropoxysilane, ethyltrimethoxysilane, methylethyldiethoxysilane, n-propyltriethoxysilane, n-/i-octyltrimethoxysilane, propylsilanol, octylsilanols and corresponding oligomers or condensates, 1-methacryloyloxymethyltrimethoxysilane, 2-methacryloyloxyethyltrimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, 3-methacryloyloxyisobutyltrimethoxysilane, 3-methacryloyloxypropylmethyldialkoxysilane, 3-methacryloyloxypropylsilanol and corresponding oligomers or condensates, 3-glycidyoxypropyltrimethoxysilane, 3-glycidyoxypropylsilanol and corresponding oligomers or condensates or hydrolyzates, cocondensates or else block cocondensates or cocondensates based on at least two from the group of n-propyltriethoxysilane, n-/i-octyltriethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, 3-glycidyoxypropyltrimethoxysilane and 3-polyetherpropyltriethoxysilane.

Said additives may simultaneously fulfill the functions of a silicon or carbon supplier and of a processing assistant, especially in the shaping processes known per se to those skilled in the art, and/or the function of a binder, especially of a binder which is substantially thermally resistant in the range from RT to 300°C. To prepare granules, preference is given to spraying powder with the binder in aqueous or alcoholic solution

and then to supplying it to a shaping process in which the drying can be effected simultaneously; alternatively, the drying can also be effected after the shaping. In order that the process gases formed can flow efficiently through the formulation in the course of reduction to pure silicon, preference is given to shaping high-porosity tablets, pellets
5 or briquets from the formulations.

Preferred binders give rise to essentially dimensionally stable formulations in the temperature range from 150 to 300°C; particularly preferred binders give rise to dimensionally stable formulations in the temperature range from 200 to 300°C. In
10 particular cases, it may also be preferred to prepare formulations which enable essentially dimensionally stable formulations in the temperature range from above 300°C up to 800°C or higher, more preferably up to 1400°C. These formulations can preferably be used in the reduction to pure silicon. The high-temperature binders are based essentially on predominant Si-O-substrate crosslinking, the substrate meaning
15 generally all components condensable with silanol groups or functional groups of the formulation.

A preferred formulation comprises silicon carbide and/or activated carbon, i.e., for example, graphite, or mixtures thereof and a further pure carbon source, for example
20 thermal black, and the thermally stable binders mentioned, especially high-temperature binders.

Generally, all solid reactants, such as silicon dioxide, the pure carbon source and optionally silicon carbide may be used in the process or may be present in the
25 composition in a form which offers the greatest possible surface area for the reaction to proceed. According to the invention, a formulation is added in the form of a briquet.

The purified silicon oxide can be reduced with one or more pure carbon sources and/or the activator in an industrial furnace, such as a light arc furnace, in a thermal reactor, in
30 an induction furnace, rotary tube furnace and/or in a microwave furnace, for example with a fluidized bed and/or rotary tube.

Generally, the reaction can be effected in customary melting furnaces for preparing silicon, such as metallurgical silicon, or other suitable melting furnaces, for example induction furnaces. The design of such melting furnaces, especially preferably electrical furnaces, which use an electrical light arc as the energy source, is sufficiently well known to those skilled in the art. In direct current furnaces, they have a melting electrode and a base electrode or, as alternating current furnaces, typically three melting electrodes. The light arc length is regulated by means of an electrode regulator. The light arc furnaces are based generally on a reaction chamber made of refractory material, in the lower region of which liquid silicon can be tapped or drained off. The raw materials are added in the upper region, in which the graphite electrodes to generate the light arc are also disposed. These furnaces are usually operated at temperatures in the region around 1800°C. The person skilled in the art is additionally aware that the furnace structures themselves must not contribute to contamination of the silicon prepared.

According to the invention, the purified silicon oxide is reduced with one or more pure carbon sources in a reaction chamber lined with high-purity refractory materials and optionally using electrodes which consist of high-purity material, as explained below. Customary electrodes are made of high-purity graphite and are consumed during the reaction, and so they generally have to be repositioned continuously.

The fused or molten silicon obtained in accordance with the invention by the reduction is obtained in the form of molten pure silicon; more particularly, it is suitable as solar silicon or suitable for preparing solar silicon; optionally, it is purified further by zone melting or by controlled solidification, which is known per se to those skilled in the art.

Alternatively or additionally, the silicon can be solidified, comminuted and classified further by means of the different magnetic behavior of the comminuted fragments. More particularly, the fraction enriched with impurities by means of zone melting or controlled solidification can subsequently be used to prepare organosilanes. The process of magnetic classification is known to those skilled in the art. For magnetic classification of silicon from the reaction of purified silicon oxide and one or more pure carbon sources,

the entire disclosure content of WO 03/018207 is incorporated into the subject matter of the present application, with the modification that the silicon supplied to the magnetic separation originates from the reaction of purified silicon oxide and at least one pure carbon source. The invention provides a corresponding magnetic separation of the pure silicon prepared in accordance with the invention or of silicon purified further by zone melting of the pure silicon.

The particular process steps which are optional for the overall process for preparing pure silicon and are preferably effected in combination will be explained in more detail hereinafter, each of which makes a crucial synergistic contribution to the economic viability of the overall process.

Detailed description of component steps of the preparation of the purified SiO₂

In step a.2) of the process described in general terms above, an aqueous phase with a content of from 2 to 35% by weight of SiO₂ is preferably added to an acidifying agent for the precipitation, in order to form an acidic precipitation suspension.

In a first preferred variant, the precipitation suspension into which the silicon oxide dissolved in the aqueous phase is added dropwise always has to be acidic. In this variant, an aqueous phase with a content of from 2 to 35% by weight, preferably from 15 to 35% by weight and more preferably from 20 to 30% by weight of SiO₂ is used.

In a second preferred variant, the aqueous active silica must, immediately after contact with the cation exchanger, be added dropwise to an acidic initial charge. In this variant, an aqueous phase with a content of from 2 to 6% by weight or from 7 to 17% by weight of SiO₂ is used. "Acidic" is understood to mean a pH below 6.5, especially below 5.0, preferably below 3.5, more preferably below 2.5, and according to the invention from below 2.0 to below 0.5. The aim is generally that the pH does not vary locally too much, in order to obtain reproducible precipitation suspensions. Both the mean pH and the particular local pH should therefore exhibit only a variation of plus/minus 0.5, preferably of plus/minus 0.2.

According to the invention, the pH during the precipitation in the precipitation suspension at the addition site, preferably in the middle of the precipitation suspension, is less than 2, preferably less than 1.5, more preferably less than 1, most preferably less than 0.5. The pH of the precipitation suspension can be kept constant at these pH values by adding the acidifying agent, moving the precipitation suspension, such as stirring, or by other measures. One means is that of continuously irrigating a fluid, continuously descending film of an acidifying agent on an inclined surface with the aqueous phase of the silicon oxide, or alkali metal waterglass, or by means of injecting the aqueous phase into the acidifying agent.

It will be clear to those skilled in the art that the dilute or undiluted acidifying agents or mixtures of acidifying agents used must not entrain any impurities into the process which do not remain dissolved in the aqueous phase of the precipitation suspension. In each case, the acidifying agents must not have any impurities that would precipitate with the silicon oxide in the course of acidic precipitation, unless they can be kept in the precipitation suspension by means of added complexing agents or washed out with the later washing media.

The inventive acidic precipitation of active silicas in the aqueous phase in an acidifying agent to form a precipitation suspension, i.e. a precipitation in an acidic precipitation suspension, is followed by the removal of the purified silicon oxide, especially of the purified silicon dioxide, optionally followed by washing of the silicon oxide with an aqueous, especially acidic medium, and optional washing to neutrality of the isolated, purified silicon oxide. Washing to neutrality can be effected with high-purity demineralized water. The removal can be effected by customary measures sufficiently well known to those skilled in the art, such as filtration, decanting, centrifugation, sedimentation, with the proviso that these measures do not worsen the degree of contamination of acid-precipitated, purified silicon oxide again.

Preferred acidifying agents are strong mineral acids such as hydrochloric acid, phosphoric acid, nitric acid and/or sulfuric acid. According to the invention, high-purity is high-purity acids are used.

- 5 Washing media may preferably be aqueous solutions of organic water-soluble acids, such as formic acid, acetic acid, fumaric acid, oxalic acid, or other organic acids which are known to those skilled in the art and do not themselves contribute to the contamination of the silicon oxide purified if they cannot be removed completely with high-purity water. Generally, preference is therefore given to all organic, water-soluble
10 acids, especially consisting of the elements C, H and O, both from acidifying agents and in the washing medium, because they do not themselves contribute to contamination of the subsequent reduction step.

- Inventive washing media are aqueous solutions of the acidifying agents, preferred acids
15 being organic acids such as formic acid and/or acetic acid. The washing medium may, if required, also comprise a mixture of water and organic solvents. Appropriate solvents are high-purity alcohols, such as methanol, ethanol; a possible esterification does not disrupt the subsequent reduction to silicon.

- 20 To stabilize acid-soluble metal complexes, a metal complexing agent, such as EDTA or else a peroxide, can be added to the precipitation suspension or else to a washing medium for colored marking, as an "indicator" of undesired metal contamination. For example, hydroperoxide can be added to the precipitation suspension or to the washing medium in order to indicate titanium impurities present by means of color. Marking is
25 generally also possible with other organic complexing agents which do not in turn have a disruptive effect in the subsequent reduction process. These are generally all complexing agents based on the elements C, H and O.

- The purified silicon oxide obtained by acidic precipitation can, if necessary, be
30 concentrated further and/or else be subjected to a thermal aftertreatment. Equally, the still-moist or aqueous, purified silicon oxide, possibly still as a sol, can be mixed with a pure carbon source.

The step of concentration of the aqueous phase which is effected in step a.2) can be effected by adding the aqueous phase from step d) to an acidifying agent or by adding an acidifying agent. According to the invention, the acidic aqueous phase which comes
5 from the cation exchanger in step d) must be transferred directly into the acidifying agent or be contacted with the acidifying agent, especially without being concentrated beforehand.

An essential process feature is the control of the pH of the silicon dioxide and of the
10 reactor media in which the silicon dioxide is present during the different process steps. The inventive precipitation of purified silicon oxide from silicon oxide dissolved in the aqueous phase, especially silicon oxide dissolved fully, is carried out in an acidifying agent. According to the invention, the acidifying agent is an aqueous solution with a pH below 2; after addition of the silicon dioxide dissolved in the aqueous phase, it is also
15 referred to as the precipitation suspension.

At a very low pH, the surface is even positively charged, and so metal cations are repelled by the silica surface. When these metal ions are then washed out, provided that the pH is very low, they can be prevented from accumulating on the surface of the
20 inventive silicon dioxide. When the silica surface assumes a positive charge, this additionally prevents silica particles from accumulating on one another, thus forming cavities in which impurities could be intercalated.

Accordingly, the precipitation is more preferably carried out as early as in step a.2),
25 especially in step a.3), preferably immediately after the discharge, i.e. the recovery of the aqueous phase of an active silica in step d). The precipitation may comprise the following steps:

- I. preparing an initial charge composed of an acidifying agent having a pH of less
30 than 2, preferably less than 1.5, more preferably less than 1, most preferably less than 0.5,
- II. providing the aqueous phase from step d)

III. adding the aqueous phase from step d) comprising the aqueous silica to the initial charge from step II. in such a way that the pH of the resulting precipitation suspension always remains at a value of less than 2, preferably less than 1.5, more preferably less than 1 and most preferably less than 0.5

5 IV. removing and washing the resulting silicon dioxide, the washing medium having a pH of less than 2, preferably less than 1.5, more preferably less than 1 and most preferably less than 0.5

V. drying the resulting silicon dioxide. The invention also provides purified silica obtainable by this process.

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In step I., an initial charge composed of an acidifying agent or an acidifying agent and water is prepared in the precipitation vessel. The water is preferably distilled or demineralized water.

15 The acidifying agent may be the acidifying agent which is also used in step IV. to wash the filtercake. The acidifying agent may be hydrochloric acid, phosphoric acid, nitric acid, sulfuric acid, chlorosulfonic acid, sulfuryl chloride or perchloric acid, in concentrated or dilute form, or mixtures of the aforementioned acids. In particular, it is possible to use hydrochloric acid, preferably from 2 to 14 N, more preferably from 2 to 12 N, even more preferably from 2 to 10 N, especially preferably from 2 to 7 N and very
20 especially preferably from 3 to 6 N, phosphoric acid, preferably from 2 to 59 N, more preferably from 2 to 50 N, even more preferably from 3 to 40 N, especially preferably from 3 to 30 N and very especially preferably from 4 to 20 N, nitric acid, preferably from 1 to 24 N, more preferably from 1 to 20 N, even more preferably from 1 to 15 N,
25 especially preferably from 2 to 10 N, sulfuric acid, preferably from 1 to 37 N, more preferably from 1 to 30 N, even more preferably from 2 to 20 N, especially preferably from 2 to 10 N. Very particular preference is given to using concentrated sulfuric acid.

In a preferred variant of the precipitation process according to the invention, a peroxide
30 is added to the initial charge in step I. as well as the acidifying agent, which causes a yellow/brown color with titanium(IV) ions under acidic conditions. The peroxide is more preferably hydrogen peroxide or potassium peroxodisulfate. The yellow/brown color of

the reaction solution allows the degree of purification during the wash step d to be appreciated very clearly.

- 5 This is because it has been found that specifically titanium is a very persistent impurity which accumulates readily on the silicon dioxide even at pH values above 2. The inventors have found that, when the yellow color disappears in stage IV., the desired purity of the purified silicon oxide, especially of the silicon dioxide, has generally been attained, and the silicon dioxide, from this time, can be washed with distilled or demineralized water until a neutral pH of the silicon dioxide has been attained. In order
10 to achieve this indicator function of the peroxide, it is also possible to add the peroxide not in step I., but in step II. to the active silica, or in step III. as a third stream. In principle, it is also possible to add the peroxide only after step III. and before step IV. or during step IV.
- 15 All aforementioned variants and mixed forms thereof are subjects of the present inventions. Preference is given, however, to the variants in which the peroxide is added in step I. or II., since it can fulfill a further function in this case as well as the indicator function. Without being bound to a particular theory, the inventors are of the view that some – especially carbon-containing – impurities are oxidized by reaction with the
20 peroxide and removed from the reaction solution. Other impurities are converted by oxidation to a better soluble form which can thus be washed out. The precipitation process according to the invention thus has the advantage that no calcination step need be carried out, although this is of course possible as an option.
- 25 In step III. of the precipitation process according to the invention, the aqueous phase of the active silica from step d) is added directly to the initial charge and the silicon dioxide is thus precipitated. It should be ensured that the acidifying agent is always present in excess. The silicate solution is therefore added in such a way that the pH of the reaction solution is always less than 2, preferably less than 1.5, more preferably less than 1,
30 even more preferably less than 0.5 and especially preferably from 0.01 to 0.5. If necessary, further acidifying agent can be added. The temperature of the reaction

solution is kept at from 20 to 95°C, preferably from 30 to 90°C, more preferably from 40 to 80°C, by heating or cooling the precipitation vessel during the addition of the active.

The inventors have found that particularly readily filterable precipitates are obtained when the aqueous active silica enters the initial charge and/or precipitation suspension in droplet form. In a preferred embodiment of the invention, it is therefore ensured that the active silica enters the initial charge and/or precipitation suspension in droplet form. This can be achieved, for example, by introducing the silica into the initial charge by dropwise addition. The equipment may be metering equipment which is mounted outside the initial charge/precipitation suspension and/or is immersed in the initial charge/precipitation suspension.

Alternatively, the solution can be agitated very slowly, e.g. stirred or circulated by pump, in order that the pH at the dropwise addition site does not rise above pH 2, preferably not above 1.5, more preferably not above 1.0, most preferably not above 0.5. Preference is given to moving the vessel or the metering unit above the initial charge/precipitation suspension in order to be able to maintain the pH as described above and simultaneously to distribute the incoming active silica only to a minor degree as it enters the initial charge/precipitation suspension. This results in rapid gelation at the outer shell of the incoming active silica before impurities can be incorporated in the interior of the particles. Optimal selection of the flow rate of the initial charge/precipitation suspension or movement of the vessel or of the metering unit thus allows the purity of the resulting product to be improved.

Combination of optimized movement or flow rate with a very substantially droplet-shaped introduction of the active silica allows this effect to be enhanced once more, such that one embodiment of the process according to the invention in which the active silica is introduced in droplet form into an initial charge/precipitation suspension at a flow rate, measured in an area of the surface of the reaction solution up to 10 cm below the reaction surface, of from 0.001 to 10 m/s, preferably from 0.005 to 8 m/s, more preferably from 0.01 to 5 m/s, very particularly from 0.01 to 4 m/s, especially preferably from 0.01 to 2 m/s and very especially from 0.01 to 1 m/s. The metering unit is

preferably moved relative to the fixed vessel or the vessel relative to the metering unit at from 0.0001 to 10 m/s. Preference is given to moving the metering unit, because only this ensures constant movement with time.

5 Without being bound to a particular theory, the inventors are of the view that the acidic conditions in the initial charge/reaction solution together with the dropwise addition of the aqueous active silica lead to the droplet of silica starting to gelate/precipitate at its surface immediately on contact with the acid.

10 The inventive purified silicon oxides, especially silicon dioxides, are characterized in that their impurity profile corresponds to that defined further above under "Definitions", where the sum of the impurities plus sodium and potassium is less than 5 ppm, preferably less than 4 ppm, more preferably less than 3 ppm, even more preferably from 0.5 to 3 ppm and especially preferably from 1 ppm to 3 ppm.

15 The silicon oxide prepared in accordance with the invention can be pressed by processes known to those skilled in the art to granules or briquets. When the particles are ground, i.e. they are present in conventional particulate form, they may preferably have a mean particle size d_{50} of from 1 to 100 μm , more preferably from 3 to 30 μm and
20 most preferably from 5 to 15 μm . The particles are preferably present in a mean particle size d_{50} of from 0.1 to 10 mm, more preferably from 0.3 to 9 mm and most preferably from 2 to 8 mm.

The high-purity silicon dioxide thus obtained can be dried and processed further. The
25 drying can be effected by means of all processes known to those skilled in the art, for example belt driers, tray driers, drum driers, etc., as mentioned at the outset.

