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POLYSILANE-BASED CERAMIC PRECURSOR COMPOSITIONS AND CERAMICS OBTAINED BY
PYROLYSIS OF THE SAID COMPOSITIONS
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- (57) Claim

1. Ceramic precursor composition characterized in
that it comprises

- at least one precursor comprising a plurality
of units of formula:



- and at least one precursor comprising a plu-
rality of units of formula:



in which formulae the available valencies of the silicon
and nitrogen atoms are linked to a saturated or unsatura-
ted aliphatic hydrocarbon radical or to a mono- or
polycyclic aryl, alkylaryl or arylalkyl radical, it being
possible for these substituents to be different or

identical, it being possible for at least one of the available valencies of the silicon atom or of the nitrogen atoms in formula I and/or the nitrogen atom in formula II to carry a hydrogen atom, and it being possible for the silicon atom of formula II to carry a second hydrogen atom, the nitrogen atom in the same formula II then carrying a methyl radical.

5. Composition according to any one of Claims 1 to 4, characterized in that it comprises from 10 to 90% by weight of precursor(s) of formula I and from 90 to 10% by weight of precursor(s) of formula II.

10. The ceramic materials obtained by pyrolysis of the compositions according to any one of Claims 1 to 7 or 9 at a temperature of the order of 800 to 1500°C.

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

POLYSILANE-BASED CERAMIC PRECURSOR COMPOSITIONS AND
CERAMICS OBTAINED BY PYROLYSIS OF THE SAID COMPOSITIONS

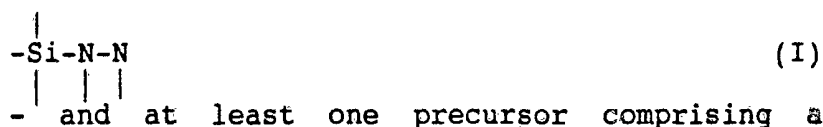
The following statement is a full description of this invention, including the best method of performing it known to us

POLYSILAZANE-BASED CERAMIC PRECURSOR COMPOSITIONS AND
CERAMICS OBTAINED BY PYROLYSIS OF THE SAID COMPOSITIONS

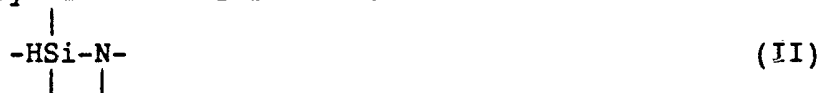
The present invention relates to a polysilazane-based ceramic precursor composition. It also relates to ceramic materials resulting from the shaping and the
5 pyrolysis of the said composition.

The ceramic precursor composition in accordance with the invention comprises:

- at least one precursor comprising a plurality
10 of units of formula:



plurality of units of formula:



15 in which formulae the available valencies of the silicon and nitrogen atoms are linked to a saturated or unsaturated aliphatic hydrocarbon radical or to a mono- or polycyclic aryl, alkylaryl or arylalkyl radical, it being possible for these substituents to be different or
20 identical, it being possible for at least one of the available valencies of the silicon atom or of the nitrogen atoms in formula I and/or the nitrogen atom in formula II to carry a hydrogen atom, and it being possible for the silicon atom of formula II to carry a
25 second hydrogen atom, the nitrogen atom in the same formula II then carrying a methyl radical.

The expression "available valencies" is employed in this case to take account of the bonds between the units of formulae I or II in the polymeric chain sequences of the precursors.

5 As specific examples of the substituents of the silicon or nitrogen atoms in the above formulae mentioned will be made in particular of saturated aliphatic hydrocarbon radicals containing from 1 to 8 carbon atoms, unsaturated radicals such as vinyl or allyl, alicyclic radicals containing from 3 to 7 carbon atoms, and phenyl, benzyl, phenylethyl, tolyl, xylyl or naphthyl radicals.

10 The silicon atom of formula I preferably carries a hydrogen atom or a methyl substituent, the second substituent of the silicon atom of formula I being a methyl, ethyl, phenyl or, more preferably, vinyl substituent. In
15 formula II the silicon atom preferably carries a methyl radical.

