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PROCESS FOR THE PRODUCTION OF METAL NITRIDE SINTERED BODIES
AND RESULTANT SILICON NITRIDE AND ALUMINUM NITRIDE SINTERED BODIES

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OF METAL NITRIDE SINTERED BODIES AND
RESULTANT SILICON NITRIDE AND ALUMINUM
NITRIDE SINTERED BODIES (National
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54 Title: Process for the Production of Metal Nitride Sintered
Bodies and Resultant Silicon Nitride and Aluminum
Nitride Sintered Bodies

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Patent Claims

1. Process for the production of metal nitride sintered products, characterized by the fact that metal nitride powder is mixed, shaped to the desired form and heated under reduced pressure, inert gas, CO gas and/or hydrogen gas with at least one binding agent from the following group:

- (1) compounds in which the silicon is bound only to carbon;
- (2) compounds with Si-H bonds in addition to Si-C bonds;
- (3) compounds with Si-Hal bonds;
- (4) compounds with Si-Si bonds;
- (5) compounds with Si-N bonds and
- (6) high molecular weight organosilicon compounds in which silicon and carbon are main structural components and which are formed by polycondensation of at least one of the organosilicon compounds from groups (1) through (5) above and from
- (7) organoalkoxy- (or -aryloxy-)silanes;
- (8) compounds with Si-OH bonds;
- (9) compounds with Si-O-Si bonds;
- (10) esters of organosilicon compounds and
- (11) peroxides of organosilicon compounds

to form metal nitride sintered products.

2. Process according to Claim 1, characterized by the fact that the metal nitride sintered product is heated to a temperature of 800 to 1400°C in an oxidizing atmosphere to remove free carbon contained in the metal nitride sintered product.

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3. Process according to Claim 1, characterized by the fact that the binding agent is added in an amount of from 0.3 to 45% by weight.

4. Process according to Claim 1, characterized by the fact that the shaped briquette is heated to a temperature of 800 to 2200°C.

5. Process according to Claim 1, characterized by the fact that the mixture of metal nitride powder and binding agent is pressed by means of a hot-press procedure, during which sintering takes place.

6. Process according to Claim 1, characterized by the fact that the metal nitride sintered product is impregnated with a liquid form of the organosilicon compound or high molecular weight organosilicon compound under reduced pressure, and the impregnated metal nitride sintered product is then heated under vacuum, inert gas, CO gas and/or hydrogen gas.
7. Process according to Claim 6, characterized by the fact that the subsequent treatment of impregnation and heating is carried out or repeated two or more times.
8. Process according to Claim 6, characterized by the fact that the impregnated metal nitride sintered product is heated to a temperature of 800 to 2200°C.
9. Process according to Claim 6, characterized by the fact that the liquid form of the organosilicon compound or high molecular weight organosilicon compound is produced by dissolving same in a solvent.
10. Process according to Claim 1, characterized by the fact that Si_3N_4 or AlN is used as the metal nitride. /3
11. Si_3N_4 sintered products characterized by a content of SiC binding agent, flexural strength of no less than 5 kg/mm², effective density of no more than 3.05 g/cm³ and high dimensional accuracy.
12. AlN sintered products characterized by a content of SiC binding agent, flexural strength of no less than 3 kg/mm^{3*}, effective density of no more than 3.0 g/cm³ and high dimensional accuracy.

* (Translator's note: appears to be misprint in German original; should be kg/mm²)

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Process for the Production of Metal Nitride Sintered Bodies
and Resultant Silicon Nitride and
Aluminum Nitride Sintered Bodies

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The invention concerns a process for the manufacture of metal nitride sintered bodies and, in particular, a process in which a mixture of metal nitride powders is shaped and heated together with a binding agent.

Of the metal nitrides, Si_3N_4 and AlN were used especially frequently because of their excellent properties at high temperatures; sintered bodies of these metal nitrides were made according to the following processes:

(1) Production of Si_3N_4 Sintered Bodies

In general, silicon powders are shaped and the briquettes are heated in nitrogen or ammonia gas, resulting in simultaneous nitride formation and sintering. However, the self-sintering capacity of Si_3N_4

is low and the sintered bodies made from Si_3N_4 according to the /5
conventional processes have a porosity of about 20% and a low density
of roughly 1.2 to 2.7 g/cm^3 , which is far below the theoretical value
of 3.18 g/cm^3 , and they become markedly oxidized at temperatures of
about 1200°C. According to a relatively new process, MgO , Al_2O_3 , Y_2O_3
and similar compounds are added to Si_3N_4 powder and the mixture is
ground, shaped and sintered, resulting in dense Si_3N_4 sintered bodies
with high oxidation resistance.