If necessary, the resulting silicon oxide can be subjected to a thermal aftertreatment, especially to a calcination, preferably at temperatures in the range from 900 to 2000°C,
30 more preferably around 1400°C, in order to remove nitrogen-, sulfur-containing impurities.

The purified silicon oxide, especially the purified silicon dioxide, obtainable in accordance with the invention by gel formation or precipitation after step a.2) or a.3), preferably after a.2), and especially subsequent calcination at temperatures up to 1400°C, has a content of the elements aluminum, boron, calcium, iron, nickel,
5 phosphorus, titanium and/or zinc, in each case individually or in combination, as has been and is defined above.

As described above, the silicon oxide essentially dissolved in the aqueous phase can be prepared in different ways. At this point, another specific variant of the overall process is
10 disclosed, in which silicon oxide essentially dissolved in the aqueous phase is contaminated, i.e. in which contaminated silicon oxide is first dissolved and then purified in accordance with the invention to thus obtain high-purity silicon oxide.

The invention thus provides, in this process variant, for the use of at least one silicon
15 oxide containing impurities for preparing silicon, especially suitable as solar silicon or suitable for preparing solar silicon, preferably pure silicon as defined above, in a process comprising the following steps:

- a) converting the silicon oxide containing impurities to a silicate dissolved in the
20 aqueous phase,
- b) purifying the silicate dissolved in the aqueous phase by contacting with a strongly acidic cation exchange resin, especially of the hydrogen type; further steps according to at least one of Claims 2 to 8 can advantageously be carried out,
- c) obtaining a precipitate of purified silicon oxide and
- 25 d) converting the silicon oxide thus obtained to silicon in the presence of one or more carbon sources and optionally by addition of an activator.

More particularly, step b) is effected according to the above remarks regarding the purification of an essentially dissolved silicon oxide, especially according to at least one
30 of the steps according to claims 2 to 8, preferably by the processes I. to V. detailed above.

A silicon oxide containing impurities is considered to be a silicon oxide with a boron, phosphorus, aluminum, iron, titanium, sodium and/or potassium content of greater than 1000 ppm by weight, especially greater than 100 ppm by weight; a silicon oxide is preferably still considered to be contaminated silicon oxide when the total content of the
5 above impurities is above 10 ppm by weight.

A silicon oxide containing impurities is also considered to be a silicon dioxide having a content of the following elements, in each case individually or in any combinations of parts or else all of:

- 10
- a. aluminum more than 6 ppm, especially more than 5.5 ppm, preferably also more than 3.5 ppm, more preferably also more than 0.85 ppm, and/or
 - b. boron more than 10 ppm, preferably also more than 5.5 ppm, more preferably more than 3.5 ppb, even more preferably more than 15 ppb, and/or
 - 15 c. calcium more than 2 ppm, especially also more than 0.35 ppm, more preferably more than 0.015 ppm, and/or
 - d. iron more than 23 ppm, especially more than 15 ppm, preferably more than 0.65 ppm, and/or
 - e. nickel more than 15 ppm, especially more than 5.5 ppm, especially more than
20 0.055 ppm, and/or
 - f. phosphorus more than 15 ppm, especially more than 5.5 ppm, more preferably more than 0.1 ppm, or else more than 15 ppb, and/or
 - g. titanium more than 2.5 ppm, especially more than 1.5 ppm, and/or
 - h. zinc more than 3.5 ppm, especially more than 1.5 ppm, more preferably more than
25 0.35 ppm,

and the sum of the abovementioned impurities plus sodium and potassium is especially greater than 10 ppm, especially also more than 5 ppm, preferably more than 4 ppm, more preferably more than 3 ppm, most preferably more than 1 ppm or else more than
30 0.5 ppm.

Even in the case of a boron content of less than 0.5 ppm, especially also less than 0.1 ppm, and/or a phosphorus content of more than 1 ppm or else more than 0.5 ppm, a silicon oxide is considered to be a silicon oxide containing impurities when only the content of at least one element selected from the group of aluminum, calcium, iron,
5 nickel, titanium, zinc exceeds the limit specified above.

The purified silicon oxides, especially high-purity silicon dioxides, are, in accordance with the invention, processed further to give pure to high-purity silicon for the solar industry. According to the invention, the purified silicon oxides, especially high-purity
10 silicon dioxides, are reacted with a pure carbon source, such as a high-purity carbon, silicon carbide and/or pure sugars.

More particularly, the silicon oxide purified by all the processes described in detail above, preferably the high-purity silicon dioxide, can be used as a starting material in
15 the overall process according to the invention. In this case, it can be used for further conversion to high-purity silicon, i.e. the reduction step, but it can also be used in one process variant as a high-purity defoamer in the preparation of high-purity carbon. This process variant is described below. Finally, the silicon oxide purified by all the processes described in detail above can also be used for preparation of silicon carbide,
20 which is described below.

Preparation of the carbon source by sugar pyrolysis using silicon oxide as a defoamer

25 In addition to the other carbon sources mentioned in this description, preferably the natural carbon sources listed therein, it is also possible to obtain carbon from carbohydrates. To prepare the high-purity carbon, in this preferred variant (component process) of the overall process according to the invention for preparing pure silicon, a carbon source should preferably be used, especially a pure carbon source, in which the
30 carbon is obtained by industrial pyrolysis of at least one carbohydrate or of a carbohydrate mixture, especially of a crystalline sugar, at elevated temperature with addition of silicon oxide.

It has been found that, surprisingly, addition of silicon oxide, preferably SiO_2 , especially precipitated silica and/or fumed silica, allows the foam formation effect to be suppressed.

5

It is also possible to operate this industrial process for pyrolysis of carbohydrates in a simple and economically viable manner without disruptive foam formation. Furthermore, in the performance of the process, no caramel formation is observed either.

Furthermore, it was advantageously possible in a preferred embodiment, since it is particularly energy-saving (low-temperature method), to lower the pyrolysis temperature from, for example, 1600°C to about 700°C . The process is advantageously operated above a temperature of 400°C , preferably in the range from 800 to 1600°C , more preferably in the range from 900 to 1500°C , especially at from 1000 to 1400°C , advantageously to obtain a graphite-containing pyrolysis product.

15

When a graphite-containing pyrolysis product is preferred, the desired pyrolysis temperatures are from 1300 to 1500°C . The pyrolysis is advantageously performed under protective gas and/or reduced pressure (vacuum). For example at a pressure of from 1 mbar to 1 bar (ambient pressure), especially from 1 to 10 mbar. The feedstocks need not be dried, especially in the case of pyrolysis with a microwave. The reactants may have residual moisture. Appropriately, the pyrolysis apparatus used is dried before the start of pyrolysis and is purged to virtually free it of oxygen by purging with an inert gas, such as nitrogen or Ar or He. Preference is given to working with argon or helium. The pyrolysis time is generally in the range from 1 minute to 48 hours, preferably in the range from 1/4 hour and 18 hours, especially in the range from. hour to 12 hours at said pyrolysis temperature; the heating time until the desired pyrolysis temperature is attained may simultaneously be within the same order of magnitude, especially in the range from 1/4 hour to 8 hours.

The process is generally performed batchwise; but it can likewise be effected continuously.

A resulting carbon-based pyrolysis product contains carbon, especially with graphite fractions and silica and optionally fractions of other carbon forms, such as coke, and is particularly low in impurities, for example boron, phosphorus, arsenic and aluminum compounds. For instance, the pyrolysis product can advantageously be used as a
5 reducing agent in the overall process according to the invention. In particular, the graphite-containing pyrolysis product, owing to its conductivity properties, can be used in a light arc reactor.

The present invention therefore provides a process for technical, i.e. industrial, pyrolysis
10 of a carbohydrate or carbohydrate mixture at elevated temperature with addition of silicon oxide, especially purified silicon oxide.

The carbohydrate components used in the pyrolysis are preferably monosaccharides, i.e. aldoses or ketoses, such as trioses, tetroses, pentoses, hexoses, heptoses,
15 particularly glucose and fructose, but also oligo- and polysaccharides based on said monomers, such as lactose, maltose, sucrose, raffinose – to name just a few or the derivatives thereof – up to and including starch, including amylose and amylopectin, the glycogens, the glycosans and fructosans – to mention just a few polysaccharides. However, it is also possible to use all carbohydrates/sugars described in detail below for
20 the preparation of SiC in the purities stated there.

Optionally, the aforementioned carbohydrates can be purified additionally by a treatment using an ion exchanger, in which case the carbohydrate is dissolved in a suitable solvent, advantageously water, conducted through a column filled with an ion
25 exchange resin, preferably an ionic or cationic resin, the resulting solution is concentrated, for example by removing solvent fractions by heating – especially under reduced pressure – and the carbohydrate thus purified is advantageously obtained in crystalline form, for example by cooling the solution and then removing the crystalline fractions, by means of methods including filtration or centrifuging. However, it is also
30 possible to use a mixture of at least two of the aforementioned carbohydrates as the carbohydrate or carbohydrate component in the pyrolysis.

Particular preference is given to using a crystalline sugar available in economically viable amounts, a sugar, as can be obtained in a manner known per se, for example, by crystallization of a solution or a juice from sugarcane or beets, i.e. conventional crystalline sugar, for example refined sugar, preferably crystalline sugar with the substance-specific melting point/softening range and a mean particle size of from 1 μm to 10 μm , more preferably from 10 μm to 1 cm , especially from 100 μm to 0.5 cm . The particle size can be determined, for example – but not exclusively – by means of screen analysis, TEM, SEM or light microscopy. It is also possible to use a carbohydrate in dissolved form, for example – but not exclusively – in aqueous solution, in which case the solvent admittedly evaporates more or less rapidly before attainment of the actual pyrolysis temperature.

The silicon oxide component used in the pyrolysis is preferably SiO_x where x = from 0.5 to 1.5, SiO , SiO_2 , silicon oxide (hydrate), aqueous or water-containing SiO_2 , in the form of fumed or precipitated silica, moist, dry or calcined, for example Aerosil® or Sipernat®, or a silica sol or gel, porous or dense silica glass, quartz sand, quartz glass fibers, for example light guide fibers, quartz glass beads, or mixtures of at least two of the aforementioned components. Preference is given to using, in the pyrolysis, silica with an internal surface area of from 0.1 to 600 m^2/g , more preferably from 10 to 500 m^2/g , especially from 100 to 200 m^2/g . The inner or specific surface area can be determined, for example, by the BET method (DIN ISO 9277). Preference is given to using silica with a mean particle size of from 10 nm to 5 mm , especially from 1 to 500 μm . Here too, the particle size can be determined, inter alia, by means of TEM (transmission electron microscopy), SEM (scanning electron microscopy) or light microscopy. Very particular preference is given to using a silicon oxide obtained by the above-described process component.

According to the invention, the purified silicon oxide, especially high-purity silicon oxide, as defined above is used in the pyrolysis. The silica used in the pyrolysis advantageously has a high (99%) to ultrahigh (99.9999%) purity, and the content of impurities, such as boron, phosphorus, arsenic and aluminum compounds, should in total advantageously be ≤ 10 ppm by weight, especially ≤ 1 ppm by weight, preferably

from ≤ 0.5 ppm by weight to 0.0001 ppb by weight. According to the invention, the purified silicon oxide, i.e. especially the silicon dioxide obtained by gel formation or precipitation in a.2) or a.3) and especially a thermal aftertreatment, for example a calcination, is used. The determination of

5

Thus, in the pyrolysis, carbohydrate defoamer, i.e. silicon oxide component, calculated as SiO_2 , can be used in a weight ratio of from 1000:0.1 to 0.1:1000. The weight ratio of carbohydrate component to silicon oxide component can preferably be adjusted to from 100:1 to 1:100, more preferably to from 50:1 to 1:50, most preferably to

10

The apparatus used for the performance of the pyrolysis may, for example, be an induction-heated vacuum reactor, in which case the reactor can be designed in stainless steel, and covered or lined with a suitable inert substance with regard to the reaction, for example with high-purity SiC , Si_3N_3 , high-purity quartz or silica glass, high-purity carbon or graphite.

15

However, it is also possible to use other suitable reaction vessels, for example an induction furnace with a vacuum chamber to accommodate an appropriate reaction crucible or bath.

20

In general, the pyrolysis is performed as follows:

the reactor interior and the reaction vessel are suitably dried and purged with an inert gas which may be heated, for example, to a temperature in the range from room temperature to 300°C . Subsequently, the carbohydrate or carbohydrate mixture to be pyrolyzed, in addition to the silicon oxide as the defoamer component, is introduced into the reaction chamber or the reaction vessel of the pyrolysis apparatus. The feedstocks may be intimately mixed beforehand, degassed under reduced pressure and transferred into the prepared reactor under protective gas. This reactor may already be slightly

25

30

reaction mixture. Especially through the addition of silicon oxide, it is advantageous to very substantially prevent foam formation in the reaction mixture.

After the pyrolysis reaction has ended, the pyrolysis product can be thermally
5 aftertreated for a certain time, advantageously at a temperature in the range from 1000 to 1500°C. In general, a pyrolysis product or a composition which comprises pure to high-purity carbon is thus obtained. According to the invention, the pyrolysis product is preferably used as a reducing agent for the preparation of solar silicon in the overall process.

10 To this end, the pyrolysis product can be converted to a defined form with addition of further components, especially convert to a defined form with addition of SiO₂ purified in accordance with the invention, activators such as SiC, binders such as organosilanes, organosiloxanes, carbohydrates, silica gel, natural or synthetic resins, and high-purity
15 processing assistants, such as pressing, tableting or extrusion assistants, such as graphite, for example by granulation, pelletizing, tableting, extrusion – to name just a few examples.

The present invention thus also provides a composition or the pyrolysis product as
20 obtained after the pyrolysis.

The present invention therefore likewise provides a pyrolysis product with a content of carbon relative to silicon oxide (calculated as silicon dioxide) of from 400:0.1 to 0.4:1000, especially from 400:0.4 to 4:10, preferably from 400:2 to 4:1.3, more
25 preferably from 400:4 to 40:7.

More particularly, the direct pyrolysis product is notable for its high purity and usability for the preparation of polycrystalline silicon, especially of solar silicon for photovoltaic systems, but also for medical applications. Such a composition (also known as
30 pyrolyzate or pyrolysis product for short) may, in accordance with the invention, be used feedstock in the preparation of solar silicon by reduction of SiO₂, especially by reduction of the purified silicon oxide, at high temperature, especially in a light arc furnace.

According to the invention, the direct process product is used to react purified silicon oxide with a pure carbon source in the process according to the invention. Another alternative is to use the direct process product in a simple and economically viable manner as a carbon-containing reducing agent in a process of the documents cited, as disclosed, for example, by US 4,247,528, US 4,460,556, US 4,294,811 and WO 2007/106860.

The present invention also provides for the use of a composition (pyrolysis product) as a feedstock in the preparation of solar silicon by reduction of SiO_2 , especially by reduction of the purified silicon oxide, at high temperature, especially in a light arc furnace.

Preparation of high-purity SiC from SiO_2 and use thereof in the process according to the invention

A further inventive aspect of the overall process for preparing pure silicon comprises the use of silicon carbide as an activator and/or as a pure carbon source, in which case the silicon carbide must be a pure silicon carbide.

The preparation of silicon carbide, especially for use in the process according to the invention for preparing pure silicon, will first be explained hereinafter, and then a process in which the silicon carbide is used as an activator, reaction initiator, reaction accelerant or else as a pure carbon source in the preparation of silicon.

Generally, the silicon carbide can be purchased and/or may be silicon carbide to be recycled or waste product, provided that it meets the purity demands for this process. The pure silicon carbide can likewise be obtained by reacting silicon oxide and a carbon source comprising at least one carbohydrate at elevated temperature and be used in the process according to the invention, e.g. as the material for producing electrodes or the high-purity refractory materials for lining the reactor, especially of the first layer of the reaction chamber or of the reactor. This aspect will be explained in detail elsewhere. The carbon source used which comprises at least one carbohydrate, especially pure carbon source, is preferably crystalline sugar.

In this aspect of the invention, a process is disclosed for preparing pure to high-purity silicon carbide and/or silicon carbide-graphite particles by reaction of silicon oxide, especially purified silicon oxide, and a carbon source comprising a carbohydrate, especially carbohydrates, at elevated temperature, more particularly an industrial process for preparing silicon carbide or for preparing compositions comprising silicon carbide, and the isolation of the reaction products. This aspect of the invention further relates to a pure to high-purity silicon carbide, to compositions comprising it, to use as a catalyst and to use in the production of electrodes or as a material of electrodes and other articles.

According to the aspect of the invention, one task was to prepare pure to high-purity silicon carbide from significantly less expensive raw materials, and to overcome the process disadvantages to date in the known processes, which deposit hydrolysis-sensitive and self-igniting gases to give silicon carbide.

It has been found that, surprisingly, by reacting mixtures of silicon dioxide, especially of silicon oxide purified in accordance with the invention, and sugar with subsequent pyrolysis and/or high-temperature calcination, depending on the mixing ratio, it is possible to inexpensively prepare high-purity silicon carbide in a carbon matrix and/or silicon carbide in a silicon dioxide matrix and/or a silicon carbide comprising carbon dioxide and/or silicon dioxide in a composition. Preference is given to preparing the silicon carbide in a carbon matrix. In particular, it is possible to obtain silicon carbide particles with an outer carbon matrix, preferably with a graphite matrix on the inner and/or outer surface of the particles.

Thereafter, the silicon carbide can be obtained in a simple manner by passive oxidation with air in pure form, especially by oxidatively removing the carbon. Alternatively, the silicon carbide can be purified further and/or deposited by sublimation at high temperatures and optionally under high vacuum. Silicon carbide can be sublimed at temperatures around 2800°C.

Silicon carbide can be obtained in pure form by aftertreating the silicon carbide in a carbon matrix by passive oxidation with oxygen, air and/or $\text{NO}_x \cdot \text{H}_2\text{O}$, for example at temperatures around 800°C . In this oxidation process, carbon or the carbon-containing matrix can be oxidized and removed from the system as process gas, for example as carbon monoxide. The purified silicon carbide may then comprise one or more silicon oxide matrices or possibly small amounts of silicon.

The silicon carbide itself is relatively oxidation-resistant to oxygen at temperatures above 800°C . In direct contact with oxygen, it forms a passivating layer of silicon dioxide (SiO_2 , "passive oxidation"). At temperatures above about 1600°C with a simultaneous deficiency of oxygen (partial pressure below approx. 50 mbar), the glasslike SiO_2 does not form, but rather the gaseous SiO ; there is then no longer any protective effect, and the SiC is combusted rapidly ("active oxidation"). This active oxidation proceeds when the free oxygen in the system has been used up.