20 The precursor compositions in accordance with the invention may comprise from 10 to 90% by weight of precursor(s) of formula I and 90 to 10% of precursor(s) of formula II. The said compositions preferably comprise from 10 to 70% by weight of precursor(s) of formula I and from 90 to 30% by weight of precursor(s) of formula II. Among these compositions, those comprising 10 to 55% of
25 precursor(s) of formula I will also advantageously be chosen.

The precursors of formula I can be prepared by reaction of at least one halosilane of formula:



with at least one hydrazine of formula:



in which formulae Y denotes a halogen, and especially chlorine, atom, a denotes a number between 1 and 4 inclusive, and preferably approximately 2, the free valency or valencies of silicon and of nitrogen being linked to an unsaturated aliphatic hydrocarbon radical or one of the other atoms or radicals referred to within the description of formula (I), at least two of the available valencies of the nitrogen atoms being linked to hydrogen atoms.

15 The precursors of formula II can be prepared by reaction of a hydrohalosilane of formula:

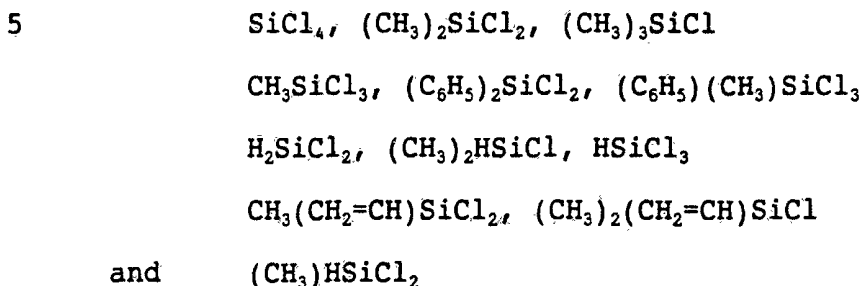


with ammonia or an amine -NH_2 , where $c = 2$ in formula V, in which formulae the symbol Y of formula V has the meaning given above, $b = 1, 2$ or 3 , $c = 4 - b$, the free valency or valencies of silicon and optionally of nitrogen are linked to one of the hydrocarbon radicals referred to above or to a hydrogen atom (in the case of hydrohalosilane).

25 By way of alternative form, the precursors of formula I can be prepared by reaction of a precursor of formula II, obtained, for example, in the way indicated

above, with a hydrazine of formula IV.

By way of specific examples of the halosilanes of formula (III) or (IV), particular mention will be made of the products corresponding to the following formulae:



10 From the preferred meaning given in the case of
a it follows that one or more dihalosilanes or a mixture
comprising one or more dihalosilanes and a mono- or a
trihalosilane and/or SiCl_4 is, or are, advantageously
employed in the invention. The percentage of chlorine
15 atoms contributed by the trihalosilane to the mixture
with the dihalosilane preferably does not exceed 70%. In
the case of monohalosilane or of SiCl_4 , this percentage
preferably does not exceed 30%.

 Specified examples of the hydrazines of formula
20 (IV) which will be mentioned in particular are unsub-
stituted hydrazine (N_2H_4), methylhydrazine, ethyl-
hydrazine, phenylhydrazine, cyclohexylhydrazine, di-
methylhydrazine, diethylhydrazine, diphenylhydrazine,
dibenzylhydrazine, α -naphthylhydrazine, diisopropyl-
25 hydrazine, ditolylhydrazines, diisobutylhydrazine, (2,3-
dimethylphenyl)hydrazine and di(α -naphthyl)hydrazine.

To prepare the precursors of formula I by the first abovementioned process, hydrazine IV is advantageously employed in a quantity such as to make the number of moles of hydrazine greater than the number of moles of halogen Y atoms added to the number of moles of silicon atoms. This excess may be, for example up to 20%.

10 The abovementioned reaction is advantageously conducted in the presence of a tertiary amine such as triethylamine, trimethylamine, triphenylamine or pyridine.