One Si_3N_4 sintered product known as "Sialon", with a high density close
to the theoretical value, was recently produced by adding several
percent Al_2O_3 or Y_2O_3 as binding agent to Si_3N_4 powders in a hot-press
process. However, inclusion of various impurities such as MgO , Al_2O_3 ,
 Y_2O_3 and similar compounds in the sintered products cannot be avoided
in the processes described above.

(2) Production of AlN Sintered Bodies

Generally, aluminum nitride powders are subjected to a hot-press
process, or aluminum nitride alone is shaped and sintered, or aluminum
nitride is added to aluminum powder and the mixture is subjected to
a nitriding and sintering treatment. Irrespective of the hot-press
process, these procedures do not produce sintered bodies of sufficient
density, and high treatment temperatures of about 1700 to 2000 °C /6
are required and the strength of the resulting AlN sintered products
is low. Indeed, sintered products with relatively high density of
roughly 98% of the theoretical value can be obtained using the hot-
press process, but their strengths are at most about 30 kg/mm^2 , which
is far from a satisfactory strength value. Recently, it was reported
that an AlN fibrous structure was formed by sintering a mixture of AlN
with small amounts of Y_2O_3 , resulting in AlN sintered products of high
mechanical strength.

In the procedures described above, however, inclusion of Y_2O_3 as an
impurity in the sintered product cannot be avoided, just as in the
production of Si_3N_4 sintered bodies.

In other words, if Si_3N_4 or AlN sintered products are produced
according to the above procedures (1) or (2) and are used as tubes,
crucibles or boats in the production of high-purity metals, the oxides
used as binding agents -- MgO , Al_2O_3 , Y_2O_3 in the case of Si_3N_4

sintered products and Y_2O_3 in the case of AlN sintered products -- react with the metal or metals at high temperatures and the resulting sintered products have a low thermal shock strength, thereby limiting the usefulness of such sintered products with oxide inclusions.

The goal of the invention, therefore, is a process for the production of metal nitride sintered bodies with high strength and other excellent properties such as high corrosion resistance and thermal / 7 shock resistance, and in which the previously known faults of the metal nitride sintered products are avoided.

According to the invention, metal nitride powders are mixed with at least one of the binding agents from the following group of organo-silicon compounds:

- (1) compounds in which Si is bound only to C ("which have only Si-C bonds");
- (2) compounds with Si-H bonds in addition to Si-C bonds;
- (3) compounds with Si-Hal bonds;
- (4) compounds with Si-Si bonds;
- (5) compounds with Si-N bonds; and
- (6) high molecular weight organosilicon compounds in which silicon and carbon are main structural components and which are obtained from polycondensation reactions of at least one of the organosilicon compounds (1) to (5) above; as well as from
- (7) organoalkoxy- (or aryloxy-) silanes (with Si-OR);
- (8) compounds with Si-OH bonds;
- (9) compounds with Si-O-Si bonds;
- (10) esters of organosilicon compounds; and
- (11) peroxides of organosilicon compounds.

The mixture is shaped to the desired form and the briquette is heated in vacuum, inert gas, CO gas and/or hydrogen gas, whereby the above organosilicon compounds and high molecular weight organosilicon compounds are thermally decomposed and the volatile components are evaporated, while the remaining carbon and silicon react to form SiC, and the above mixture can be sintered at a lower sintering temperature than in conventional processes.

Metal nitrides which can be used within the framework of the invention

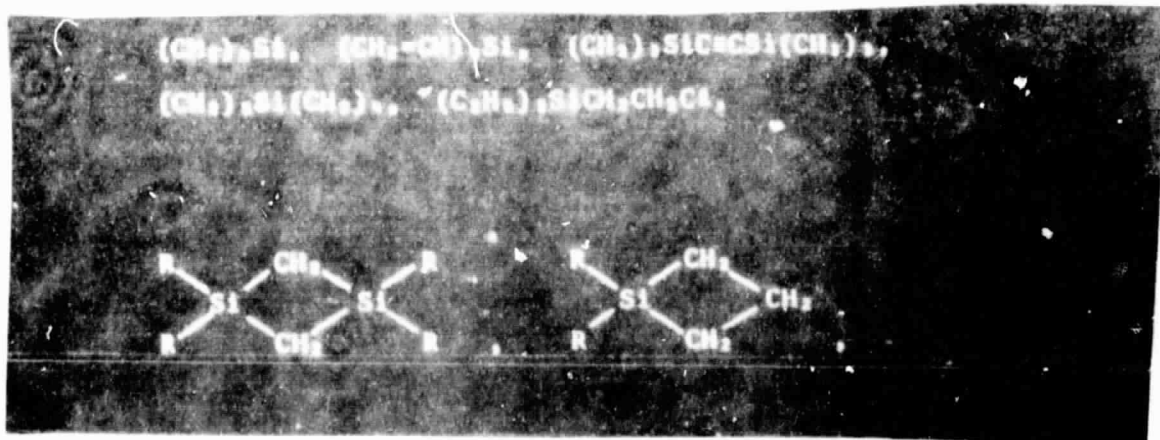
include Si_3N_4 , AlN , HfN , TaN , ZrN , TiN , ScN , UN , ThN , NbN , VN , CrN , BN , Be_3N_2 , etc. The use of fine-grained metal nitrides permits lower sintering temperatures and more dense sintered products. /8