A carbon-based reaction product obtained in accordance with the invention or a reaction product with a carbon matrix, especially a pyrolysis product, contains carbon, especially in the form of coke and/or carbon black, and silica, and also optional fractions of other carbon forms, such as graphite, and is particularly low in impurities, for example the elements boron, phosphorus, arsenic, iron and aluminum, and compounds thereof.

The pyrolysis and/or calcination product can preferably be used as a reducing agent in the preparation of silicon carbide from sugar coke and silica at high temperature. In particular, the inventive carbon- or graphite-containing pyrolysis and/or calcination product is used for the production of electrode material owing to its conductivity properties, for example in a light arc reactor, or as a catalyst, and according to the invention as a raw material for the preparation of pure silicon, especially for solar silicon preparation. The silicon carbide obtainable can also be used for the production of the refractory high-purity materials for the lining of the reactors, of a reaction chamber or for the lining of other installations, inlets or outlets.

The high-purity silicon carbide can likewise be used as an energy source and/or as an additive for producing high-purity steels.

The present invention therefore provides a process for preparing pure to high-purity
5 silicon carbide by reacting silicon oxide, especially purified silicon oxide according to the
above definition, especially purified silicon dioxide, and a carbon source comprising at
least one carbohydrate, especially a pure carbon source, at elevated temperature, and
more particularly the isolation of the silicon carbide. The invention also provides a
silicon carbide or a composition comprising silicon carbide obtainable by this process,
10 and also the pyrolysis and/or calcination product obtainable by the process according to
the invention, and more particularly the isolation thereof.

According to the invention, the process is an industrial process, preferably an industrial
scale process, for industrial reaction or industrial pyrolysis and/or calcination of a pure
15 carbohydrate or carbohydrate mixture at elevated temperature with addition of silicon
oxide, especially purified silicon dioxide, and the material conversion thereof. In a
particularly preferred process variant, the industrial process for preparing high-purity
silicon carbide consists of the reaction of pure carbohydrates, optionally of carbohydrate
mixtures, with silicon oxide, especially purified silicon dioxide, and silicon oxide formed
20 in situ, at elevated temperature, especially in the range from 400 to 3000°C, preferably
at from 1400 to 1800°C, more preferably in the range from about 1450 to below about
1600°C.

According to the invention, a pure to high-purity silicon carbide is optionally isolated with
25 a carbon matrix and/or silicon oxide matrix or a matrix comprising carbon and/or silicon
oxide; more particularly, it is isolated as the product, possibly with a content of silicon.
The isolated silicon carbide may have any crystalline phase, for example an α - or β -
silicon carbide phase, or mixtures of these or further silicon carbide phases. Generally,
a total or more than 150 polytype phases of silicon carbide are known. The pure to high-
30 purity silicon carbide obtained by the process preferably comprises only a small amount,
if any, of silicon or is infiltrated with silicon only to a minor degree, especially in the
range from 0.001 to 60% by weight, preferably in the range from 0.01 to 50% by weight,

more preferably in the range from 0.1 to 20% by weight, in relation to the silicon carbide comprising the matrices mentioned and optionally silicon. According to the invention, generally no silicon forms in the calcination or high-temperature reaction, because there is no agglomeration of the particles and generally no formation of a melt. Silicon would
5 form only with formation of a melt. The further content of silicon can be controlled by infiltration with silicon.

Pure or high-purity silicon carbide is interpreted as defined at the start of this description under "Definitions".

10 The pure to high-purity silicon carbides or high-purity compositions can be obtained by using the reaction participants, the carbohydrate-containing carbon source and the silicon oxide used, and also the reactors, reactor components, feedlines, storage containers of the reactants, the reactor lining, jacket, and any reaction gases or inert
15 gases added, with a purity needed for this purpose in the process according to the invention.

The pure to high-purity silicon carbide or the high-purity composition as defined above, especially comprising a content of carbon, for example in the form of coke, carbon
20 black, graphite; and/or silicon oxide, especially in the form of SiO_2 , or preferably in the form of reaction products of the purified silicon oxide, has a contamination profile with boron and/or phosphorus or with boron- and/or phosphorus-containing compounds which is preferably below 100 ppm for the element boron, especially in the range from 10 ppm to 0.001 ppt, and below 200 ppm for phosphorus, especially in the range from
25 20 ppm to 0.001 ppt. The content of boron in a silicon carbide is preferably in the range from 7 ppm to 1 ppt, preferably in the range from 6 ppm to 1 ppt, more preferably in the range from 5 ppm to 1 ppt or lower, or, for example, in the range from 0.001 ppm to 0.001 ppt, preferably in the region of the analytical detection limit. The content of phosphorus in a silicon carbide should preferably be in the range from 18 ppm to 1 ppt,
30 preferably in the range from 15 ppm to 1 ppt, more preferably in the range from 10 ppm to 1 ppt or lower. The content of phosphorus is preferably in the region of the analytical detection limit. The units ppm, ppb and/or ppt should be understood throughout as

proportions of the weights, especially in mg/kg, µg/kg, ng/kg or in mg/g, µg/g or ng/g, etc.

The carbon sources comprising at least one carbohydrate used in the process according to the invention, especially a pure carbon source, are, in accordance with the invention, carbohydrates or saccharides, or mixtures of carbohydrates or suitable derivatives of the carbohydrates. It is possible to use the naturally occurring carbohydrates, anomers thereof, invert sugars, or else synthetic carbohydrates. It is equally possible to use carbohydrates which have been obtained by biotechnology means, for example by fermentation. The carbohydrate or derivative is preferably selected from a monosaccharide, disaccharide, oligosaccharide or polysaccharide, or a mixture of at least two of the saccharides mentioned. The following carbohydrates are more preferably used in the process: monosaccharides, i.e. aldoses or ketoses, such as trioses, tetroses, pentoses, hexoses, heptoses, particularly glucose and fructose, but also corresponding oligo- and polysaccharides based on said monomers, such as lactose, maltose, sucrose, raffinose, to name just a few; it is equally possible to use derivatives of the carbohydrates mentioned provided that they have the purity requirements specified – up to and including cellulose, cellulose derivatives, starch, include amylose and amylopectin, glycogen, the glycosans and fructosans – to name just a few polysaccharides. However, it is also possible to use a mixture of at least two of the aforementioned carbohydrates as the carbohydrate or carbohydrate component in the process according to the invention.

Generally, it is possible to use all carbohydrates, derivatives of the carbohydrates and carbohydrate mixtures in the process according to the invention, which preferably have a sufficient purity, especially with regard to the elements boron, phosphorus and/or aluminum. Overall, the elements mentioned should be present as an impurity in the carbohydrate or the mixture in a total of below 100 µg/g, especially from below 100 µg/g to 0.001 µg/g, preferably from below 10 µg/g to 0.001 µg/g, more preferably from below 5 µg/g to 0.01 µg/g. The carbohydrates for use in accordance with the invention consist of the elements carbon, hydrogen, oxygen, and may have the contamination profile specified.

Appropriately, it is also possible to use carbohydrates consisting of the elements carbon, hydrogen, oxygen and nitrogen, possibly with the aforementioned contamination profile, in the process, if a doped silicon carbide or a silicon carbide with proportions of silicon nitride is to be prepared. To prepare silicon carbide with proportions of silicon nitride, the silicon nitride not being considered as an impurity in this case, chitin can appropriately also be used in the process.

Further carbohydrates obtainable on the industrial scale are lactose, hydroxypropylmethylcellulose (HPMC) and further customary tableting assistants which can optionally be utilized to formulate the silicon oxide with customary crystalline sugars.

More preferably, in the process according to the invention, a crystalline sugar available in economic amounts is, a sugar as can be obtained, for example, by crystallization of a solution or from a juice from sugarcane or beets in a manner known per se, i.e. commercial crystalline sugar, especially crystalline sugar in food quality. The sugar or the carbohydrate can, if the contamination profile is suitable for the process, of course generally also be used in the process in liquid form, as a syrup, in solid phase, i.e. including amorphous form. There is optionally then a preceding formulation and/or drying step.

The sugar may also have been prepurified by means of ion exchangers in the liquid phase, optionally in demineralized water or another suitable solvent or solvent mixture, in order to remove any specific impurities which are less efficiently removable by means of crystallization. Useful ion exchangers include strongly acidic, weakly acidic, amphoteric, neutral or basic ion exchangers. The selection of the correct ion exchanger is familiar to those skilled in the art as such depending on the impurities to be removed. Subsequently, the sugar can be crystallized, centrifuged and/or dried, or mixed with silicon oxide and dried. The crystallization can be effected by cooling or adding an antisolvent, or other methods familiar to those skilled in the art. The crystalline fractions can be removed by means of filtration and/or centrifugation.

According to the invention, the inventive carbon source containing at least one carbohydrate, or the carbohydrate mixture, especially a pure carbon source, has the following contamination profile: boron less than 2 [$\mu\text{g/g}$], phosphorus less than 0.5 [$\mu\text{g/g}$] and aluminum less than 2 [$\mu\text{g/g}$], preferably less than 1 [$\mu\text{g/g}$], especially iron less than 60 [$\mu\text{g/g}$], the content of iron preferably being less than 10 [$\mu\text{g/g}$], more preferably less than 5 [$\mu\text{g/g}$]. Overall, the aim in accordance with the invention is to use carbohydrates in which the content of impurities, such as boron, phosphorus, aluminum and/or arsenic etc., is below the limit of detection technically possible in each case.

The carbohydrate source comprising at least one carbohydrate, according to the invention the carbohydrate or the carbohydrate mixture, preferably has the following contamination profile of boron, phosphorus and aluminum, and possibly of iron, sodium, potassium, nickel and/or chromium. The contamination with boron (B) is especially in the range from 5 to 0.00001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from 2 to 0.00001 $\mu\text{g/g}$, according to the invention from below 2 to 0.00001 $\mu\text{g/g}$. The contamination with phosphorus (P) is especially in the range from 5 to 0.00001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from 1 to 0.00001 $\mu\text{g/g}$, according to the invention from below 0.5 to 0.00001 $\mu\text{g/g}$. The contamination with iron (Fe) is in the range from 100 to 0.00001 $\mu\text{g/g}$, especially in the range from 55 to 0.00001 $\mu\text{g/g}$, preferably from 2 to 0.00001 $\mu\text{g/g}$, more preferably from below 1 to 0.00001 $\mu\text{g/g}$, according to the invention from below 0.5 to 0.00001 $\mu\text{g/g}$. The contamination with sodium (Na) is especially in the range from 20 to 0.00001 $\mu\text{g/g}$, preferably from 15 to 0.00001 $\mu\text{g/g}$, more preferably from 12 to 0.00001 $\mu\text{g/g}$, according to the invention from below 10 to 0.00001 $\mu\text{g/g}$. The contamination with potassium (K) is especially in the range from 30 to 0.00001 $\mu\text{g/g}$, preferably from 25 to 0.00001 $\mu\text{g/g}$, more preferably from below 20 to 0.00001 $\mu\text{g/g}$, according to the invention from below 16 to 0.00001 $\mu\text{g/g}$. The contamination with aluminum (Al) is especially in the range from 4 to 0.00001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from 2 to 0.00001 $\mu\text{g/g}$, according to the invention from below 1.5 to 0.00001 $\mu\text{g/g}$. The contamination with nickel (Ni) is especially in the range from 4 to 0.000001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from below 2 to 0.00001 $\mu\text{g/g}$,

according to the invention from below 1.5 to 0.00001 $\mu\text{g/g}$. The contamination with chromium (Cr) is especially in the range from 4 to 0.00001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from below 2 to 0.00001 $\mu\text{g/g}$, according to the invention from below 1 to 0.00001 $\mu\text{g/g}$.

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According to the invention, a crystalline sugar, for example refined sugar is used, or a crystalline sugar is mixed with water-containing silicon dioxide or a silica sol, dried and used in the process in particulate form. Alternatively, any desired carbohydrate, especially sugar, invert sugar or syrup, can be mixed with a dry, water-containing or aqueous silicon oxide, silicon dioxide, silica having a water content or a silica sol or the silicon oxide components specified below, optionally sent to a drying step and used in the process in the form of particles, preferably with a particle size of from 1 nm to 10 mm.

15 Typically, sugar with a mean particle size of from 1 nm to 10 cm, especially from 10 μm to 1 cm, preferably from 100 μm to 0.5 cm, is used. Alternatively, it is possible to use sugar with a mean particle size in the micrometer range down to the millimeter range, preference being given to the range from 1 micrometer to 1 mm, more preferably from 10 micrometers to 100 micrometers. The particle size can be determined by methods including screen analysis, TEM (transmission electron microscopy), SEM (scanning electron microscopy) or light microscopy. It is also possible to use a dissolved carbohydrate in the form of a liquid, syrup, paste, in which case the high-purity solvent evaporates before the pyrolysis. Alternatively, there may be a preceding drying step to recover the solvent.

25

Preferred raw materials as the carbon source, especially as the pure carbon source, are also all organic compounds known to those skilled in the art which comprise at least one carbohydrate and which satisfy the purity demands, for example solutions of carbohydrates. The carbohydrate solution used may also be an aqueous-alcoholic solution or a solution containing tetraethoxysilane (Dynasylan® TEOS) or a tetraalkoxysilane, the solution being evaporated and/or pyrolyzed before the actual pyrolysis.

30

The silicon oxide or silicon oxide component used is preferably an SiO , more preferably an SiO_x where $x =$ from 0.5 to 1.5, SiO , SiO_2 , silicon oxide (hydrate), aqueous or water-containing SiO_2 , a silicon oxide in the form of fumed or precipitated silica, moist, dry or
5 calcined, for example Aerosil® or Sipernat®, or a silica sol or gel, porous or dense silica glass, quartz sand, quartz glass fibers, for example light guide fibers, quartz glass beads, or mixtures of at least two of the aforementioned silicon oxide forms. In the manner known to those skilled in the art, the particle sizes of the individual components are matched to one another.

10 In the context of the present invention, a sol is understood to mean a colloidal solution in which the solid or liquid substance is dispersed in ultrafine distribution in a solid, liquid or gaseous medium (see also Römpp Chemie Lexikon).

The particle size of the carbon source comprising a carbohydrate and also the particle
15 size of the silicon oxide are more particularly matched to one another in order to enable good homogenization of the components and suppress separation before or during the process.

Preference is given to using a porous silica, especially with an internal surface area of
20 from 0.1 to 800 m^2/g , preferably from 10 to 500 m^2/g or from 100 to 200 m^2/g , and especially with a mean particle size of 1 nm and greater, or else of from 10 nm to 10 mm, especially silica with high (99.9%) to ultrahigh (99.9999%) purity, where the content of impurities, such as boron, phosphorus, arsenic and aluminum compounds, is in total advantageously less than 10 ppm by weight in relation to the overall
25 composition. The purity is determined by the sample analysis known to those skilled in the art, for example by detection in ICP-MS (analysis for the determination of trace contamination). Particularly sensitive detection is possible by electron spin spectrometry. The internal surface area can be effected, for example, by the BET method (DIN ISO 9277, 1995).

30 A preferred mean particle size of the silicon oxide is in the range from 10 nm to 1 mm, especially in the range from 1 to 500 μm . The particle size can be determined by

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methods including TEM (transmission electron microscopy), SEM (scanning electron microscopy) or light microscopy.

Suitable silicon oxides generally include all compounds and/or minerals which contain a silicon oxide, provided that they have a suitable purity for the process and hence for the process product and do not introduce any disruptive elements and/or compounds into the process or do not burn without residue. As detailed above, pure or high-purity silicon oxide-containing compounds or materials are used in the process. According to the invention, a purified silicon oxide according to the above definition and/or prepared by the process component described above is used in the process for preparing silicon carbide.

In the case of use of the different silicon oxides, especially of the different silicas, etc., depending on the pH of the particle surface, the agglomeration may be different during the pyrolysis. Generally, in the case of relatively acidic silicon oxides, enhanced agglomeration of the particles is observed as a result of the pyrolysis. Therefore, for the preparation of less agglomerated pyrolyzates and/or calcination products, it may be preferable to use silicon oxides with neutral to basic surfaces in the process, for example with pH values between 7 and 14.

According to the invention, silicon oxide comprises a silicon dioxide, especially a fumed or precipitated silica, preferably a fumed or precipitated silica of high or ultrahigh purity, according to the invention a purified silicon oxide. Ultrahigh purity is understood to mean a silicon oxide, especially a silicon dioxide, in which the contamination of the silicon oxide with boron and/or phosphorus or for boron- and/or phosphorus-containing compounds should be below 10 ppm for boron, especially in the range from 10 ppm to 0.001 ppt, and below 20 ppm for phosphorus, especially in the range from 20 ppm to 0.001 ppt. The boron content is preferably in the range from 7 ppm to 1 ppt, preferably in the range from 6 ppm to 1 ppt, more preferably in the range from 5 ppm to 1 ppt or lower, or, for example, in the range from 0.001 ppm to 0.001 ppt, preferably in the region of the analytical detection limit. The phosphorus content of the silicon oxides should preferably be in the range from 18 ppm to 1 ppt, preferably in the range from

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15 ppm to 1 ppt, more preferably in the range from 10 ppm to 1 ppt or lower. The phosphorus content is preferably in the region of the analytical detection limit.

Also appropriate are silicon oxides, such as quartz, quartzite and/or silicon dioxides
5 prepared in a customary manner. These may be the silicon dioxides present in the crystalline polymorphs, such as moganite (chalcedone), α -quartz (low quartz), β -quartz (high quartz), tridymite, cristabolite, coesite, stishovite or else amorphous SiO_2 , especially when they meet the purity demands specified. In addition, it is possible with preference to use silicas, especially precipitated silicas or silica gels, fumed SiO_2 , fumed
10 silica or silica in the process and/or the composition. Customary fumed silicas are amorphous SiO_2 powders with an average diameter of from 5 to 50 nm and with a specific surface area of from 50 to 600 m^2/g . The above enumeration should not be considered to be conclusive; it is clear to the person skilled in the art that he or she can also use other silicon oxide sources suitable for the process in the process when the
15 silicon oxide source has an appropriate purity or after it has been purified.