The main function of this amine is to limit the formation of a hydrazine hydrohalide through the formation of a hydrohalide of this amine.

15 As a general rule, the quantity of amine is at least one molecule of amine per atom of halogen Y. This ratio is preferably in excess, for example by 20%. When an amine is employed the number of moles of hydrazine may be higher than the number of moles of silicon atoms alone.

20 If an excess of halosilane is employed within the meaning intended above, it is advantageous, after having reacted hydrazine with the halosilane(s), to introduce an excess of a reactant which makes it possible to limit the halogen content of the final product, it being possible
25 for this reactant to be, as a general rule, for example, an amine or ammonia.

This reaction is advantageously conducted in an inert atmosphere, for example under a stream of nitrogen.

The temperature is generally between -10 and 100°C. The abovementioned reactants (halosilane and hydrazine) may be employed alone, the tertiary amine being added if appropriate. A solvent for the final polysilazane may be preferably employed, and this can be chosen especially from optionally halogenated aliphatic or aromatic hydrocarbons such as toluene, methylene chloride, benzene, xylene, hexane, or ethers such as isopropyl ether or diethyl ether.

The reaction may be conducted at atmospheric pressure, under pressure, or under reduced pressure. The operation is preferably carried out at atmospheric pressure.

At the end of the reaction, whose length may be between a few tens of minutes and a few hours, the hydrohalides are removed, for example by filtration under reduced pressure or under nitrogen pressure, and the solvent which may have been employed and the excess hydrazine or tertiary amine are removed, for example by evaporation under reduced pressure. Polysilazanes are thus recovered in the form of rigid or resinous solids or of a more or less viscous oil.

To prepare the precursors of formula II a quantity of ammonia or of amine is advantageously employed such as to make the number of moles of ammonia or of

amine greater than the number of moles of halogen Y atoms added to the number of moles of silicon atoms. This excess may be up to 20%. The ammonia may be used in diluted form, for example with nitrogen. The reaction may
5 take place at a temperature which may be between -20°C and 100°C or the temperature of the optional solvent, when this temperature is below 100°C at atmospheric pressure. It is also possible to operate at sub-atmospheric or superatmospheric pressure.

10 The reaction is advantageously conducted in an organic solvent medium. Examples of such solvents which may be mentioned in particular are optionally chlorinated hydrocarbons such as methylene chloride, carbon tetra-
chloride, toluene and benzene.

15 The hydrogen halide acid formed during this reaction precipitates in the form of ammonium halide, which can be removed by filtration. The solvent for the polysilazane can be removed by evaporation.

20 One or more cyclic or linear polysilazanes containing units of formula II can be generally recovered at the end of this reaction, which can last from a few tens of minutes to a few hours.

25 To implement the second process for the preparation of the precursors of formula I a hydrazine IV may be reacted with a precursor of formula II, prepared, for example, as described above.

As a general rule, a sufficient quantity of hydrazine is used to permit the substitution of the -NH- groups in formula II by the -N-N- groups of formula I.

5 The hydrazine of formula IV is advantageously used in anhydrous form and the reaction temperature may vary, for example, between 20 and 100°C at atmospheric pressure. The reaction is accompanied by a release of ammonia, the end of this release signifying the end of the reaction, following a period which can last from a
10 few tens of minutes to a few hours. It is advantageous to introduce an organic solvent into the reaction mixture, it being possible for this to be chosen, for example, from the products mentioned above. After separation of the dense phase containing the excess unreacted hydrazine
15 and evaporation of the solvent, a polyhydrosilazane containing a plurality of units of formula I is collected in the form of a viscous liquid.

The compositions in accordance with the invention may be prepared merely by mixing the precursors of
20 formula I and II, preferably under an inert atmosphere, for example under nitrogen. This mixing may be performed at ambient temperature and more generally between 0 and 100°C.

The compositions may then be shaped at ambient
25 temperature or after heating to a temperature which may be up to 300°C.