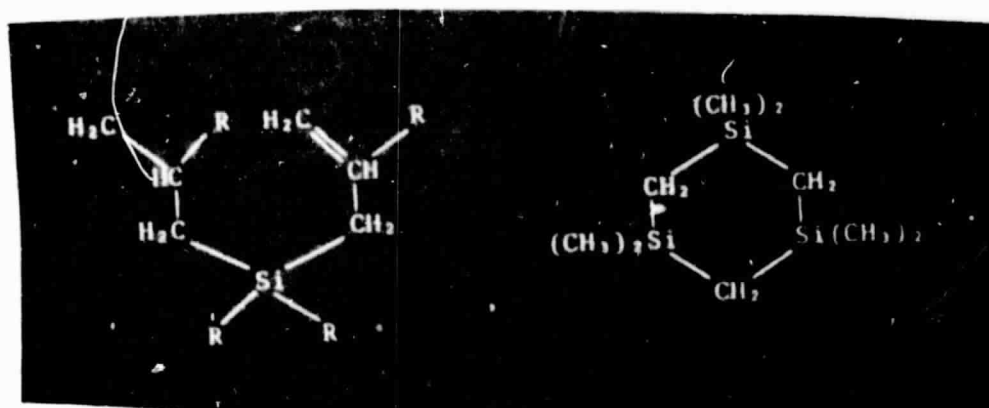
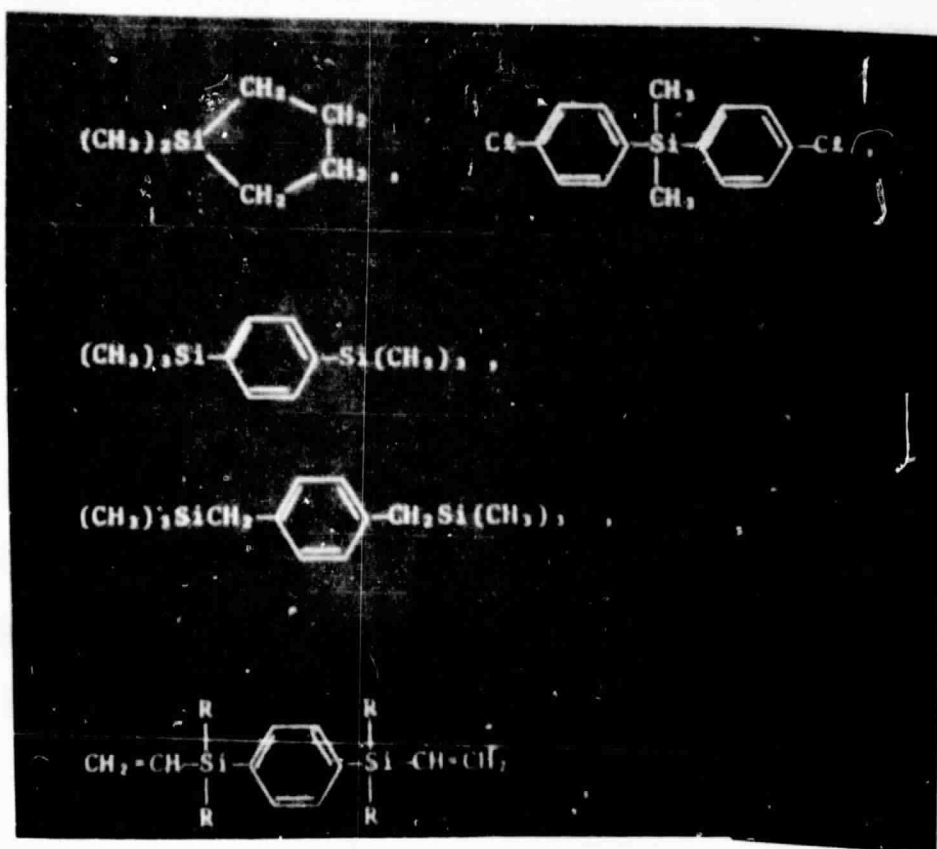
The binding agents to be used according to the invention include the organosilicon compounds (1) to (5) mentioned earlier and the polycondensed, high-molecular organosilicon compounds having a molecular weight of 100 - 600,000. If the above organosilicon compounds (1) to (5) or the high molecular weight organosilicon compounds are mixed with the metal nitrides and the resulting mixture is shaped and heated, the named compounds are thermally decomposed and hydrogen, chlorine or a portion of the carbon volatilizes, while the remaining carbon and silicon react at a temperature higher than about 1250°C to form SiC , resulting in a sintered product which contains essentially SiC as well as Si_3N_4 or AlN as the main component. With regard to the above-named compounds (1) to (5), various oxygen-containing organosilicon compounds can be used in the formation of the sintered product, but in such cases small amounts of silicon dioxide are formed, which can detract from the properties of the sintered product and thereby limit the usefulness of same.