The silicon oxide, especially SiO_2 , can be initially charged and/or used in pulverulent, particulate, porous or foamed form, or as an extrudate, as a pressing and/or as a porous glass body, optionally together with further additives, especially together with the
20 carbon source comprising at least one carbohydrate, and optionally a binder and/or shaping assistant.

Preference is given to using a pulverulent, porous silicon dioxide in the form of a shaped body, especially as an extrudate or pressing, more preferably together with the carbon
25 source comprising a carbohydrate in an extrudate or pressing, for example in a pellet or briquet. Generally, all solid reactants, such as silicon dioxide, and optionally the carbon source comprising at least one carbohydrate in a mold are used in the process or are present in a composition which offers a greatest possible surface area for the progress of the reaction. In addition, an increased porosity is desirable for rapid removal of the
30 process gases. According to the invention, it is therefore possible to use a particulate mixture of silicon dioxide particles with a coating of carbohydrate. In a particularly

preferred embodiment, this particulate mixture is present in the form of a composition or of a kit, especially packaged.

The amounts of feedstocks used and also the particular ratios of silicon oxide, especially silicon dioxide, and the carbon source comprising at least one carbohydrate are guided by the circumstances known to those skilled in the art and/or requirements, for example, in a subsequent process for silicon preparation, sintering processes, processes for producing electrode material or electrodes.

In the process according to the invention, the carbohydrate can be used in a weight ratio of carbohydrate to silicon oxide, especially of the silicon dioxide, in a weight ratio of from 1000:0.1 to 1:1000 in relation to the total weight. Preference is given to using the carbohydrate or the carbohydrate mixture in a weight ratio relative to the silicon oxide, especially the silicon dioxide, of from 100:1 to 1:100, more preferably from 50:1 to 1:5, most preferably from 20:1 to 1:2, preferred ranges being from 2:1 to 1:1. In a preferred variant, carbon via the carbohydrate is used in the process in excess in relation to the silicon to be converted in the silicon oxide. When the silicon oxide is used in excess in an appropriate embodiment, it should be ensured in the selection of the ratio that the formation of silicon carbide is not suppressed.

Likewise in accordance with the invention, the carbon content of the carbon source comprising a carbohydrate relative to the silicon content of the silicon oxide, especially of the silicon dioxide, is in a molar ratio of from 1000:0.1 to 0.1:1000 in relation to the overall composition. In the case of use of customary crystalline sugars, the preferred range of moles of carbon introduced via the carbon source comprising a carbohydrate to moles of silicon introduced via the silicon oxide compound is in the range from 100 mol:1 mol to 1 mol:100 mol (C to Si in the reactants); more preferably, C and Si are present in a ratio of from 50:1 to 1:50, even more preferably from 20:1 to 1:20, according to the invention in the range from 3:1 to 2:1 or to 1:1. Preference is given to molar ratios in which the carbon is added via the carbon source in approximately equimolar amounts or else in excess relative to the silicon in the silicon oxide.

The process component typically has a multistage configuration. In a first process step, the carbon source comprising at least one carbohydrate is pyrolyzed in the presence of silicon oxide with graphitization; more particularly, carbon-containing pyrolysis products, for example coatings containing proportions of graphite and/or carbon black, form on and/or in the silicon oxide component, such as SiO_x where $x =$ from 0.5 to 1.5, SiO , SiO_2 , silicon oxide (hydrate). The pyrolysis is followed by the calcination. The pyrolysis and/or calcination can be effected successively in one reactor or separately from one another in different reactors. For example, the pyrolysis is effected in a first reactor and the subsequent calcination, for example, in a microwave with a fluidized bed. It is familiar to those skilled in the art that the reactor internals, vessels, inlets and/or outlets, furnace internals themselves must not contribute to contamination of the process products.

The process component is generally conducted in such a way that the silicon oxide and the carbon source comprising at least one carbohydrate are fed to a first reactor for the pyrolysis in intimately mixed, dispersed or homogenized form or in a formulation. This can be effected continuously or batchwise. Optionally, the feedstocks are dried before being supplied to the actual reactor; adhering water or residual moisture may preferably remain in the system. The overall process is divided into a first phase in which the pyrolysis is effected, and into a further phase in which the calcination takes place.

The reaction can be effected at temperatures from 150°C , preferably from 400 to 3000°C , in which, in a first pyrolysis step (low-temperature method), a reaction can be effected at relatively low temperatures, especially at from 400 to 1400°C , and a subsequent calcination at higher temperatures (high-temperature method), especially at from 1400 to 3000°C , preferably at from 1400 to 1800°C . The pyrolysis and calcination can be effected in direct succession in one process or in two separate steps. For example, the process product of the pyrolysis can be packaged as a composition and be used later by a further processor to prepare silicon carbide or silicon.

Alternatively, the reaction of silicon oxide, especially purified silicon oxide, and the carbon source comprising a carbohydrate, especially the pure carbon source, may

commence with a low temperature range, for example from 150°C, preferably at 400°C, and be increased continuously or stepwise, for example up to 1800°C or higher, for example around 1900°C. This mode of operation may be favorable for removal of the process gases formed.

5

In a further alternative process regime, the reaction can be effected directly at high temperatures, especially at temperatures of from above 1400°C to 3000°C, preferably in the range from 1400°C to 1800°C, more preferably in the range from 1450 to below about 1600°C. In order to prevent decomposition of the silicon carbide formed, the reaction is preferably performed in a low-oxygen atmosphere at temperatures below the decomposition temperature, especially below 1800°C, preferably below 1600°C. The process product isolated in accordance with the invention is high-purity silicon carbide as defined below.

15 The actual pyrolysis (low-temperature step) takes place generally at temperatures below about 800°C. The pyrolysis can be carried out, depending on the desired product, at atmospheric pressure, under reduced pressure or else under elevated pressure. When vacuum or low pressure is employed, the process gases can be removed efficiently, and highly porous, particulate structures are typically obtained after the
20 pyrolysis. Under conditions in the region of standard pressure, the porous, particulate structures are typically relatively highly agglomerated. When pyrolysis is effected under elevated pressures, the volatile reaction products may then condense on the silicon oxide particles and possibly react with themselves or with reactive groups of the silicon dioxide. For example, decomposition products formed from the carbohydrates, such as
25 ketones, aldehydes or alcohols, may react with free hydroxyl groups of the silicon dioxide particles. This significantly reduces the pollution of the environment with process gases. The resulting porous pyrolysis products are somewhat more highly agglomerated in this case.

30 In addition to pressure and temperature which, according to the desired pyrolysis product, are freely selectable within wide limits and the exact matching to one another is known per se to those skilled in the art, the pyrolysis of the carbon source containing at

least one carbohydrate can additionally be effected in the presence of moisture, especially of residual moisture of the reactants, or else by addition of moisture, in the form of condensed water, water vapor or hydrate-containing components, such as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, or other hydrates familiar to those skilled in the art. The presence of moisture has, more particularly, the effect that the carbohydrate pyrolyzes more readily and that a complicated predrying of the reactants can be dispensed with. The process is more preferably carried out to prepare silicon carbide by reaction of silicon oxide, especially purified silicon oxide, and a carbon source comprising at least one carbohydrate, especially a pure carbon source, at elevated temperature, especially at the start of pyrolysis, in the presence of moisture; moisture may also be present during the pyrolysis or is metered in.

The pyrolysis is effected generally, especially in the at least one first reactor, at around 700°C in the low-temperature method, typically in the range from 200°C to 1600°C , more preferably in the range from 300°C to 1500°C , especially at from 400 to 1400°C , preference being given to obtaining a graphite-containing pyrolysis product. The pyrolysis temperature is preferably considered to be the internal temperature of the reaction participants. The pyrolysis product is preferably obtained at temperatures from around 1300 to 1500°C .

The process is generally operated in the low-pressure range and/or under an inert gas atmosphere. Preferred inert gases are argon or helium. Nitrogen may likewise be appropriate, i.e. when, in the calcination step, the intention is that silicon nitride forms as well as silicon carbide or n-doped silicon carbide, which may be desired according to the process regime. In order to prepare n-doped silicon carbide in the calcination step, nitrogen can be added to the process in the pyrolysis and/or calcination step, optionally also via the carbohydrates, such as chitin. The preparation of specifically p-doped silicon carbide may likewise be appropriate; in this specific exception, the aluminum content, for example, may be higher. The doping can be effected by means of aluminum-containing substances, for example by means of trimethylaluminum gas.

Depending on the pressure in the reactor, more or less agglomerated and more or less porous pyrolysis products and compositions can be prepared in this process step.

Under reduced pressure, generally a lower level of agglomerated pyrolysis products with an elevated porosity are obtained than under standard pressure or elevated

5 pressure.

The pyrolysis time may be in the range from 1 minute to typically 48 hours, especially in the range from 15 minutes to 18 hours, preferably in the range from 30 minutes to about 12 hours, at the pyrolysis temperatures specified. The heating phase up to the pyrolysis

10 temperature should generally be included in this.

The pressure range is typically from 1 mbar to 50 bar, especially from 1 mbar to 10 bar, preferably from 1 mbar to 5 bar. According to the pyrolysis product desired and, in order to minimize the formation of carbon-containing process gases, the pyrolysis step in the

15 process can also be effected within a pressure range from 1 to 50 bar, preferably at from 2 to 50 bar, more preferably at from 5 to 50 bar. The person skilled in the art is aware that the pressure to be selected is a compromise between gas removal, agglomeration and reduction of the carbon-containing process gases.

20 The pyrolysis of the reaction participants, such as silicon oxide and the carbohydrate, is followed by the calcination step. A calcination (high-temperature range) is understood to mean a process section in which the reaction participants react essentially to give high-purity silicon carbide, optionally containing a carbon matrix and/or a silicon oxide matrix and/or mixtures thereof. In this step, the pyrolysis products are converted further to

25 silicon carbide and water of crystallization is optionally evaporated and the process products are sintered. The calcination step (high-temperature step) generally follows the pyrolysis directly, but it can also be carried out at a later time, for example when the pyrolysis product is sold on. The temperature ranges of the pyrolysis and calcination step may overlap somewhat. The calcination is typically performed at from 1400 to

30 2000°C, preferably in the range from 1400 to 1800°C. When the pyrolysis is effected at temperatures below 800°C, the calcination step may also extend to a temperature range of from 800°C to about 1800°C. For improved heat transfer, high-purity silicon oxide

spheres, especially quartz glass spheres and/or silicon carbide spheres, or generally quartz glass and/or silicon carbide particles, can be used in the process. These heat transferers are preferably used in rotary tube furnaces, or else in microwave furnaces. In microwave furnaces, the microwaves can be absorbed into the quartz glass particles and/or silicon carbide particles, such that the particles heat up. The spheres and/or particles are preferably well-distributed in the reaction system in order to enable homogeneous heat transfer.

The calcination, i.e. the high-temperature area of the process, is effected typically within the pressure range from 1 mbar to 50 bar, especially in the range from 1 mbar to 1 bar (ambient pressure), especially at from 1 to 250 mbar, preferably at from 1 to 10 mbar. A useful inert gas atmosphere is that specified above. The calcination time depends on the temperature and the reactants used. In general, it is in the range from 1 minute and may typically be 48 hours, especially in the range from 15 minutes to 18 hours, preferably in the range from 30 minutes to about 12 hours, at the calcination temperatures specified. The heating phase up to the calcination temperature should generally be included.

The reaction of silicon oxide and the carbon source containing a carbohydrate can also be effected directly in the high-temperature range, in which case the gaseous reaction participants formed and process gases must be able to outgas efficiently out of the reaction zone. This can be ensured by means of a loose bed or a bed comprising shaped bodies of silicon oxide and/or of the carbon source or preferably comprising shaped bodies comprising silicon dioxide and the carbon source (carbohydrate). The gaseous reaction products and process gases may especially be water vapor, carbon monoxide and conversion products. At high temperatures, especially in the high-temperature range, predominantly carbon monoxide forms.

The conversion to silicon carbide at elevated temperature, especially of the calcination step, is effected preferably at a temperature of from 400 to 3000°C, preference being given to effecting the calcination in the high-temperature range from 1400 to 3000°C, preferably at from 1400°C to 1800°C, more preferably from 1450 to 1500 and 1700°C.

The temperature ranges should not be restricted to those disclosed, since the temperatures attained also depend directly on the reactors used. The temperature data are based on measurements with standard high-temperature sensors, for example encapsulated sensors (PtRhPt element), or alternatively via the color temperature by visual comparison with an incandescent element.

Useful reactors for use in the process according to the invention include all reactors known to those skilled in the art for a pyrolysis and/or calcination. It is therefore possible to utilize, for the pyrolysis and subsequent calcination to form SiC and optional graphitization, all laboratory reactors known to those skilled in the art, pilot plant reactors or preferably industrial scale reactors, for example rotary tube reactors or else a microwave reactor, as is known for the sintering of ceramics.

The microwave reactors can be operated in the high-frequency (HF) range, the "high-frequency range" being understood in the context of the present invention to mean from 100 MHz to 100 GHz, especially in the range from 100 MHz to 50 GHz or else from 100 MHz to 40 GHz. Preferred frequency ranges are, for instance, in the range from 1 MHz to 100 GHz, from 10 MHz to 50 GHz being particularly preferred. The reactors can be operated in parallel. Particular preference is given to using magnetrons at 2.4 MHz for the process.

The high-temperature reaction can also be effected in customary melting furnaces for producing steel or silicon, such as metallurgical silicon, or other suitable melting furnaces, for example induction furnaces. The design of such melting furnaces, especially preferably electrical furnaces, which use an electric light arc as the energy source is sufficiently well known to those skilled in the art and does not form part of this application. In direct current furnaces, they have one melt electrode and one base electrode, or, in the form of alternating current furnaces, typically three melting electrodes. The light arc length is regulated by means of an electrode regulator. The light arc furnaces are generally based on a reaction chamber made of refractory material. The raw materials, especially the pyrolyzed carbohydrate on silica/SiO₂, are added in the upper region, in which the graphite electrodes to generate the light arc are

also disposed. These furnaces are usually operated at temperatures in the region of 1800°C. It is additionally known to those skilled in the art that the furnace internals themselves must not contribute to contamination of the silicon carbide prepared.

- 5 The invention also provides a composition comprising silicon carbide, optionally with a carbon matrix and/or silicon oxide matrix or a matrix comprising silicon carbide, carbon and/or silicon oxide and optionally silicon, which is obtainable by the process component according to the invention, especially by the calcination step, and is especially isolated. "Isolation" means that, after performance of the process, the
10 composition and/or the high-purity silicon carbide is obtained and isolated, especially as the product. The silicon carbide may be provided with a passivation layer, for example comprising SiO₂.

This product can then be utilized as a reaction participant, catalyst, material for
15 producing articles, for example filters, shaped bodies or green bodies, and also in further applications familiar to those skilled in the art. A further important application is the utilization of the composition comprising silicon carbide as a reaction initiator and/or reaction participant and/or in the production of electrode material or in the production of silicon carbide with sugar coke and silica.

20 The invention also provides the pyrolysis product and optionally calcination product, especially a composition obtainable by the process according to the invention and especially the pyrolysis and/or calcination product isolated from the process component, with a content of carbon relative to silicon oxide, especially silicon dioxide, of from
25 400:0.1 to 0.4:1000.

The conductivity of the process products, especially of the high-density compressed pulverulent process products, measured between pointed electrodes, is preferably in the range from κ [m/Ω.m²] = $1 \cdot 10^{-1}$ to $1 \cdot 10^{-6}$. A low conductivity is desired for the
30 particular silicon carbide process product, which correlates directly with the purity of the process product.

The composition or the pyrolysis and/or calcination product preferably has a graphite content of from 0 to 50% by weight, preferably from 25 to 50% by weight, in relation to the overall composition. According to the invention, the composition or the pyrolysis and/or calcination product has a proportion of silicon carbide of from 25 to 100% by weight, especially from 30 to 50% by weight, in relation to the overall composition.

The invention also provides a silicon carbide with a carbon matrix comprising coke and/or carbon black and/or graphite or mixtures thereof and/or with a silicon oxide matrix comprising silicon dioxide, silica and/or mixtures thereof, or with a mixture of the aforementioned components, obtainable by the process according to the invention, especially according to any one of claims 1 to 10. More particularly, the SiC is isolated and used further as detailed below.

The content of the elements boron, phosphorus, arsenic and/or aluminum is in total preferably below 10 ppm by weight in the silicon carbide according to the definition of the invention.

The invention also provides a silicon carbide, optionally with carbon components and/or silicon oxide components, or mixtures comprising silicon carbide, carbon and/or silicon oxide, especially silicon dioxide, with a content of the elements boron, phosphorus, arsenic and/or aluminum of less than 100 ppm by weight in total in the silicon carbide. The contamination profile of the high-purity silicon carbide with boron, phosphorus, arsenic, aluminum, iron, sodium, potassium, nickel, chromium is preferably from below 5 ppm to 0.01 ppt (by weight), especially from below 2.5 ppm to 0.1 ppt. More preferably, the silicon carbide obtained by the process according to the invention, optionally with carbon and/or Si_yO_z matrices, has a contamination profile as defined above comprising the elements B, P, Na, S, Ba, Zr, Zn, Al, Fe, Ti, Ca, K, Mg, Cu, Cr, Co, Zn, Ni, V, Mn and/or Pb, and mixtures of these elements.

In particular, the silicon carbide obtainable, in total, has a content of carbon relative to silicon oxide, especially silicon dioxide, of from 400:0.1 to 0.4:1000; it, especially the composition, preferably has a graphite content of from 0 to 50% by weight, more preferably from 25 to 50% by weight. The proportion of silicon carbide is especially in

the range from 25 to 100% by weight, preferably from 30 to 50% by weight, in the silicon carbide (overall) as defined above.

In one variant, the invention provides for the use of silicon carbide or of a composition or
5 of a pyrolysis and/or calcination product of the process in the preparation of pure silicon,
especially in the preparation of solar silicon. The invention provides, more particularly,
the use in the preparation of solar silicon by reduction of silicon dioxide, especially of
purified silicon dioxide, at high temperatures, or in the preparation of silicon carbide by
reaction of coke, especially of sugar coke, and silicon dioxide, especially of silica,
10 preferably of fumed or precipitated silica or silica purified by means of ion exchangers,
or SiO_2 , at high temperatures, as an abrasive, insulator, as a refractory material, such
as thermal tiles, or in the production of articles or in the production of electrodes.