Solutions of the said compositions may be used to form coatings on substrates such as metals (metallic silicon, steel, molybdenum, nickel-rich alloys) or ceramics, it being possible for the thickness of such coatings to be of the order of 0.01 to 100 μm . Where the coating contains an additive such as silicon carbide or nitride powders, this thickness may be up to several millimetres.

The use of hydrogenated precursors ($-\text{SiH}-\text{N}-\text{N}-$ and $-\text{SiH}-\text{N}-$) enables the viscosity of the compositions to be controlled, the former being used to increase the viscosity and the latter to decrease it. Furthermore, such precursors result in thermally crosslinkable products, and this is of advantage in some applications, such as spinning.

The shaped compositions can then be pyrolysed by heating to a temperature of the order of 800 to 1500°C to a ceramic containing Si, N and optionally O and/or C.

The pyrolysis may be conducted in an inert atmosphere, that is to say under nitrogen or argon, or in an ammonia atmosphere if it is desired to lower the carbon content of the ceramic or even to remove it.

After pyrolysis, the precursor compositions in accordance with the invention produce ceramics in a ceramic yield which is higher both than the arithmetic mean of the mixture of the two precursors and, in some cases, than the yield observed separately with the

precursors of formulae I and II.

In the examples, the ceramic yield values (= weight of ceramic obtained/weight of precursor employed $\times$ 100) have been measured by thermogravimetric analysis without confinement and under a nitrogen purge. The temperature rise was 100°C/hour and was followed by a plateau of one hour at 1000°C, the maximum temperature.

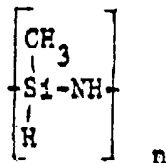
EXAMPLES 1 TO 5

A - Synthesis of an ammonolysate of $\text{CH}_3\text{SiHCl}_2$
(precursor 1A)

The reaction takes place in a jacketed reactor fitted with a thermometer, a stirring system and a condenser (15°C).

After the reactor has been purged with nitrogen, 800 ml of toluene and 1.2 moles of $\text{CH}_3\text{SiHCl}_2$ are poured into it at 15°C. The reactor is cooled to 2°C and 4.66 moles of NH_3 diluted with 2.33 moles of N_2 are introduced at a constant rate with stirring over 6 hours. During the last hour the reactor temperature is raised to 20°C. Gentle stirring is continued for 15 hours at 15°C. The ammonium chloride is filtered off under nitrogen and is washed with two 300-ml portions of toluene. The solvent is then evaporated from the ammonolysate solution at 60°C in vacuum with the aid of a rotary evaporator. The evaporation is finished off by leaving the residue for $\frac{1}{2}$ hour at 60°C at approximately 5 mm Hg. 56 g of ammonolysate are collected, which corresponds to a 79.1% yield

based on the formation of units:



This ammonolysate has a viscosity of approximately 0.4 poises at 25°C.

B - Synthesis of a hydrazine derivative of

5 CH₃SiCH=CH₂Cl₂ (precursor 1B)

The apparatus described above under A is employed. 600 ml of toluene, 0.8 moles of methylvinyl-dichlorosilane CH₃SiCH=CH₂Cl₂, 0.2 moles of methyltri-chlorosilane and 2.64 moles of triethylamine are poured
10 into the reactor at ambient temperature. 1.2 moles of hydrazine are run in over 30 min, with stirring, while the reactor temperature is maintained at 15°C. The reactor is heated to 70°C while stirring is continued. After 6 hours 0.5 moles of ammonia are introduced, still
15 at 70°C and with stirring. The reactor is cooled to 15°C and left for 15 hours with gentle stirring. The precipitate is filtered off under nitrogen and is washed with two 400-ml portions of toluene. The solvent is then evaporated from the solution at 60°C under vacuum with
20 the aid of a rotary evaporator. The evaporation is finished off by leaving the residue for ½ hour at 60°C at approximately 5 mm Hg. Approximately 83 g of

polysilazane (precursor 1B) are collected. It contains approximately 0.64 moles of N-N bond per 100 g of product.