In the following, examples are presented for the above-mentioned organosilicon compounds (1) to (5) used as binding agents.

(1) Compounds in which the silicon is bound only to carbon:

This group includes silicon hydrocarbons such as R_4Si , $\text{R}_3\text{Si}(\text{R}'\text{SiR}_2)_n$, $\text{R}'\text{SiR}_3$ and carbo-functional derivatives of same, such as, for example:



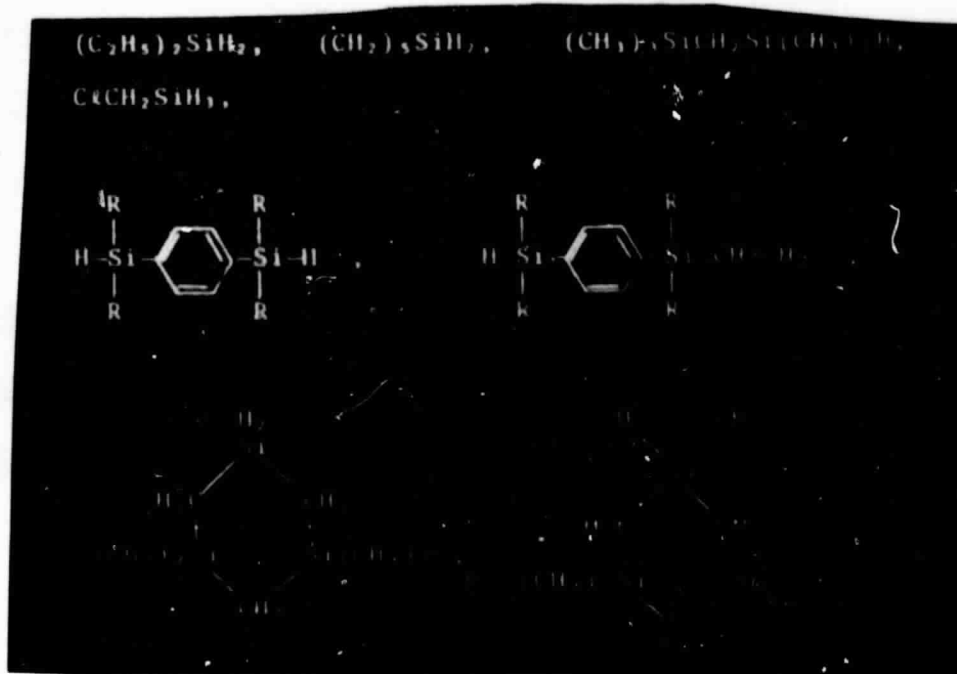


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(2) Compounds with Si-H bonds in addition to Si-C bonds:

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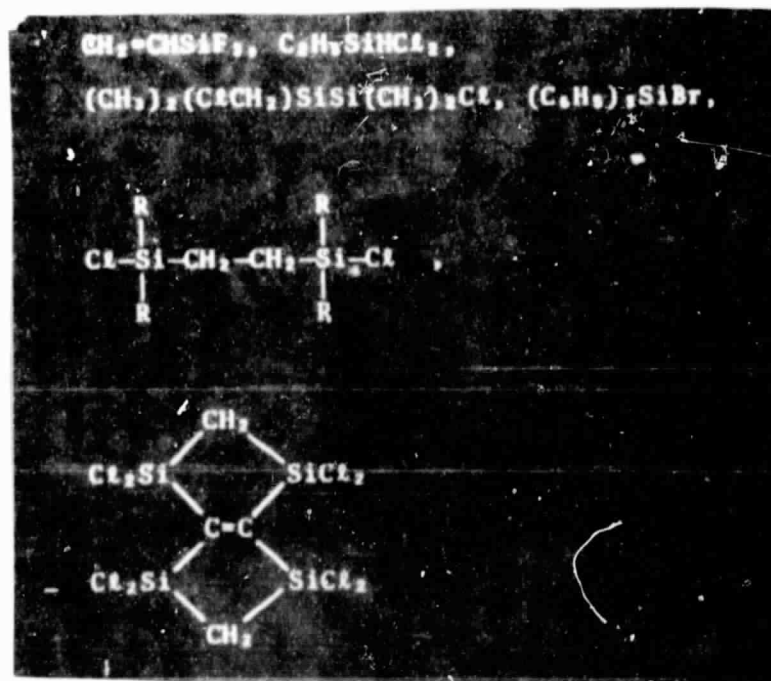
This group includes mono-, di- and triorganosilanes such as, for example:



(3) Compounds with Si-Hal bonds:

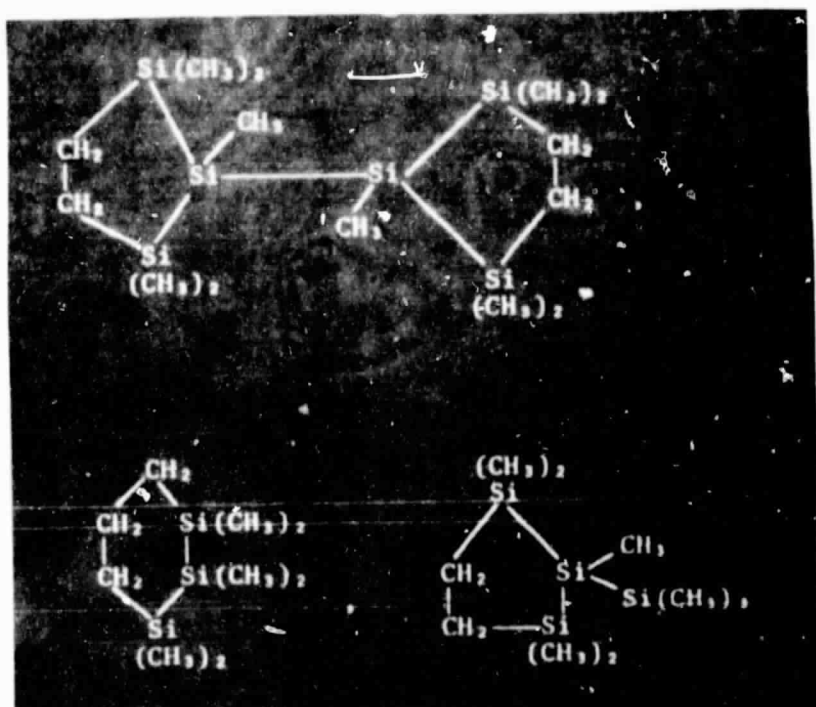
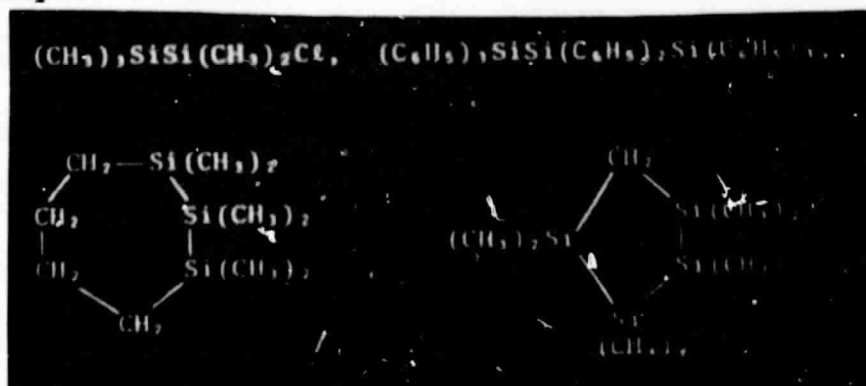
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This group includes organohalosilanes such as, for example:



(4) Compounds with Si-Si bonds:

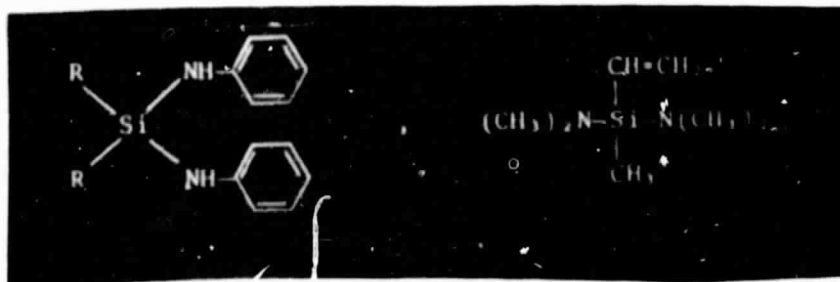
Examples include:



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(5) Compounds with Si-N bonds:

This group includes silylamines such as, for example:

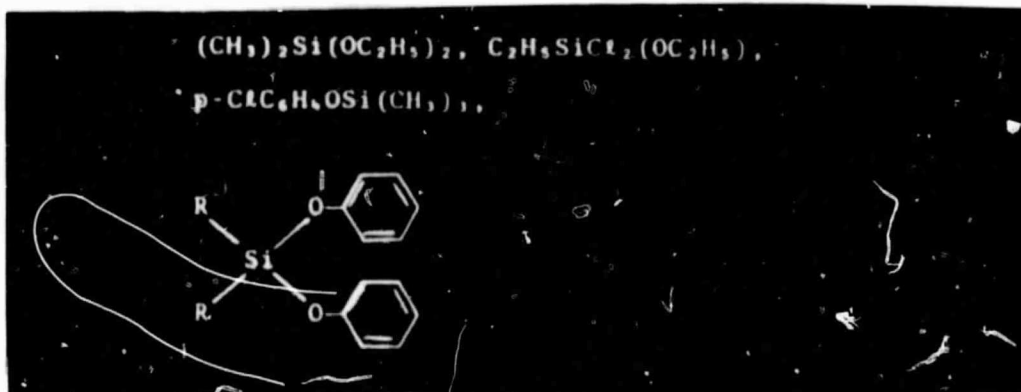


In the above structures, R indicates an alkyl or aryl group.

According to the invention, the binding agent can be an organosilicon compound from groups (1) to (5) above or from the high molecular weight organosilicon compounds formed from polycondensation of the former, or compounds formed from the following organosilicon compounds (groups 7 through 11) by means of radiation, thermal reaction or addition of polycondensation catalysts according to known processes.

(7) Organoalkoxy- (or -aryloxy-) silanes (with Si-OR):

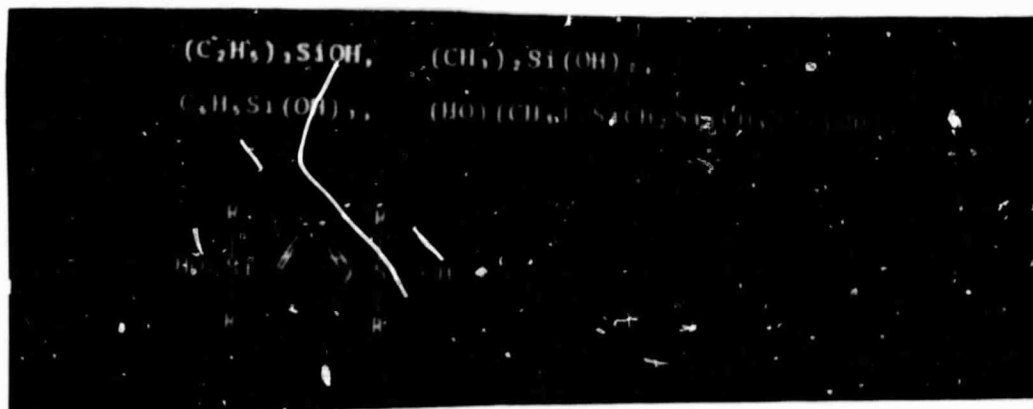
Examples include:

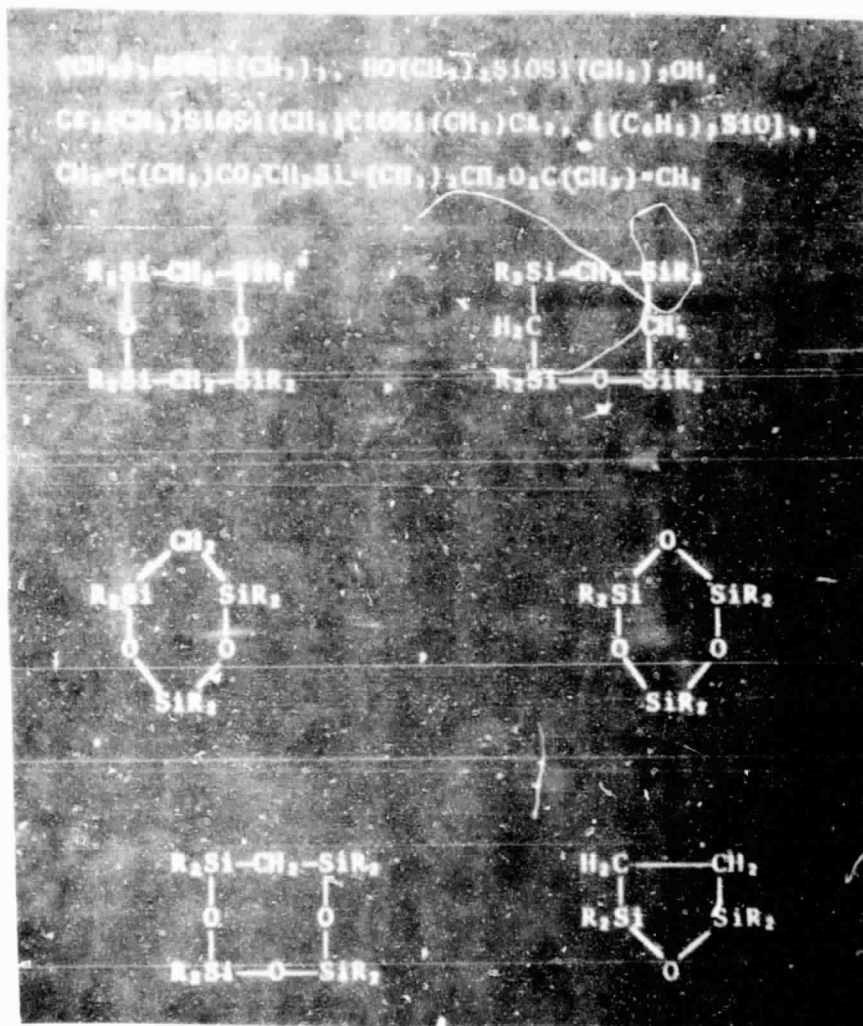


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(8) Compounds with Si-OH bonds:

This group includes organosilanes or organosilanols such as, for example:



$$\begin{aligned} & \text{CH}_3(\text{CH}_2)_4\text{COO}(\text{CH}_2)_4\text{NO}(\text{CH}_2)_4\text{SO}_3(\text{CH}_2)_4\text{OH}, \\ & \text{CF}_3(\text{CH}_2)_4\text{SO}_3(\text{CH}_2)_4\text{CO}_2(\text{CH}_2)_4\text{Cl}, \quad [(\text{C}_6\text{H}_5)_4\text{SO}_3], \\ & \text{CH}_3-\text{C}(\text{CH}_3)_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}_2-\text{CH}_2\text{O}_2\text{C}(\text{CH}_2)_4-\text{CH}_3 \end{aligned}$$


(10) Esters of organosilicon compounds:

$$(\text{CH}_3)_2\text{Si}(\text{OCOCH}_3)_2$$

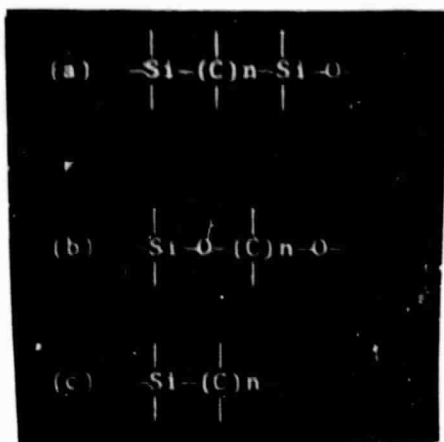
(11) Peroxides of organosilicon compounds such as, for example:



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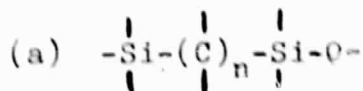
In the above formulas, R once again indicates an alkyl or aryl group.

From these starting materials, high molecular weight organosilicon compounds are obtained, in which silicon and carbon are the main structural components. For example, compounds with the following molecular structures are produced:



(d) Compounds with the above structural components (a) through (c) forming at least a partial structure in linear, cyclic and three-dimensional structures or mixtures of compounds with the above structural components (a) through (c).