The invention also provides for the use of silicon carbide or of a composition or a
15 pyrolysis and/or calcination product obtainable by the process according to the invention
as a catalyst, especially in the preparation of silicon, preferably in the preparation of
purified silicon, especially in the preparation of solar silicon, especially in the preparation
of solar silicon by reduction of silicon dioxide at high temperatures, and optionally in the
preparation of silicon carbide for semiconductor applications or for use as a catalyst in
20 the preparation of ultrahigh-purity silicon carbide, for example by sublimation, or as a
reactant in the preparation of silicon or in the preparation of silicon carbide, especially
from coke, preferably from sugar coke, and silicon dioxide, preferably with silica, at high
temperatures, or for use as a material of articles or as an electrode material, especially
for electrodes of light arc furnaces. The use as a material of articles, especially
25 electrodes, includes the use of the material as a material for the articles or else the use
of further-processed material for the production of the articles, for example of sintered
material or of abrasives.

The invention further provides for the use of at least one carbohydrate, especially a pure
30 silicon carbide especially isolable as a product in the preparation of pure to ultrapure
silicon carbide, or of a composition containing silicon carbide or a pyrolysis and/or

calcination product containing silicon carbide, especially in the presence of silicon oxide, preferably in the presence of silicon oxide and/or silicon dioxide.

Preference is given to using a selection from at least one carbohydrate and a silicon
5 oxide, especially a purified silicon dioxide, especially without further components, to
prepare silicon carbide, the silicon carbide, a composition containing silicon carbide or a
pyrolysis and/or calcination product, being isolated as the reaction product.

The invention also provides for the use of a composition, especially a formulation, or a
10 kit comprising at least one carbohydrate and silicon oxide, especially purified silicon
oxide, in the process according to the invention. The invention therefore also provides a
kit containing separate formulations, especially in separate containers, such as vessels,
pouches and/or cans, especially in the form of an extrudate and/or powder of silicon
oxide, especially of purified silicon oxide, preferably of purified silicon dioxide, optionally
15 together with pyrolysis products of carbohydrates on SiO_2 and/or the carbon source
comprising at least one carbohydrate, especially for use according to the above
remarks. It may be preferred when the silicon oxide is present in a container in the kit
directly with the carbon source comprising a carbohydrate, especially a pure carbon
source, for example is impregnated with it or the carbohydrate is supported on SiO_2 ,
20 etc., in the form of tablets, as a granule, extrudate, briquet, especially as a pellet or
briquet, and optionally further carbohydrate and/or silicon oxide as a powder in a
second container.

The invention further provides for the use of an article, especially a green body, shaped
25 body, sintered body, an electrode, a heat-resistant component, comprising an inventive
silicon carbide or an inventive composition containing silicon carbide, and optionally
further customary additives, assistants, pigments or binders in the overall process
according to the invention. The invention thus provides an article containing an inventive
silicon carbide which is prepared using the inventive silicon carbide, and use thereof in
30 the overall process according to the invention.

Use of SiC as activator in the reduction of the silicon oxide with the carbon source

As explained at the outset, silicon carbide can also be added in the process according
5 to the invention for preparing pure silicon.

According to the invention, the economic viability of the process for preparing pure silicon can be enhanced considerably by the addition of an activator which fulfills the function of a reaction initiator, reaction accelerant and/or as a carbon source. At the
10 same time, the activator, i.e. reaction initiator and/or reaction accelerant, should be very substantially pure and inexpensive. Particularly preferred reaction initiators and/or reaction accelerants should themselves not introduce any disruptive impurities into the silicon melt or preferably only introduce impurities in very small amounts for the reasons stated above.

15 The process according to the invention can be carried out in different ways; in a particularly preferred variant, a silicon oxide, especially silicon dioxide, preferably a silicon dioxide purified by acidic precipitation, is converted at elevated temperature by adding silicon carbide as a pure carbon source or as an activator to the silicon oxide, according to the invention to the purified silicon oxide, or silicon carbide (SiC) is added
20 to the process in a composition containing silicon oxide; it is particularly preferred when the silicon oxide, especially the silicon dioxide, and the silicon carbide are added in an approximately stoichiometric ratio, i.e. about 1 mol of SiO_2 to 2 mol of SiC to prepare silicon; more particularly, the reaction mixture for preparing silicon consists of silicon
25 oxide and silicon carbide.

A further advantage of this process regime is that the addition of SiC results in correspondingly less CO being released per unit of Si formed. The gas loading, which crucially limits the process, is thus lowered advantageously. Addition of SiC advantageously makes possible process intensification.

30 In a further particularly preferred variant, the purified silicon oxide, especially silicon dioxide, is converted at elevated temperature by adding and reacting silicon carbide and

a further pure carbon source to the silicon oxide or silicon carbide and a pure carbon source, especially a second pure carbon source, in a composition containing silicon oxide. In this variant, the concentration of silicon carbide can be lowered to such an extent that it acts more as a reaction initiator and/or reaction accelerant and less as a reactant. It is preferably also possible in the process to react about 1 mol of silicon dioxide with about 1 mol of silicon carbide and about 1 mol of a second carbon source.

According to the invention, to the process for preparing silicon by converting purified silicon oxide at elevated temperature, the silicon carbide is added to the silicon oxide or optionally to a composition containing the purified silicon oxide; in particular, the energy source used is an electrical light arc. The purpose is to add a silicon carbide as an activator, i.e. as a reaction initiator and/or reaction accelerant and/or as a carbon source, i.e. as a reactant, to the process and/or to add it to the process in a composition.

The silicon carbide is thus supplied separately to the process. Preference is given to adding silicon carbide to the process or to the composition as a reaction initiator and/or reaction accelerant. Since silicon carbide itself decomposes only at temperatures of from about 2700 to 3070°C, it was surprising that it can be added to the process for preparing silicon as a reaction initiator and/or reaction accelerant or as a reactant or else as a heat transferer. It has been observed in an experiment that, entirely surprisingly, after ignition of an electrical light arc, the reaction between silicon dioxide and carbon, especially graphite, which starts up and proceeds very slowly, the addition of small amounts of pulverulent silicon carbide led to a very significant increase in the reaction within a short time. The occurrence of luminescence phenomena was observed and, surprisingly, the entire subsequent reaction continued within intensive, bright light, more particularly up to the end of the reaction.

As a further or second pure carbon source, especially in addition to the silicon carbide, compounds or materials which do not consist of silicon carbide, do not have any silicon carbide or do not contain any silicon carbide are defined in connection with the process for preparing silicon. The second carbon source thus does not consist of silicon carbide,

has no silicon carbide or contains no silicon carbide. The function of the second carbon source is more that of a pure reactant, whereas the silicon carbide is also a reaction initiator and/or reaction accelerant. Useful second carbon sources include in particular sugar, graphite, coal, charcoal, carbon black, coke, bituminous coal, brown coal, activated carbon, petroleum coke, wood as woodchips or pellets, rice husks or stalks, carbon fibers, fullerenes and/or hydrocarbons, especially gaseous or liquid hydrocarbons, and mixtures of at least two of the compounds mentioned, provided that they have a sufficient purity and do not contaminate the process with undesired compounds or elements. The second carbon source is preferably selected from the compounds mentioned. The contamination of the further or second pure carbon source with boron and/or phosphorus and for boron- and/or phosphorus-containing compounds should be less than 10 ppm for boron, especially in the range from 10 ppm to 0.001 ppt, and less than 20 ppm for phosphorus, especially in the range from 20 ppm to 0.001 ppt, in parts by weight. The ppm, ppb and/or ppt units should be understood throughout as proportions of the weight in mg/kg, µg/kg, etc.

The content of boron is preferably in the range from 7 ppm to 1 ppt, preferably in the range from 6 ppm to 1 ppt, more preferably in the range from 5 ppm to 1 ppt or less, for example in the range from 0.001 ppm to 0.001 ppt, preferably in the region of the analytical detection limit. The phosphorus content should preferably be in the range from 18 ppm to 1 ppt, preferably in the range from 15 ppm to 1 ppt, more preferably in the range from 10 ppm to 1 ppt or lower. The phosphorus content is preferably in the region of the analytical detection limit. Generally, these limits are the aim for all reactants or additives to the process in order to be suitable for preparing solar and/or semiconductor silicon.

The silicon oxide used is preferably an above-defined purified or high-purity silicon oxide, especially a purified or high-purity silicon dioxide. In addition to the silicon oxide purified in accordance with the invention, it is possible to use further correspondingly pure silicon oxides in the process for preparing pure silicon.

It may also be appropriate to add further suitable silicon oxides in addition to the purified silicon oxide; these are quartz, quartzite and/or silicon dioxides prepared in a customary manner. These may be silicon dioxides which occur in crystalline polymorphs, such as moganite (chalcedone), α -quartz (low quartz), β -quartz (high quartz), tridymite, cristabolite, coesite, stishovite or else amorphous SiO_2 . In addition, it is possible with preference to use silicas, fumed SiO_2 , fumed silica or silica in the process and/or the composition. Typical fumed silicas are amorphous SiO_2 powders with an average diameter of from 5 to 50 nm and with a specific surface area of from 50 to 600 m^2/g . The above list should not be considered to be conclusive; it is clear to those skilled in the art that he or she can also use other silicon oxide sources suitable for the process in the process and/or the composition.

Preference is given to using purified silicon oxide, especially purified silicon dioxide, and silicon carbide and optionally a second carbon source, especially a second pure carbon source, in the process, in the following molar ratios and/or percentages by weight specified, where the figures may be based on the reactants and more particularly on the reaction mixture in the process:

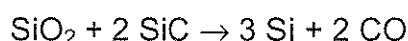
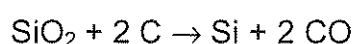
for 1 mol of a silicon oxide, for example silicon monoxide, such as Patinal[®], it is possible to add about 1 mol of a second pure carbon source and silicon carbide in small amounts as a reaction initiator or reaction accelerant. Customary amounts of silicon carbide as a reaction initiator and/or reaction accelerant are from about 0.0001% by weight to 25% by weight, preferably from 0.0001 to 20% by weight, more preferably from 0.0001 to 15% by weight, especially from 1 to 10% by weight, based on the total weight of the reaction mixture, especially comprising silicon oxide, silicon carbide and a second carbon source, and optionally further additives.

It may likewise be particularly preferred to add to the process, for 1 mol of a purified silicon oxide, especially silicon dioxide, about 1 mol of pure silicon carbide and about 1 mol of a second carbon source, especially of a pure source. When a silicon carbide containing carbon fibers or other similar carbon-containing compounds is used, the amount of second carbon source in mole can be lowered correspondingly. For 1 mol of silicon dioxide, it is possible to add about 2 mol of a second carbon source and silicon

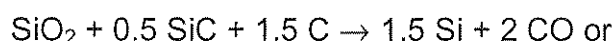
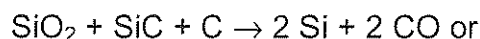
carbide in small amounts as a reaction initiator or reaction accelerant. Customary amounts of silicon carbide as a reaction initiator and/or reaction accelerant are from about 0.0001% by weight to 25% by weight, preferably from 0.0001 to 20% by weight, more preferably from 0.0001 to 15% by weight, especially from 1 to 10% by weight, based on the total weight of the reaction mixture, especially comprising silicon oxide, silicon carbide and a second carbon source, and optionally further additives.

In a preferred alternative, for 1 mol of silicon dioxide, about 2 mol of silicon carbide can be used as a reactant in the process, and a second carbon source may optionally be present in small amounts. Customary amounts of the second carbon source are from about 0.0001% by weight to 29% by weight, preferably from 0.001 to 25% by weight, more preferably from 0.01 to 20% by weight, even more preferably from 0.1 to 15% by weight, especially from 1 to 10% by weight, based on the total weight of the reaction mixture, especially comprising silicon dioxide, silicon carbide and a second carbon source, and optionally further additives.

In stoichiometric terms, silicon dioxide can especially be reacted according to the following reaction equations with silicon carbide and/or a second carbon source:



or



Because the purified silicon dioxide can react in a molar ratio of 1 mol with 2 mol of silicon carbide and/or the second carbon source, there is the possibility of controlling the process via the molar ratio of silicon carbide and of the further or second pure carbon source. Silicon carbide and the second carbon source should preferably be used in the process or be present in the process together in an approximate ratio of 2 mol to 1 mol of silicon dioxide. Thus, the 2 mol of silicon carbide and optionally of the second carbon source may be composed of 2 mol of SiC to 0 mol of second carbon source up to

0.00001 mol of SiC to 1.99999 mol of second carbon source (C). The ratio of silicon carbide to the second carbon source preferably varies within the stoichiometric about 2 mol for reaction with about 1 mol of silicon dioxide according to Table 1:

5 **Table 1**

Reaction:	Silicon dioxide in mol	Silicon carbide (SiC) in mol	Second carbon source (C) in mol
No. 1	1	2	0
No. 2	1	1.99999	0.00001
No. ∞	1	To 0.00001	to 1.9999
		where SiC + C always adds up to about 2 mol.	

For example, the 2 mol of SiC and optionally C are composed of from 2 to 0.00001 mol of SiC and from 0 to 1.99999 mol of C, especially of from 0.0001 to 0.5 mol of SiC and from 1.9999 to 1.5 C for 2 mol, preferably from 0.001 to 1 mol of SiC and from 1.999 to 1 C for 2 mol, more preferably from 0.01 to 1.5 mol of SiC and from 1.99 to 0.5 C for 2 mol; it is especially preferred to use from 0.1 to 1.9 mol of SiC and from 1.9 to 0.1 C for 2 mol for about 1 mol of silicon dioxide in the process according to the invention.

Useful silicon carbides for use in the process according to the invention or the inventive composition include preferably pure to ultrahigh-purity silicon carbides according to the above definition, and generally all polytype phases; the silicon carbide may optionally be coated with a passivating layer of SiO₂. Some polytype phases with different stability can be used with preference in the process because they are allow, for example, the reaction profile or the commencement of reaction in the process to be controlled. High-purity silicon carbide is colorless and is used in the process with preference. In addition, the silicon carbide used in the process or in the composition may be technical SiC (carborundum), metallurgical SiC, SiC bonding matrices, open-pore or dense silicon carbide ceramics, such as silicatically bonded silicon carbide, recrystallized SiC (RSiC),

reaction-bonded, silicon-infiltrated silicon carbide (SiSiC), sintered silicon carbide, hot (isostatically) pressed silicon carbide (HpSiC, HiPSiC) and/or liquid-phase sintered silicon carbide (LPSSiC), carbon fiber-reinforced silicon carbide composite materials (CMC, ceramic matrix composites) and/or mixtures of these compounds, with the

5 proviso that the contamination is so low that the silicon prepared is suitable for preparing solar silicon and/or semiconductor silicon. The aforementioned silicon carbides can also be added to the process according to the invention in small amounts provided that the total contamination of the pure silicon corresponds to that according to the invention. It is therefore also possible to supply silicon carbides in certain amounts
10 to recycling in the process according to the invention, provided that the total contamination of the pure silicon prepared is attained. The person skilled in the art is aware of how the total contamination of the resulting pure silicon can be controlled by addition of different batches and varying contamination profiles.

15 The contamination of the silicon carbide suitable for the process with boron and/or phosphorus or with boron- and/or phosphorus-containing compounds is preferably less than 10 ppm for boron, especially in the range from 10 ppm to 0.001 ppt, and less than 20 ppm for phosphorus, especially in the range from 20 ppm to 0.001 ppt. The boron content in a silicon carbide is preferably in the range from 7 ppm to 1 ppt, preferably in
20 the range from 6 ppm to 1 ppt, more preferably in the range from 5 ppm to 1 ppt or less, or, for example, in the range from 0.001 ppm to 0.001 ppt, preferably in the region of the analytical detection limit. The phosphorus content of a silicon carbide should preferably be in the range from 18 ppm to 1 ppt, preferably in the range from 15 ppm to 1 ppt, more preferably in the range from 10 ppm to 1 ppt or lower. The phosphorus content is
25 preferably in the region of the analytical detection limit.

Since silicon carbides are increasingly being used as a composite material, for example for producing semiconductors, brake disk materials or heat shields and further products, the process according to the invention and the composition or formulation offers a
30 means of recycling these products after use or the waste or rejects obtained in the production thereof in an elegant manner. The sole prerequisite for the silicon carbides to

be recycled is a purity sufficient for the process; preference is given to recycling silicon carbides which satisfy the above specifications for boron and/or phosphorus.

The silicon carbide may be added to the process a) in pulverulent, particulate and/or in piece form and/or b) in a porous glass, especially quartz glass, in an extrudate and/or pressing, such as pellet or briquet, especially in an above-described formulation,
5 optionally together with further additives.

All reaction participants, i.e. the purified silicon oxide, silicon carbide and any further pure carbon sources may each be added to the process separately or continuously or
10 batchwise in compositions or formulations. The silicon carbide is preferably added in such amounts and in the course of the process as to achieve a particularly economically viable process regime. It may therefore be advantageous when the silicon carbide is added continuously and stepwise, in order to maintain a continuing acceleration of the reaction.

15 The reaction can be effected in customary melting furnaces for preparing silicon, as described at the outset.

As detailed above, the silicon carbide, according to the contamination profile of the other reactants, can be used in the form of silicon carbide, in the form of pure silicon
20 carbide or else in the form of ultrahigh-purity silicon carbide, or else as a mixture thereof. The silicon carbides are preferably formulated beforehand in mixtures, especially briqueted. It is generally the case that the more highly contaminated the silicon carbide is, the smaller its amount will be in the process.

25 The process can be carried out in such a way that

a) the silicon carbide and purified silicon oxide, especially silicon dioxide, and optionally a further pure carbon source are each supplied separately to the process, especially to the reaction chamber, and are optionally then mixed, and/or

b) the silicon carbide, together with purified silicon oxide, especially silicon dioxide, and
30 optionally a further pure carbon source in a formulation and/or

- c) the purified silicon oxide, especially silicon dioxide, together with a pure carbon source in a formulation, especially in the form of an extrudate or pressing, preferably as a pellet or briquet, and/or
- d) the silicon carbide in a composition with the further pure carbon source is supplied or
5 added to the process. This formulation may be a physical mixture, an extrudate or pressing or else a carbon fiber-reinforced silicon carbide.

As already detailed for the silicon carbide, the silicon carbide and/or silicon oxide and optionally at least one further pure carbon source can be supplied to the process as
10 material to be recycled. The sole prerequisite on the compounds to be recycled is that they possess a sufficient purity in order to form, in the process, silicon from which solar silicon and/or semiconductor silicon can be produced.