5 C - Preparation and pyrolysis of mixtures of precursors 1A and 1B

The precursors 1A and 1B are mixed under nitrogen and in various proportions. The ceramic yields under nitrogen at 1000°C are then determined.

The results are collated in the table below.

10

EXAMPLES	*	1	2	3	4	5	*
Polysilazane 1A (% by weight)	100	80	60	50	40	20	0
Polysilazane 1B (% by weight)	0	20	40	50	60	80	100
Ceramic yield (% by weight)	41.8	68	68.2	67.2	62.8	62	59.7

15

20

* by way of comparison

EXAMPLES 6 TO 10

25 A - Preparation of a hydrazine derivative of $(CH_3)_2SiCl_2$

The procedure is as in part B of Example 1, but with 1 mole of dimethyldichlorosilane, 3 moles of

triethylamine and 1.4 moles of hydrazine, and no ammonia is introduced at the end of reaction. The mixture is heated to 60°C for 6 hours.

After evaporation of the solvent, 73.5 g are collected of a liquid polysilazane, which will be called precursor 2A.

B - Preparation and pyrolysis of mixtures of precursors 1A and 2A

The precursors 1A and 2A are mixed under nitrogen and in various proportions. The ceramic yields under nitrogen at 1000°C are then determined.

The results are collated in the table below.

EXAMPLES	*	6	7	8	9	10	*
Precursor 1A (% by weight)	100	90	80	60	50	30	0
Precursor 2A (% by weight)	0	10	20	40	50	70	100
Ceramic yield (% by weight)	41.8	43.9	44	40.25	38.05	23.6	2.2

* by way of comparison

It is found that the combination of the two precursors 1A and 2A also results in a ceramic yield which is higher than the arithmetic mean of the mixture

of the two precursors.

EXAMPLE 11

A - Synthesis of a hydrazine derivative of
 $\text{CH}_3\text{SiHCl}_2$ (precursor 11A)

5 The apparatus described in Example 1A is employed. 600 ml of toluene, 1 mole of hydromethyldichlorosilane ($\text{CH}_3\text{SiHCl}_2$) and 2.4 moles of triethylamine are poured into the reactor at ambient temperature. Water at 15°C is passed through the reactor jacket. 1.2 moles of
10 anhydrous hydrazine are run in over 1 hour, the reactor being stirred. It is found that the temperature rises from 16.5 to 23°C. After the introduction of hydrazine the reactor temperature is raised to 70°C and stirring is continued for 6 hours. The reactor is then returned to
15 15°C and is left for 15 hours with gentle stirring. The precipitate is filtered off under nitrogen and washed with three 300-ml portions of toluene.

 A toluene solution of polysilazane at a concentration of $\approx 4.6\%$ by weight is thus obtained. When
20 the solvent is evaporated from 100 g of the said solution in a rotary evaporator as indicated in the preceding examples, 4.6 g of infusible and insoluble solid cross-linked polysilazane are obtained. This polysilazane gives a ceramic yield of 72%.

B - Preparation and pyrolysis of mixtures of precursors 1A and 11A

The precursor 1A and toluene solution of precursor 11A are mixed in various proportions. The solvent is then evaporated off using a rotary evaporator as described in the preceding examples. The viscosities and the ceramic yields under nitrogen at 1000°C are then determined.

The results are collated in the table below:

10	Polysilazane 1A (% by weight)	100	75	50	25	0
15	Polysilazane 11A (% by weight)	0	25	50	75	100
20	Viscosity (poise) at 20°C	0.4	143	3200	> 20000	infusible crosslinked solid
	Ceramic yield at 1000°C under N ₂	41.8	65.2	67.2	69.4	72

It should be noted that these mixtures continue to progress towards higher viscosities at ambient temperature and that this change is proportionally faster the higher the temperature and the higher the proportion of polysilazane 11A. It can be ascertained, in fact, that the viscosity of the mixture of 25% of 1A and 75% of 11A at 70°C changes from 1000 p to 8000 p in 30 minutes.