Equally, it is possible in the process according to the invention, in addition to purified
15 silicon oxide, also to use silicon oxides which are to be recycled and are of sufficient purity. These include quartz glasses, for example broken glass. To take just a few, these may be Suprasil, SQ 1, Herasil, Spektrosil A. The purity of these quartz glasses can be determined, for example, via the absorptions at different wavelengths, such as at 157 nm or 193 nm. The second carbon source used may, for example, be virtually spent
20 electrodes which have been converted to a desired form, for example in powder form.

The pure silicon prepared or obtained by the process according to the invention is, according to the invention, optionally after zone melting/controlled solidification, suitable as solar silicon. It is preferably suitable a) for further processing in the process for
25 preparing solar silicon or semiconductor silicon.

The contamination of the silicon prepared with boron- and/or phosphorus-containing compounds should correspond to the spectrum defined at the start of this description, but may also be in the range from less than 10 ppm to 0.0001 ppt for boron, especially
30 in the range from 5 ppm to 0.0001 ppt, preferably in the range from 3 ppm to 0.0001 ppt or more preferably in the range from 10 ppb to 0.0001 ppt, after more preferably in the range from 1 ppb to 0.0001 ppt and for phosphorus in the range from less than 10 ppm

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to 0.0001 ppt, especially in the range from 5 ppm to 0.0001 ppt, preferably in the range from 3 ppm to 0.0001 ppt or more preferably in the range from 10 ppb to 0.0001 ppt, more preferably in the range from 1 ppb to 0.0001 ppt, reported in parts by weight.

There is generally no lower limit in the range of impurities, and the limit is instead
5 determined solely by the current detection limits of the analytical methods.

According to the invention, the pure silicon has the contamination profile of boron, aluminum, calcium, iron, nickel, phosphorus, titanium and/or zinc specified at the outset.

10 Appropriately, the molten silicon can be subjected to a treatment with rare earth metals in order to remove carbon, oxygen, nitrogen, boron or any other impurities present from the molten silicon.

The invention also provides a composition which is especially suitable for use in the
15 above process for preparing silicon and whose quality is preferably suitable as solar silicon or for production of solar silicon and/or semiconductor silicon, said composition comprising silicon oxide and silicon carbide and optionally a second carbon source, especially a pure second carbon source. Useful purified silicon oxide, especially silicon dioxide, silicon carbide and optionally a second carbon source, includes especially that
20 specified above, and preferably also satisfies the purity requirements listed there.

The silicon carbide may also be present in the formulation, according to the above remarks, a) in pulverulent, particulate and/or piece form, and/or b) present in a porous glass, especially quartz glass, in an extrudate and/or pellet, optionally together with
25 further additives. In further embodiments, the formulation may comprise silicon-infiltrated silicon carbide and/or silicon carbide containing carbon fibers. These formulations are preferable when corresponding silicon carbides are to be sent to recycling because they cannot be used in another way, for example production rejects or spent products. When the purity is sufficient for the process according to the
30 invention, it is possible in this way to send silicon carbides, silicon carbide ceramics, such as hotplates, brake disk material, back to recycling. In general, these products, as a result of the production, already have a sufficient purity. The invention may therefore

also provide the recycling of silicon carbides in a process for preparing silicon. The binders used may be the above-defined binders, especially the thermally resistant or highly thermally resistant binders for producing the formulation.

- 5 The invention likewise provides for the use of the silicon prepared by the process according to the invention as a base material for solar cells and/or semiconductors or especially as a starting material for preparing solar silicon.

Reactors suitable for use in the overall process according to the invention

10

The invention also provides a reactor, an apparatus and electrodes, especially suitable for preparation of solar silicon or semiconductor silicon.

15

In order to be able to prepare silicon of high purity, it is necessary to use reduction furnaces by which contamination with impurities can be very substantially avoided, more preferably prevented. Suitable reactors and apparatus of this kind is, for example, the subject of a further invention. To prevent contamination in the reduction, it is proposed there in accordance with the invention to line the reactors with the pure to high-purity graphites, silicon carbides, or else to manufacture the electrodes therefrom.

20

The boron, phosphorus, arsenic, aluminum, iron, sodium, potassium, nickel, chromium content is, for each element in pure silicon carbide, preferably from less than 5 ppm to 0.01 ppt (by weight), and, in high-purity silicon carbide, especially from less than 2.5 ppm to 0.1 ppt. The silicon carbide obtained from the reaction of a silicon oxide and
25 a pure carbohydrate source, especially purified sugar, optionally with carbon and/or Si_yO_z matrices, more preferably has an impurity profile as defined at the start of the description for SiC.

30

A particularly preferred pure to high-purity silicon carbide or a high-purity composition contains or consists of silicon carbide, carbon, silicon oxide and optionally small amounts of silicon, the high-purity silicon carbide or the high-purity composition having especially a contamination profile of boron, phosphorus, arsenic, aluminum, iron,

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sodium, potassium, nickel, chromium, sulfur, barium, zirconium, zinc, titanium, calcium, magnesium, copper, chromium, cobalt, zinc, vanadium, manganese and/or lead of less than 100 ppm for pure silicon carbide, preferably from less than 20 ppm to 0.001 ppt for high-purity silicon carbide, more preferably in the range from 10 ppm to 0.001 ppt in relation to the high-purity overall composition or the high-purity silicon carbide.

The silicon carbide is more preferably obtained from the reaction of a purified silicon oxide and a pure carbohydrate source, especially pure sugar, as described above. During the reaction, the silicon content can be controlled via the reaction conditions or else by adding separate silicon. The silicon carbide is preferably prepared by the process explained above for preparing silicon carbide.

Corresponding limits for aluminum, boron, calcium, iron, nickel, phosphorus, titanium, zinc apply to a high-purity graphite. These are specifically:

- boron less than 5.5 [$\mu\text{g/g}$], especially in the range from 5 to 0.000001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from 2 to 0.00001 $\mu\text{g/g}$, according to the invention from less than 2 to 0.00001 $\mu\text{g/g}$,
- phosphorus less than 5.5 [$\mu\text{g/g}$], from 5 to 0.000001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from less than 1 to 0.00001 $\mu\text{g/g}$, according to the invention from less than 0.5 to 0.00001 $\mu\text{g/g}$,
- aluminum in the range from 4 to 0.000001 $\mu\text{g/g}$, preferably from 3 to 0.00001 $\mu\text{g/g}$, more preferably from less than 2.5 to 0.00001 $\mu\text{g/g}$, according to the invention from 2 to 0.00001 $\mu\text{g/g}$,
- iron in the range from 100 to 0.000001 $\mu\text{g/g}$, preferably in the range from 60 to 0.00001 $\mu\text{g/g}$, especially in the range from 10 to 0.000001 $\mu\text{g/g}$, preferably from 5 to 0.00001 $\mu\text{g/g}$, more preferably from 2 to 0.00001 $\mu\text{g/g}$, even more preferably from below 1 to 0.00001 $\mu\text{g/g}$, according to the invention from less than 0.5 to 0.00001 $\mu\text{g/g}$,
- sodium (Na) in the range from 20 to 0.000001 $\mu\text{g/g}$, preferably from 15 to 0.00001 $\mu\text{g/g}$, more preferably from less than 12 to 0.00001 $\mu\text{g/g}$, according to the invention from less than 10 to 0.00001 $\mu\text{g/g}$,

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- potassium (K) in the range from 30 to 0.000001 µg/g, preferably from 25 to 0.00001 µg/g, more preferably from less than 20 to 0.00001 µg/g, according to the invention from less than 16 to 0.00001 µg/g,
 - nickel (Ni) in the range from 4 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from less than 2 to 0.00001 µg/g, according to the invention from less than 1.5 to 0.00001 µg/g,
 - chromium (Cr) in the range from 4 to 0.000001 µg/g, preferably from 3 to 0.00001 µg/g, more preferably from less than 2 to 0.00001 µg/g, according to the invention from less than 1 to 0.00001 µg/g.
- Preference is given to minimal contamination with the particular elements, more preferably less than 100 ppm, most preferably less than 10 ppb or less than 1 ppb.

Test methods:

Determination of the pH of the precipitation suspension

The process based on DIN EN ISO 787-9 serves to determine the pH of an aqueous suspension of silicon dioxide.

Before the performance of the pH measurement, the pH meter (calimatic 766 pH meter from Knick, with temperature sensor) and the pH electrode (N7680 combination electrode from Schott) should be calibrated using buffer solutions at 20°C. The calibration function should be selected such that the two buffer solutions used encompass the expected pH of the sample (buffer solutions with pH 4.00 and 7.00, pH 7.00 and pH 9.00 and, if appropriate, pH 7.00 and 12.00).

Determination of the content of impurities:

Method description for determination of trace elements in silica by means of high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS)
(analogously to test report A080007580)

1-5 g of sample material are weighed accurately to ± 1 mg into a PFA cup. 1 g of mannitol solution (approx. 1%) and 25-30 g of hydrofluoric acid (approx. 50%) are

added. After tilting briefly, the PFA cup is heated to 110°C in a heating block, such that the silicon present in the sample as hexafluorosilicic acid and the excess hydrofluoric acid evaporate off slowly. The residue is dissolved with 0.5 ml of nitric acid (approx. 65%) and a few drops of hydrogen peroxide solution (approx. 30%) for about 1 hour and
5 made up to 10 g with ultrapure water.

To determine the trace elements, 0.05 ml or 0.1 ml is taken from the digestion solutions, in each case transferred into a polypropylene sample tube, admixed with 0.1 ml of indium solution ($c = 0.1 \text{ mg/l}$) as an internal standard and made up to 10 ml with dilute nitric acid (approx. 3%). The preparation of these two sample solutions in different
10 dilutions serves for internal quality assurance, i.e. testing whether errors have been made in the measurement or sample preparation. In principle, it is also possible to work only with one sample solution.

Multielement stock solutions ($c = 10 \text{ mg/l}$) in which all elements to be analyzed apart from indium are present are used to make up four calibration solutions ($c = 0.1; 0.5; 1.0; 5.0 \text{ } \mu\text{g/l}$), again with the addition of 0.1 ml of indium solution ($c = 0.1 \text{ mg/l}$) to end
15 volume 10 ml. In addition, blank value solutions are prepared with 0.1 ml of indium solution ($c = 0.1 \text{ mg/l}$) for end volume 10 ml.

The element contents in the blank value, calibration and sample solutions thus prepared are quantified by means of high-resolution inductively coupled mass spectrometry
20 (HR-ICPMS) and by means of external calibration. The measurement is effected with a mass resolution ($m/\Delta m$) of at least 4000, and 10 000 for the elements potassium, arsenic and selenium.

The examples which follow are intended to illustrate the present invention in detail, but
25 do not restrict it in any way.

In a general embodiment, the process for reduction of purified silicon dioxide can be carried out as follows in a general process line. Proceeding from, for example, commercial waterglass, the waterglass can be purified by, in a first step, diluting the
30 waterglass, if necessary, with demineralized water to a content of from 1 to 30% by weight, preferably from 1 to 20% by weight, more preferably from 2 to 10% by weight

and most preferably from 2 to 6% by weight. Solid constituents can be removed by customary filtering processes known to those skilled in the art.

The resulting phase is then passed through a strongly acidic cation exchanger, especially according to step c), and the active silica in aqueous phase which emerges at one end of the cation exchanger is added dropwise directly to an acidic initial charge, especially at pH 0.5, and gel formation is awaited.

Alternatively, in accordance with the invention, gel formation may follow, especially by addition of ammonia.

The resulting silicon dioxide can be removed subsequently, in which case the washing medium has a pH of less than 2, preferably less than 1. Washing is continued until the washing medium, after addition of a few drops of H_2O_2 , visually no longer has any yellow color; the purified silicon oxide can optionally be dried.

However, it is preferably admixed at least partly with with in the moist state with crystalline sugar (pure carbon source), and optionally with a thermal black and siloxanes as a binder. The resulting pasty mixture is, for example, shaped in an extruder and sent to at least partial drying. According to the invention, the moist silicon dioxide is mixed with silicon carbide and optionally sugar, shaped and then dried or calcined, in order to be sent to the reduction step as a formulation, especially as a briquet.

In a preferred alternative, the aqueous phase of the active silica which emerges from the cation exchanger may form a gel. The gel is formed under argon and can preferably be accelerated by adding purely organic amines or ammonia.

The resulting briquets may then be pyrolyzed in order to obtain a pure carbon source comprising active carbon. The pyrolyzed carbon (active carbon) is added to the later process for preparing silicon to improve the thermal and/or electrical conductivity.

A further portion of the briquets can be pyrolyzed and calcined in order to prepare silicon carbide-containing briquets. These silicon carbide-containing briquets are added to the processes according to the invention at a later stage for the reduction of the

proportion of carbon monoxide in the actual reduction step to the pure silicon. The further function of the silicon carbide is that of an activator, of a reaction accelerant and for improving the conductivity.

- 5 To reduce the purified silicon dioxide, preference is given to subjecting briquets comprising the purified silicon dioxide, thermal black and sugar, and also briquets, to the aforementioned pyrolysis and reducing briquets which have been subjected to pyrolysis and calcination to pure silicon in a light arc furnace at around 1800°C. The addition of the silicon carbide content can be used to directly control the gas loading of
10 the process with carbon monoxide. According to the invention, the reaction is effected in a light arc furnace with a reactor in the sandwich design mentioned, in which the inner lining is composed of high-purity silicon carbide. The electrodes used are preferably segmented, silicon-infiltrated silicon carbide electrodes with a carbon fiber content. At the metal tap, molten silicon may be discharged, which, if required, can be sent to
15 controlled solidification.

The resulting silicon had the required purity for solar silicon.

- Steps c), d), d.2), d.3) will be explained hereinafter in more detail for a process in which these process steps are carried out successively in order to arrive at a purified silica sol
20 suitable for gel formation.

- The person skilled in the art is aware that, a the silica sol is used as a binder, the sol may receive a higher binding strength when the particle size of the colloidal silicon dioxide in the sol is smaller. On the other hand, the sol is less stable when the particle
25 size of the colloidal silicon dioxide in the sol is smaller. Therefore, to compensate for the latter disadvantage, the SiO_2 concentration in the sol has to be reduced. When, in general, the sol is used as a binder, it is desired to have a sufficient binding power, with the presence of a high SiO_2 concentration. With regard to the particle size distribution of the colloidal silicon dioxide in a sol, a broad size distribution would impart a higher
30 binding power to the sol than a silicon dioxide with a narrow size distribution.

The process for preparing a purified silicon oxide may proceed via the formation of a stable aqueous silica sol with an SiO_2 concentration of from 30 to 50% by weight, and which contains other polyvalent metals, especially metal oxides, than silicon dioxide in an amount of 300 ppm or less, and in which the colloidal silicon dioxide grains have a mean particle size of from 10 to 30 nm (nanometers).

The alkali metal silicate for use in step c) of the process may be any which is obtainable as a commercial industrial product, but preference is given to a water-soluble alkali metal silicate with a molar ratio of silicon to alkali metals, as present herein, of from approx. 0.5 to 4.5 as $\text{SiO}_2/\text{M}_2\text{O}$ (in which M is an alkali metal, especially sodium or potassium). Especially for the preparation of the purified silicon oxide as a cheap industrial product in an industrial scale plant, sodium waterglass is used with preference, which is a cheap industrial product, and has a molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ of from approx. 2 to 4.

However, the commercial waterglass product for industrial use generally contains other polyvalent metals, especially metal oxides, than silicon dioxide as impurities in an amount of from approx. 500 to 10 000 ppm, based on the SiO_2 content in the waterglass.

In step c), an aqueous phase of an alkali metal silicate is used, which is obtained by dissolving an alkali metal silicate which contains the polyvalent metal oxides, for example of the aluminum type or iron type, in water in a concentration of from 2 to 6% by weight as the SiO_2 content, which originates from the silicate.

The strongly acidic cation exchange resin of the hydrogen type for use in step c) may be any which has been used to date for removal of alkali metal ions from waterglass-containing aqueous solutions, and this is readily available as a commercial product for industrial use. One example of the resin is Amberlite IR-120.

In step c), the abovementioned alkali metal silicate-containing, aqueous solution is contacted with the abovementioned strong cation exchange resin of the hydrogen type.

The contact is preferably effected by passing the aqueous solution through a column filled with the ion exchange resin, especially Amberlite® IR 120, at from 0 to 60°C, preferably from 5 to 50°C, and the solution passed through the column is recovered as an active silica-containing, aqueous solution with an SiO₂ concentration of from 2 to 6% by weight and a pH of from 2 to 4, in step d). The amount of the strongly acidic cation exchange resin of the hydrogen type may be such that it is sufficient for the exchange of all alkali metal ions in the alkali metal silicate-containing aqueous solution for hydrogen ions. The rate at which the solution is passed through the column is preferably from approx. 1 to 10 per hour as a space velocity. When the resulting phase d) already has a sufficient purity of polyvalent metals, it may be sent to a gel formation, especially by addition of ammonia.

If this is not the case, a strong acid comprising inorganic acids such as hydrochloric acid, nitric acid and sulfuric acid is added in step d.2) step 1). Nitric acid in particular is the most preferred for increasing the percentage of elimination of the aluminum and iron content. The strong acid is added to the active silica-containing aqueous phase, as obtained after step d), before the phase decomposes after being obtained, and is preferably added immediately after it is obtained. The amount of the strong acid to be added is such that the pH of the resulting solution is within a range from 0 to 2, preferably from 0.5 to 1.8. After the addition, the phase is kept at a temperature of from 0°C to 100°C for a period of from 0.5 to 120 hours.

The strong acidic cation exchange resin of the hydrogen type used in step d.2) step 2) may be the same as used in the preceding step c). The strongly basic anion exchange resin of the hydroxyl type used in step d.2) step 2), especially Amberlite® IR 440, may be any which has been used to date for removal of anions from a customary silica sol, and such a material is readily obtainable as a commercial product.

In step d.2) step 2), the aqueous solution obtained in step d.2) step 1) is first contacted with the above strongly acidic cation exchange resin of the hydrogen type. The contact is effected preferably by passing the aqueous solution through a column filled with the abovementioned strongly acidic cation exchange resin of the hydrogen type in an

amount sufficient for ion exchange of all metal ions in the solution, at from 0 to 60°C, preferably at from 5 to 50°C, and at a space velocity of from 2 to 20 per hour.

Subsequently, the resulting aqueous phase, preferably immediately after it has been obtained, is contacted in step d.2) step 3) with the abovementioned strongly basic anion exchange resin of the hydroxyl type at a temperature of from 0 to 60°C, preferably from 5 to 50°C. The contact can also be effected by passing the aqueous phase through a column filled with the abovementioned strongly basic anion exchange resin of the hydroxyl type at a space velocity of from 1 to 10 per hour. The resulting aqueous solution can, immediately after it is obtained, be contacted with the abovementioned strongly acidic cation exchange resin of the hydrogen type at from 0 to 60°C, preferably from 5 to 50°C. The contact can also be effected by passing the aqueous phase through a column filled with the abovementioned strongly acidic cation exchange resin of the hydrogen type in an amount sufficient for the ion exchange of all metal ions in the solution, at a space velocity of from 1 to 10 per hour. Subsequently, the aqueous phase is obtained in step d.2) step 4), and the resulting solution is an active silica-containing aqueous phase with an SiO₂ concentration of from 2 to 6% by weight and a pH of from 2 to 5. This is then used in the next step d.3) step 5).

The aqueous phase composed of sodium hydroxide or potassium hydroxide used in step d.3) step 5) can be obtained by dissolving sodium hydroxide or potassium hydroxide of a commercial product for industrial use, which preferably has a purity of 95% or more, in decationized industrial water, preferably in a concentration of from 2 to 20% by weight. In step d.3) step 5), the sodium hydroxide- or potassium hydroxide-containing aqueous solution is added to the active silica-containing aqueous solution, as obtained from step d.2) step 4), preferably immediately after it has been obtained, in a molar ratio of SiO₂/M₂O of from 60 to 200, where M is defined as mentioned above. The addition can be effected at a temperature in the range from 0°C to 60°C, but is preferably carried out at room temperature for a possibly shorter period. The addition allows a stabilized active silica-containing aqueous solution with an SiO₂ concentration of from 2 to 6% by weight and a pH of from 7 to 9 to be obtained. Even though the aqueous phase thus prepared is stable for a long period, it is preferably used in the next step d.3) step 6) within 30 hours.

The apparatus for performing step d.3) step 6) may be a customary acid-resistant, alkali-resistant and pressure-resistant vessel which is equipped, for example, with a stirrer, a temperature control device, a liquid level sensor, a pressure reducer, a liquid feed device or vapor cooling device. In step d.3) step 6), all or a portion (1/5 to 1/20) of the stabilized active silica-containing aqueous solution which has been obtained in step d.3) step 5) is first introduced into the vessel as a stock solution. In industrial scale production plants, it is preferred that the entire aqueous phase from the present step is used as the stock solution, and a further stabilized active silica-containing aqueous phase is prepared separately by the abovementioned continuous steps a) to d.3) step 5).

The newly prepared aqueous phase, in an amount of from 5 to 20 times the stock solution, is used as a feed solution within 30 hours after the separate preparation of the feed solution. When, on the other hand, a portion of from 1/5 to 1/20 of the solution as prepared in the preceding step d.2) step 5) is used as the stock solution in step d.3) step 6), the remaining aqueous phase is used as feed solution.

The liquid temperature in step d.3) step 6) in the interior of the vessel is set to from 70 to 100°C, preferably to from 80 to 100°C, while the internal pressure of the vessel is controlled such that water can evaporate from the liquid under controlled conditions. In addition, the feed rate of the feed solution and the removal rate of the water evaporated are adjusted such that the amount of liquid within the vessel remains constant and that the feed of the feed solution can be ended within a period of from 50 to 200 hours. The feed of the aqueous phase and the removal of the evaporated water are carried out constantly and continuously or at intervals during step d.3) step 6), but they are preferably carried out in such a way that the amount of the liquid within the vessel remains constant during the step. It is also likewise preferred that the feed rate of the feed solution remains constant.

The strongly acidic cation exchange resin of the hydrogen type for use in step d.3) step 7) may be the same as that used in the preceding steps c) and d.2) step 2). The

strongly basic anionic exchange resin of the hydroxyl type for use therein may likewise be a customary anion exchange resin, which is the same as used in step d.2) step 2). The stable aqueous sol can be contacted with the ion exchange resin in step d.3) step 7) in the same way as in step d.2) step 2). Particular preference is also given to
5 contacting the aqueous phase obtained from the contact with the anion exchange resin with the cation exchange resin.

The amine or preferably ammonia for use in the step for gel formation may be a commercial product for industrial use, but it is preferably a high-purity product. It is
10 desirable that it is used in the form of aqueous ammonia with an ammonia concentration of from approx. 5 to 30% by weight. Instead of ammonia, it is also possible to use quaternary ammonium hydroxides, guanidine hydroxides or water-soluble amines. However, ammonia is preferred in general, provided that it is not undesired for specific reasons.

15 In the gel formation, the abovementioned ammonia is added to the aqueous sol, in step b.2), b.3) or after step d.3) step 8), preferably immediately after formation of the sol. The addition can be effected at a temperature of from 0 to 100°C, but is preferably carried out at room temperature. The amount of ammonia to be added is preferably such that
20 the resulting silica sol may have a pH of from 8 to 10.5. Optionally, an acid or ammonia salt which is free of any kind of metal components may be added to the aqueous phase, especially to the sol, if desired, in an amount of 1000 ppm or less.

25 The mean particle size of the colloidal particles in the silica sol is calculated via the specific surface area which is measured by means of the nitrogen gas absorption method, the so-called BET method. The size of the colloidal particles can be observed with an electron microscope. The silica sol obtained in the gel formation in steps b.2), b.3) or after step d.3) step 8), which has a mean particle size of 10 nm (nanometers), has a particle size distribution from the minimum particle size of approx. 4 nm
30 (nanometers) up to the maximum particle size of approx. 20 nm (nanometers), and a further silica sol, which has a mean particle size of 30 nm (nanometers), has a particle

size distribution from the minimum particle size of approx. 10 nm (nanometers) up to the maximum particle size of approx. 60 nm (nanometers).

In a preferred process, an aqueous phase of an alkali metal ion-free active silica is formed when the alkali metal silicate-containing aqueous phase is contacted with the strongly acidic cation exchange resin of the hydrogen type. The active silica in the aqueous solution is present in the form of silica or oligomers thereof with a particle size of 3 nm or less, and the aqueous solution is unstable, such that it gels within approx. 100 hours, even in the presence of polyvalent metals such as aluminum. The higher the SiO_2 concentration in the solution or the higher the temperature of the solution, the greater the extent to which such instability is observed. When, accordingly, a large amount of silica sol is to be prepared in an industrial plant, it is advisable that the concentration of the active silica in the aqueous phase to be formed in step a) or c) does not exceed approx. 6% by weight, and that the aqueous phase which has such a reduced SiO_2 concentration is formed at room temperature. When, more particularly, the alkali metals or polyvalent metals which are present in the raw material are incorporated into the interior of the silica polymer particles, such metal is barely removed from the particles. The aqueous solution should therefore have a relatively low concentration, such that the polymerization of the silica in the solution barely proceeds. Moreover, with regard to the avoidance of gradual polymerization of the silica, which is unavoidable even at room temperature, the entire aqueous solution of the active silica formed should be used as early as possible after formation in the next step. An SiO_2 concentration in the active aqueous silica solution of less than approx. 2% by weight is inefficient, since the amount of water to be removed during the concentration step of the silica sol which is to be formed later would be too much. In step c), the SiO_2 concentration of the alkali metal silicate-containing aqueous solution is adjusted to from 2 to 6% by weight before it is contacted with the cation exchange resin, such that the SiO_2 concentration of the aqueous solution of the active silica formed in step c) may be from 2 to 6% by weight, and such that the active silica-containing aqueous phase thus formed can be used directly in the next step d.2) immediately after it has been formed or, when the purity is sufficient, is sent directly to gel formation, especially by addition of ammonia.

In step c), the aqueous phase is supplied to the cation exchange resin-filled column which is preferably used in this step advantageously at a solution flow rate of from approx. 1 to 10 per hour as the space velocity, with removal of a possibly relatively large amount of metal ions from the solution. In addition, it is desired that the solution temperature is from 0 to 60°C, such that barely any polymerization, rise in the viscosity or gelation of the active silica solution occurs during the passage through the column. In steps c), d), d.2) step 2) and d.2) step 2) to d.2) step 4), no particular conditions are needed to stabilize the active silica-containing aqueous phase. It is therefore important to maintain the abovementioned SiO₂ concentration and the temperature in these steps.

The strong acid to be added in step d.2) step 1) has the function of converting the contaminating metal components, such as alkali metals or polyvalent metals which are bound to the active silica or to the interior of the polymer thereof and which are not present in the form of dissociated ions, to dissociated ions in the solution. Since the active silica has a lower degree of polymerization, the polyvalent metals can be extracted readily from the active silica. It is also desired that the addition of the strong acid to the active silica-containing aqueous solution which is obtained in step c) is completed as early as possible.

If, however, the amount of the strong acid to be added was increased such that the pH of the resulting active silica-containing aqueous solution becomes less than 0, the removal of the anions in the subsequent steps d.2) step 2) to d.1) step 4) becomes difficult, even though the removal of the metal components in the present step d.2) step 1) would be improved. If, moreover, the strong acid is added in such an amount that the pH of the resulting solution becomes more than 2, the effect of the removal of the metal components becomes poor. Among the strong acids, nitric acid has a particularly high action for removal of metal components, such as aluminum components or iron components. The action of the strong acid for removal of the polyvalent metal components also depends on the temperature of the phase and the treatment time. When, for example, the temperature is from 0 to 40°C, the treatment time is from 10 to 120 hours; when the former is from 40 to 60°C, the latter is preferably from 2 to 10

hours, and when the former is from 60 to 100°C, the latter is preferably from 0.5 to 2 hours. If the phase is treated with the strong acid over a prolonged period, the viscosity of the aqueous phase would rise or it would gelate.

- 5 In step d.2) step 2) to d.2) step 4), the metal ions which have dissolved in the solution and the anions from the acid as added in step d.2) step 1) are removed by means of cation exchange resin and anion exchange resin. The solution from the first cation exchange resin treatment contains the anions of the acid added in step d.2) step 1), such that the dissolved metal ions quite simply remain in the solution. The amount of
10 the remaining metal ions in the solution after the anion exchange resin treatment may be such that the solution has a pH of from 5 to 7. In this case, however, the solution would gelate within approx. 1 hour. The two-stage treatment with the cation exchange resin which is carried out after removal of the anions from the solution by treatment with the anion exchange resin can also advantageously remove such undesired dissolved
15 metal ions.

Since the active silica-containing aqueous phase from step d.2) step 4) is so unstable that it gelates within 6 hours, it is employed in the next step d.3) step 5) as soon as possible, preferably immediately after formation of the solution. When the amount of the
20 amount of sodium hydroxide or potassium hydroxide to be added to the unstable active silica-containing aqueous phase is less than 60, based on the molar ratio of $\text{SiO}_2/\text{M}_2\text{O}$, the active silica is readily polymerized and, as a result, the growth of the particles in step d.3) step 6) would be insufficient or the sol formed would be unstable. When, however, on the other hand, the amount is so small that the molar ratio is more than
25 200, it would be impossible to increase the particle size of the colloidal silicon dioxide particles, even if the resulting phase is treated in the same way as in step d.3) step 6). Even though the solution obtained in step d.3) step 5) is stable for quite a long period at room temperature, the polymerization of the active silica therein would be accelerated at a high temperature. It is therefore particularly preferred that the solution obtained in step
30 d.3) step 5) is applied in the next step d.3) step 6) within 30 hours. The sodium hydroxide or potassium hydroxide to be added in step d.3) step 5) gives rise to a higher growth rate for colloidal silicon dioxide particles to a size of from 10 to 30 nm in the next

step d.3) step 6). This rate is, for example, twice that or more than that with the same molar amount of other bases, such as ammonia or amine.

Owing to such a high growth rate, the feed rate of the feed solution in step d.3) step 6) can be increased, and the production rate for the silica sol as the end product according to the invention is therefore increased to an extremely high degree. In addition, the feeding of the feed solution, which is to be carried out at such a high rate in step d.3) step 6), is also advantageous with regard to the preparation of colloidal inhomogeneous silicon dioxide particles in the silica sol formed and for broadening of the particle size distribution of the particles therein. In step d.3) step 6), water is evaporated from the sol formed simultaneously with the feeding of the feed solution. The evaporated water is removed from the reaction system to increase the preparation rate of the highly concentrated silica sol. If the liquid temperature in step d.3) step 6) is lower than 70°C, the colloidal silicon dioxide particles cannot grow sufficiently in the phase such that the resulting solution comprises colloidal silicon dioxide particles with a mean particle size of 10 nm or less. If the silica sol containing such small silicon particles is concentrated, the viscosity of the liquid increases or it gels, such that it is no longer possible to obtain a stable sol with an SiO₂ concentration of 30% by weight or more. The rate of growth would be higher if the temperature of the liquid is higher than 70°C. If, however, the temperature is higher than 100°C, the growth rate increases to such a high degree that the control of the mean particle size of the particles formed becomes difficult.

Where the amount of the feed solution to be added is less than 5 times the amount of the stock solution, the particles cannot be allowed to grow up to the mean particle size of more than 10 nm. In this case, it is likewise impossible to obtain a concentrated stable sol or silica sol with a concentration of 30% by weight or more.

The mean particle size of the colloidal purified silicon dioxide particles to be formed increases with an increasing amount of feed liquid to be fed in. If, however, the amount of the feed liquid to be fed in is more than 20 times that of the stock solution, the mean particle size of the particles to be formed disadvantageously becomes greater than 30 nm. In such a case, a sol with a high binding power cannot be obtained.

In spite of the above situation, the relationship between the amount of feed liquid and the mean particle size of the colloidal particles to be formed is influenced further by the feed rate of the feed solution. Where, for example, the feed solution is added to the stock solution in an amount of from 5 to 20 times that of the stock solution within a period of 50 hours, colloidal silicon dioxide particles with a mean particle size of greater than 10 nm cannot be formed. This is probably based on the following reasons: in step d.3) step 6), a portion of the active silica in the feed solution added does not adhere to the surface of the colloidal silicon dioxide particles, but rather forms new core particles in the aqueous phase. When, more particularly, the feed rate of the feed solution is high, the proportion of the amount of the active silica which is consumed for such new cores to that which is consumed for the growth of the silicon dioxide particles will rise. It is therefore impossible to efficiently form colloidal silicon dioxide particles with a mean particle size of 10 nm or more in this case.

The feeding of the feed solution at too high a rate should therefore be avoided.

However, the feeding of the feed solution in an amount of from 5 to 20 times the stock solution over a period of more than 200 hours is inefficient for industrial production of silica sol. For the production of sol or silica sol with a constant quality in an industrial plant, the feeding of the feed solution is preferably carried out continuously for a period of from 50 to 200 hours. If, in step d.3) step 6), the liquid level in the interior of the vessel fluctuates along the wall of the vessel owing to the feeding of the feed solution and the concentration of the liquid in the vessel, which is carried out continuously, the silica adheres to the wall of the vessel along the fluctuating liquid level, and so a favorable sol product cannot be obtained. Accordingly, in step d.3) step 6), the feed liquid of the feed solution and the removal rate of evaporated water will preferably be such that the liquid level in the vessel remains the same. If the SiO_2 concentration of the silica sol which is formed in step d.3) step 6) becomes up to more than 50% by weight, the viscosity of the resulting sol rises to an undesired value. It is therefore undesired to form such a sol with a high concentration in step d.3) step 6). In step d.3) step 6), the sodium and potassium ions supplied to the sol beforehand are removed again by the cation exchanger. For an improved removal of the potassium or sodium ions, preference is

given to working in two or more stages with one cation exchanger. The cation-free sol obtained in step d.3) step 7) does not exhibit the same instability as active silica-containing aqueous phase, but the stability is still insufficient. The treatment with the ion exchanger is therefore preferably not carried out at too high a temperature. The sol is in the step of gel formation as far as possible after completion of step d.3) step 8), preferably immediately after step d.3) step 8). For stabilization, ammonia is preferably added to the sol, as a result of which the sol obtained may have a pH of from 8 to 10.5. Ammonia can be purchased as an aqueous ammonia solution in high purity. A particular advantage of the ammonia used is that it can be evaporated readily out of the silica sol.

Examples for purification of the aqueous silicon oxide solution

Example 1

A 1000 ml glass apparatus with dropping funnel, stirrer, thermometer and pH electrode was initially charged with 700 ml of waterglass with a SiO_2 content of 25 g/l. The dropping funnel was charged with 100 ml of 10% sulfuric acid, and the waterglass was heated to 88°C with a heating mantle. From a pH of approx. 9.5, the pH electrode was installed, and sulfuric acid was used for acidification down to a pH of approx. 8.5.

A slightly turbid sol was obtained, which was first purified by means of Amberlite IR-120 cation exchanger. After a first fraction of 150 ml, the main fraction of 610 g was taken. After the cation exchanger, the solution had a pH of 1.0 and a conductivity of 43.8 ms/cm. The turbidity was about as significant as before the cation exchanger.

Thereafter, the sol was passed through an Amberlite IRA-400 anion exchanger. A first fraction of 150 ml was discarded, and the main fraction of 435 g was collected. The sol then had a pH of 6.65 and a conductivity of 54 $\mu\text{s}/\text{cm}$. The turbidity had decreased but was still very slightly visible.

Subsequently, 0.2 g of 40% potassium hydroxide solution (5 drops) was used to adjust to a final pH of 8.45 and establish a conductivity of 99 $\mu\text{s}/\text{cm}$.

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403 g (395 ml) of the sol were concentrated in a 500 ml three-neck flask with stirrer and distillation system. For this purpose, 360 ml of water were distilled off.

- 5 30 g of concentrated sol with a pH of 8.7 and an SiO_2 content of 26.8% by weight were obtained. The dried product formed glassy flakes.

The concentrated sol had the impurities specified in table 2 and was converted to high-purity silicon dioxide by gelation.

10

Example 2:

- The standard waterglass was diluted to an SiO_2 content of 4% by weight and adjusted with sulfuric acid to a pH of 1.09 (298.95 g of waterglass diluted with 1051.05 g of
15 demineralized water and added to 650 g of 10% sulfuric acid).
Subsequently, 177.5 g of 10% sodium hydroxide solution were used to establish a pH of 2.01.