The possibility of obtaining a polysilazane composition of high viscosity which crosslinks thermally so as to become infusible has thus been demonstrated. This property is advantageous for the production of ceramic fibres, because the high viscosity of the precursor is necessary for spinning and because the crosslinking of the polymer is indispensable for fixing the fibre in its shape and preventing it from melting at the beginning of pyrolysis.

EXAMPLE 12

A - Synthesis of a hydrazine derivative of a mixture of $\text{CH}_3\text{SiHCl}_2$ (80 mol%) and of $(\text{CN})_2\text{SiCl}_2$ (20 mol%)

The procedure is as in Example 11A, but a mixture of 0.8 moles of hydromethyldichlorosilane and 0.2 moles of dimethyldichlorosilane is employed instead of one mole of hydromethyldichlorosilane.

B - Preparation and pyrolysis of mixtures of precursors 1A and 12A

The precursor 1A and the solution of precursor 12A are mixed in various proportions. The solvent is then evaporated off in a rotary evaporator as described in the preceding examples. The viscosities and the ceramic yields under nitrogen at 1000°C are then determined.

The results are collated in the table below:

5	Polysilazane 1A (% by weight)	100	75	50	25	0
	Polysilazane 12A (% by weight)	0	25	50	75	100
10	Viscosity (poise) at 20°C	0.4	37.5	1530	> 20000	infusible crosslinked solid
15	Ceramic yield at 1000°C under N ₂	41.8	61.8	67.5	68.6	67.1

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

CLAIMS

1. Ceramic precursor composition characterized in that it comprises

- at least one precursor comprising a plurality of units of formula:



- and at least one precursor comprising a plurality of units of formula:



in which formulae the available valencies of the silicon and nitrogen atoms are linked to a saturated or unsaturated aliphatic hydrocarbon radical or to a mono- or polycyclic aryl, alkylaryl or arylalkyl radical, it being possible for these substituents to be different or identical, it being possible for at least one of the available valencies of the silicon atom or of the nitrogen atoms in formula I and/or the nitrogen atom in formula II to carry a hydrogen atom, and it being possible for the silicon atom of formula II to carry a second hydrogen atom, the nitrogen atom in the same formula II then carrying a methyl radical.

2. Composition according to Claim 1, characterized in that in formulae I and II the substituents of the silicon atoms are chosen from saturated aliphatic hydrocarbon radicals containing from 1 to 8 carbon atoms, unsaturated radicals such as vinyl or allyl, alicyclic radicals containing from 3 to 7 carbon atoms and phenyl, benzyl, phenylethyl, tolyl, xylyl or naphthyl radicals.

3. Composition according to either of Claims 1 and 2, characterized in that the silicon atom of formula I carries a hydrogen atom or a methyl substituent and a second substituent chosen from methyl, ethyl, phenyl or vinyl groups.

4. Composition according to any one of Claims 1 to 3, characterized in that the silicon atom of formula II carries a methyl radical.

5. Composition according to any one of Claims 1 to 4, characterized in that it comprises from 10 to 90% by weight of precursor(s) of formula I and from 90 to 10% by weight of precursor(s) of formula II.

6. Composition according to any one of Claims 1 to 4, characterized in that it comprises from 10 to 70% by weight of precursor(s) of formula I and from 90 to 30% by weight of precursor(s) of formula II.

7. Composition according to any one of Claims 1 to 4, characterized in that it comprises from 10 to 55% by weight of precursor(s) of formula I and 45 to 90% by weight of precursor(s) of formula II.

8. Process for the preparation of compositions according to any one of Claims 1 to 7, characterized in that it consists in mixing the precursors of formulae I and II at a temperature of between 0 and 100°C under inert atmosphere.

9. Compositions according to any one of Claims 1 to 7, in the form of filaments, fibres or films or coating.

10. The ceramic materials obtained by pyrolysis of the compositions according to any one of Claims 1 to 7 or 9 at a temperature of the order of 800 to 1500°C.

DATED THIS 5th day of December, 1989

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