- The solution was left to stand overnight and, the next day, added at pH 2 to an acidic
20 ion exchanger (Amberlite IR-120). Once the first fraction of 293 g had ended, a pH of approx. 1 was measured. The first fraction was discarded and the main fraction of 1882.5 g of acidic waterglass with a pH of 1.45 and a conductivity of 49.1 ms/cm was collected.

- 25 1700 g of the acidic waterglass were added to 991 g of demineralized water and 29.0 g of dissolved NaOH. This formed a white precipitate which dissolved again within a few seconds after the end of addition. The clear solution had a pH of 10.83 and a conductivity of 33.1 ms/cm. The waterglass had the impurities specified in table 2.

- 30 A portion of the waterglass thus purified was concentrated by evaporation and then added to a sulfuric acid solution (96% by weight) such that the pH of the precipitation suspension was kept below 2. After appropriate washing steps in which a pH of below 2

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was first maintained in the wash medium, filtration and drying, high-purity SiO₂ was obtained.

Table 2: Analysis results of the products from examples 1 and 2

5

Impurity	Content in	Waterglass before ion exchanger	Example 1	Example 2
Aluminum	ppm	250	0.4	8
Boron	ppm	< 2	1.6	N.D.
Calcium	ppm	25	< 1	1
Iron	ppm	48	0.2	7
Phosphorus	ppm	< 10	< 0.5	N.D.
Titanium	ppm	46	0.2	7
Zinc	ppm	1	0.5	N.D.

N.D. = not determined

10 **Examples – pyrolysis**

Comparative example 1

Commercial refined sugar was melted in a quartz tube under protective gas and then heated to about 1600°C. In the course of this, the reaction mixture foamed significantly, and some escaped – caramel formation was likewise observed, and the pyrolysis product adhered to the wall of the reaction vessel; cf. Figure 1a).

15

Example 3

Commercial refined sugar was mixed with SiO₂ (Sipernat® 100) in a weight ratio of 20:1, melted and heated to around 800°C. In the course of this, no caramel formation was observed, nor did any foam formation occur. A graphite-containing, particulate pyrolysis product was obtained, which advantageously essentially had not adhered to the wall of the reaction vessel.

20

Pyrolysis and calcination examples

Comparative example 2:

Commercial refined sugar was melted in a quartz tube and then heated to about
5 1600°C. The reaction mixture foams significantly in the course of heating and some
escaped from the quartz tube. At the same time, caramel formation is observed. The
pyrolysis product formed adheres to the wall of the reaction vessel (Figure 1a).

Example 4a:

10 Commercial refined sugar was mixed together with SiO₂ (Sipernat® 100) in a weight
ratio of 1.25:1, melted and heated to about 800°C. Caramel formation is observed; there
is no foam formation. A graphite-containing, particulate pyrolysis product is obtained,
which, more particularly, has not adhered to the wall of the reaction vessel (Figure 1b).
(Figure 2 is a microscopy image of the pyrolysis product from Example 3a).
15 The pyrolysis product has been distributed on and presumably also within the pores of
the SiO₂ particles. The particulate structure is preserved.

Example 4b:

Commercial refined sugar was mixed together with SiO₂ (Sipernat® 100) in a weight
20 ratio of 5:1, melted and first heated to about 800°C and then heated further to about
1800°C. Caramel formation is observed; there is no foam formation. A silicon carbide
with fractions of graphite is obtained. Figures 3 and 4 are microscopy images of two
samples of the calcination product. XPS spectra and determination of the binding
energies were used to demonstrate the formation of silicon carbide. In addition, Si-O
25 structures were detected. The formation of graphite was concluded by the metallic
shimmer under a light microscope.

Example 5:

In a rotary tube furnace with SiO₂ spheres for heat distribution, a fine particulate
30 formation of sugar coated onto SiO₂ particles is converted at elevated temperature. For
example, prepared by dissolving sugar in an aqueous silica solution with subsequent

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drying and, if necessary, homogenization. Residual moisture was still present in the system. About 1 kg of the formulation was used.

The residence time in the rotary tube furnace is guided by the water content of the fine particulate formulation. The rotary tube furnace was equipped with a preheating zone for drying of the formulation, then the formulation passed through a pyrolysis and calcination zone with temperatures of from 400°C to 1800°C. The residence time comprising the drying step, pyrolysis and calcination step was about 17 hours. Over the entire process, the process gases formed, such as water vapor and CO, were removed from the rotary tube furnace in a simple manner.

The SiO₂ used had a boron content of less than 0.1 ppm, a phosphorus content of less than 0.1 ppm and an iron content of less than about 0.2 ppm. The iron content of the sugar was determined to be less than 0.5 ppm before the formulation.

After the pyrolysis and calcination, the contents were determined again, which determined boron and phosphorus contents of less than 0.1 ppm, and an increase in the iron content to 1 ppm. The increased iron content can only be explained by the product coming into contact by the contact with parts of the furnace contaminated with iron.

Example 6:

Example 5 was repeated, except that the laboratory rotary tube furnace had been coated beforehand with high-purity silicon carbide. This was reacted at elevated temperature with SiO₂ spheres for heat distribution and a fine particulate formulation containing sugar, coated onto SiO₂ particles. Prepared, for example, by dissolving sugar in an aqueous silica solution with subsequent drying and, if necessary, homogenization. Residual moisture was still present in the system. About 10 g of the formulation were used.

The residence time in the rotary tube furnace is guided by the water content of the fine particulate formulation. The rotary tube furnace was equipped with a preheating zone

for drying of the formulation, then the formulation passed through a pyrolysis and calcination zone with temperatures of from 400°C to 1800°C. The residence time comprising the drying step, pyrolysis and calcination step was about 17 hours. Over the entire process, the process gases formed, such as water vapor and CO, were removed
5 from the rotary tube furnace in a simple manner.

The SiO₂ used had a boron content of less than 0.1 ppm, a phosphorus content of less than 0.1 ppm and an iron content of less than about 0.2 ppm. The iron content of the sugar was determined to be less than 0.5 ppm before the formulation.

10 After the pyrolysis and calcination, the contents were determined again, which determined boron and phosphorus contents of less than 0.1 ppm, and that the iron content was still below 0.5 ppm.

15 **Example 7:**

In a light arc furnace, a fine particulate formulation of pyrolyzed sugar on SiO₂ particles is converted at elevated temperature. The formulation of pyrolyzed sugar had been prepared beforehand by means of pyrolysis in a rotary tube furnace at about 800°C.

20 About 1 kg of the fine particulate pyrolyzed formulation was used. During the reaction in the light arc furnace, the process gas CO formed can escape easily via the intermediate spaces formed by the particulate structure of the SiO₂ particles, and be removed from the reaction chamber. The electrodes utilized were high-purity graphite electrodes, and the reactor base was likewise lined using high-purity graphite. The light arc furnace was
25 operated at from 1 to 12 kW.

After the reaction, high-purity silicon carbide with fractions of graphite, i.e. in a carbon matrix, was obtained.

The SiO₂ used had a boron content of less than 0.17 ppm, a phosphorus content of less than 0.15 ppm and an iron content of below about 0.2 ppm. The iron content of the
30 sugar was determined to be less than 0.7 ppm before the formulation.

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After the pyrolysis and calcination, the contents in the silicon carbide were determined again, which determined the boron and phosphorus contents still to be below 0.17 ppm and below 0.15 ppm respectively, and the iron content still to be below 0.7 ppm.

5 **Example 8:**

A corresponding reaction of a pyrolyzed formulation according to Example 5 was effected in a microwave reactor. To this end, 0.1 kg of a dry, fine particulate formulation of pyrolyzed sugar on SiO₂ particles was converted at frequencies above 1 Gigawatt to
10 silicon carbide in a carbide matrix. The reaction time depends directly on the power introduced and the reactants.

When a reaction is effected proceeding from carbohydrates and SiO₂ particles, the reaction times are correspondingly longer.

15

Example 9:

SiO₂ (AEROSIL[®] OX 50) and C (graphite) were reacted in a weight ratio of approx 75:25 in the presence of SiC.

20 Process procedure: an electrical light arc which serves as the energy source is ignited in a manner known per se. A creeping commencement of reaction through emergence of gaseous compounds between SiO₂ and C is observed. Subsequently, 1% by weight of pulverulent SiC is added. After a very short time, a very significant increase in the reaction is observed by the occurrence of luminescence. Subsequently, after the
25 addition of SiC, the reaction proceeded even within intense, bright orange luminescence (approx. 1000°C). The solid obtained after the reaction had ended was identified as silicon on the basis of its typical dark brown color (M. J. Mulligan et al. Trans. Soc. Can. [3] **21** III [1927] 263/4; Gmelin 15, part B p. 1 [1959]), and by means of scanning electron microscopy (SEM).

30

Example 10

SiO₂ (AEROSIL[®] OX 50) and C were reacted in a weight ratio of approx. 65:35 in the presence of SiC.

5

Process procedure: an electrical light arc which serves as the energy source is ignited in a manner known per se. The reaction between SiO₂ and C begins in a creeping manner. The occurrence of gases to be observed. 1% by weight of pulverulent SiC is added, which, after a short time, leads to a significant increase in the reaction, which is recognizable by the occurrence of luminescence. After addition of SiC, the reaction proceeded further for a certain time within intense, flickering luminescence. The solid obtained after the reaction had ended was identified as silicon by means of SEM and EDX analysis (energy-dispersive X-ray spectroscopy).

10

15 Comparative example 3

SiO₂ (AEROSIL[®] OX 50) and C were reacted in a tube as a 65:35 mixture at high temperature (> 1700°C). The reaction barely started and proceeded without noticeable advance. Bright luminescence was not observed.

Claims:

1. A process for preparing pure silicon, comprising the reduction of purified silicon oxide, preferably purified silicon dioxide, which has been purified as silicon oxide
5 essentially dissolved in the aqueous phase and, based on the silicon oxide, has a content of other polyvalent metals of less than or equal to 300 ppm, preferably less than 100 ppm, more preferably less than 50 ppm, most preferably less than 10 ppm in relation to the metal, with one or more pure carbon sources.
- 10 2. A process according to claim 1, characterized in that the aqueous purification of the silicon oxide comprises at least one process step in which the aqueous silicon oxide solution is contacted with an ion exchanger, preferably with at least one anion and/or cation exchanger.
- 15 3. A process according to claim 1 or 2, characterized in that the purified silicon oxide is obtained from the silicon oxide solution by means of gel formation or spray drying or by concentrating the silicon oxide solution to a
20 concentration greater than or equal to 10% by weight of SiO₂ with subsequent contacting with an acidifying agent.
4. A process according to claim 3, characterized in that
25 the gel formation is carried out with addition of ammonia and/or a calcination of the gel is performed at temperatures up to 1500°C, especially around 1400°C.
5. A process according to any one of claims 1 to 4, characterized in that
30 the purification of the silicon oxide essentially dissolved in the aqueous phase comprises the following steps a), b), c), d) and e):

- a) providing silicates dissolved in the aqueous phase, especially an aqueous phase with a content of from 1 to 30% by weight of SiO_2 ;
optionally adding soluble alkaline earth metal and/or transition metal salts and optionally filtering the aqueous phase to remove sparingly soluble alkaline earth metal and/or transition metal salts and/or other insoluble constituents,
5 optionally contacting the aqueous phase with an immobilized compound which complexes boron or boron compounds and
- b) optionally adjusting the aqueous phase to a content of from 2 to 6% by weight of SiO_2 , which additionally comprises other polyvalent metal oxide than silicon dioxide, and
10
- c) contacting with a strongly acidic cation exchange resin of the hydrogen type, in an amount which is sufficient for the ion exchange of essentially all other metal ions in the aqueous phase, the temperature of the aqueous phase being in the range from 0°C to 60°C ,
- 15 d) obtaining the aqueous phase of an active silica with an SiO_2 concentration of from 2 to 6% by weight and a pH of from 0 to 4,
- e) obtaining purified silicon oxide.

6. A process according to claim 5,

20 characterized in that

the aqueous phase from step d), before step e), is alternatively treated further by the following steps a.2), b.2), c.2) or d.2):

- a.2) adding to an acidifying agent or adding an acidifying agent, the aqueous phase from step d) optionally having been brought beforehand to a concentration of
25 SiO_2 greater than or equal to 10% by weight, or
- b.2) performing a gel formation, optionally followed by a thermal aftertreatment and/or spray-drying, or
- c.2) spray-drying the aqueous phase or
- d.2) further treatment by, in a first step 1), adding a strong aqueous acid to the
30 aqueous phase composed of active silica from step d), such that the pH is from 0 to 2.0, and keeping the aqueous phase thus obtained at from 0°C to 100°C for from 0.5 to 120 hours; by, in a second step 2), contacting the resulting aqueous

phase with a strongly acidic cation exchange resin of the hydrogen type in an amount which is sufficient for the ion exchange of essentially all other metal ions in the aqueous phase, the temperature of the aqueous phase being in the range from 0 to 60°C, then, in the third step 3), contacting the aqueous phase with a strongly basic anion exchange resin of the hydroxyl type in an amount which is sufficient for the ion exchange of essentially all anions in the aqueous phase, the temperature of the aqueous phase being from 0 to 60°C, then, in the fourth step 4), obtaining the aqueous phase of the resulting active silica, which is essentially free of other dissolved substances than the active silica, and has a concentration of SiO₂ of from 2 to 6% by weight and a pH of from 2 to 5.

7. A process according to claim 6,
characterized in that

the aqueous phase obtained in the fourth step 4) in d.2) is alternatively treated further by one of the following steps a.3), b.3), c.3) or d.3)

a.3) concentrating the aqueous phase from the fourth step 4) of d.2) to a concentration of SiO₂ greater than or equal to 10% by weight and adding to an acidifying agent or adding an acidifying agent or

b.3) performing a gel formation, optionally followed by a thermal aftertreatment and/or spray-drying, or

c.3) spray-drying the aqueous phase or

d.3) further treatment in a fifth step 5), by adding an aqueous sodium hydroxide and/or potassium hydroxide phase to the aqueous phase of the active silica, where the molar ratio of SiO₂/M₂O is from 60 to 200, and M is independently sodium or potassium and originates from the hydroxide added, and the SiO₂ originates from the aqueous phase of the active silica, and the temperature of the resulting aqueous phase is also kept at from 0 to 60°C and a stabilized aqueous phase of an active silica with an SiO₂ concentration of from 2 to 6% by weight and a pH of from 7 to 9 is maintained, in a sixth step 6) the stabilized aqueous phase of the active silica is partly or fully added to a vessel as a stock solution and the stock solution is kept at from 70 to 100°C, the vessel can be kept under standard pressure or under reduced pressure, more particularly the

water removed is metered in by supplying further stabilized aqueous phase of the active silica from the preceding component step d.3) step 5) essentially to the degree in which water is removed, to form a stable aqueous silica sol with an SiO_2 concentration of from 30 to 50% by weight and a particle size of the colloidal silicon dioxide of from 10 to 30 nm; in a seventh step 7), the stable aqueous silica sol is contacted with a strongly acidic cation exchange resin of the hydrogen type at from 0 to 60°C in such an amount that essentially all metal ions present in the sol are exchanged, the resulting aqueous phase is subsequently contacted with a strongly basic anion exchanger of the hydroxyl type at from 0 to 60°C in such an amount that an aqueous acidic silica sol which is essentially free of other polyvalent metals, especially metal oxides, than silicon oxide is obtained in the eighth step 8) and performing a gel formation.

8. A process according to claim 6 or 7,

characterized in that

the gel formation in step b.2), b.3) or after step d.3) step 8) is effected with addition of an amine and/or ammonia.

9. A process according to claim 8,

characterized in that

the gel formation is effected at a temperature in the range from 0 to 100°C and, more particularly, the pH is kept at from 0 to 7 to form a stable aqueous sol.

10. A process according to any of claims 1 to 9,

characterized in that

silicon carbide is added as an activator and/or carbon source in one process step, preferably in such a way that purified silicon oxide is present together with at least one pure carbon source which may be silicon carbide, and/or a silicon carbide and/or silicon

a) in a formulation comprising the purified silicon oxide and at least one pure carbon source and optionally silicon carbide and optionally silicon and/or

- b) in a formulation comprising the purified silicon oxide and optionally silicon carbide and optionally silicon and/or
- c) in a formulation comprising at least one pure carbon source and optionally silicon carbide and optionally silicon,
- 5 the particular formulation optionally containing binder.

11. A process according to any one of claims 1 to 10,
characterized in that
the pure carbon source comprises an organic compound of natural origin, a
10 carbohydrate, graphite, coke, coal, carbon black, thermal black, pyrolyzed carbohydrate, especially pyrolyzed sugar.

12. A process according to any one of claims 1 to 11,
characterized in that
15 the process comprises a step in which a carbohydrate is pyrolyzed in the presence of silicon oxide, preferably high-purity silicon dioxide, as a defoamer, and in this way at least some of the carbon required as a carbon source is obtained.

13. A process according to claim 12,
20 characterized in that
the carbohydrate, preferably an aqueous solution of a carbohydrate, is purified before the pyrolysis by contacting with at least one ion exchanger.

14. A process according to either of claims 12 and 13,
25 characterized in that
the carbohydrate, preferably an aqueous solution of a carbohydrate, and the silicon oxide, preferably the high-purity silicon dioxide, are subjected to a shaping process before the pyrolysis.

30 15. A process according to any one of claims 1 to 14,
characterized in that

the purified silicon oxide is reduced with one or more pure carbon sources in a light arc furnace, in a thermal reactor, in an induction furnace, rotary tube furnace and/or in a microwave furnace.

- 5 16. A process according to any one of claims 1 to 15,
characterized in that
the purified silicon oxide is reduced with one or more pure carbon sources in a reaction chamber lined with high-purity refractory materials and any electrodes used consist of high-purity material.

- 10 17. A process according to any one of claims 1 to 16,
characterized in that
molten pure silicon is obtained and is purified further by zone melting or controlled solidification.

- 15 18. A process according to any one of claims 1 to 17,
characterized in that
it comprises the following steps:
a) converting a silicon oxide, preferably silicon dioxide, containing impurities to
20 silicon oxide dissolved in the aqueous phase,
b) purifying the silicate dissolved in the aqueous phase by contacting with a
strongly acidic cation exchange resin, especially of the hydrogen type,
c) obtaining a precipitate of purified silicon oxide and
d) converting the purified oxide thus obtained to silicon in the presence of one or
25 more carbon sources and optionally by addition of an activator.