Compounds having the molecular structures described above include, for example, the following:

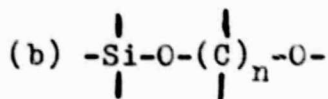


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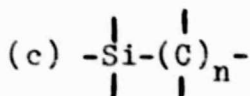
$n=1$, poly(silmethylene siloxane),

$n=2$, poly(silethylene siloxane),

$n=6$, poly(silphenylene siloxane)



- n=1, poly(methylene oxysiloxane),
n=2, poly(ethylene oxysiloxane),
n=6, poly(phenylene oxysiloxane),
n=12, poly(diphenylene oxysiloxane)



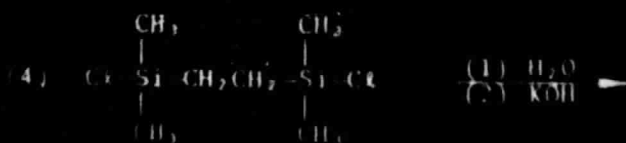
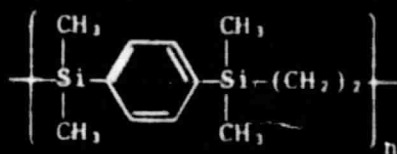
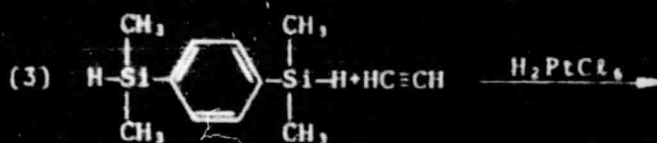
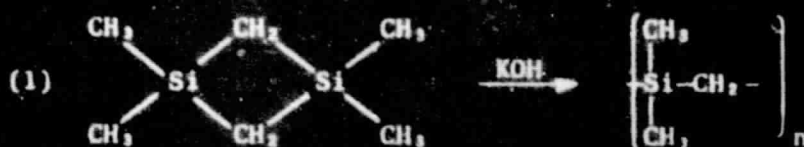
- n=1, polysilmethylene,
n=2, polysilethylene,
n=3, polysiltrimethylene,
n=6, polysilphenylene,
n=12, polysildiphenylene.

- (d) Compounds with the above structural components forming at least a partial structure in linear, cyclic and three-dimensional structures or mixtures of compounds with the above structural components (a) through (c).

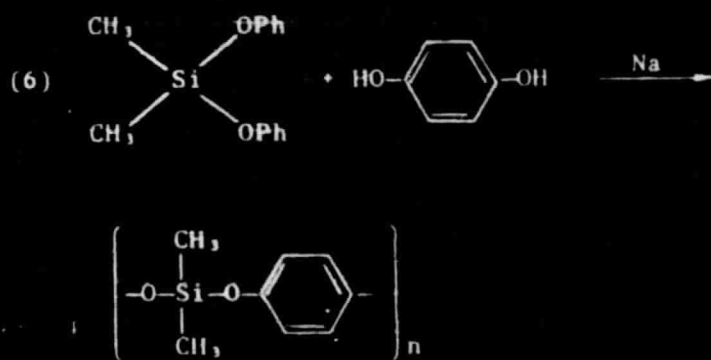
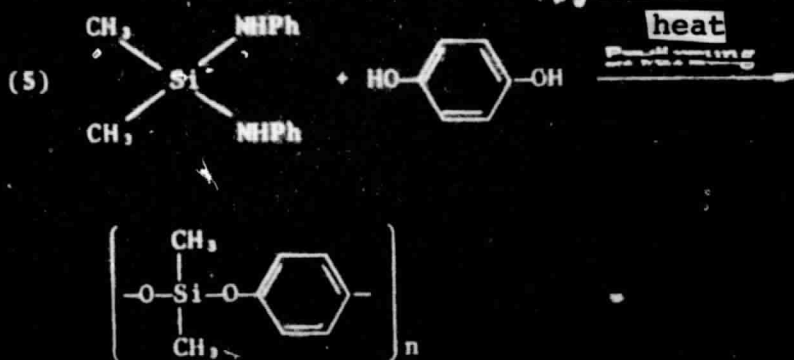
With the high molecular weight organosilicon compounds with silicon /15 and carbon as main structural components, the silicon or carbon, even if these are present in side chains, easily decompose or split off and volatilize, while silicon and carbon which form main structural components do not easily decompose or volatilize with heat, but react at high temperatures to form SiC.

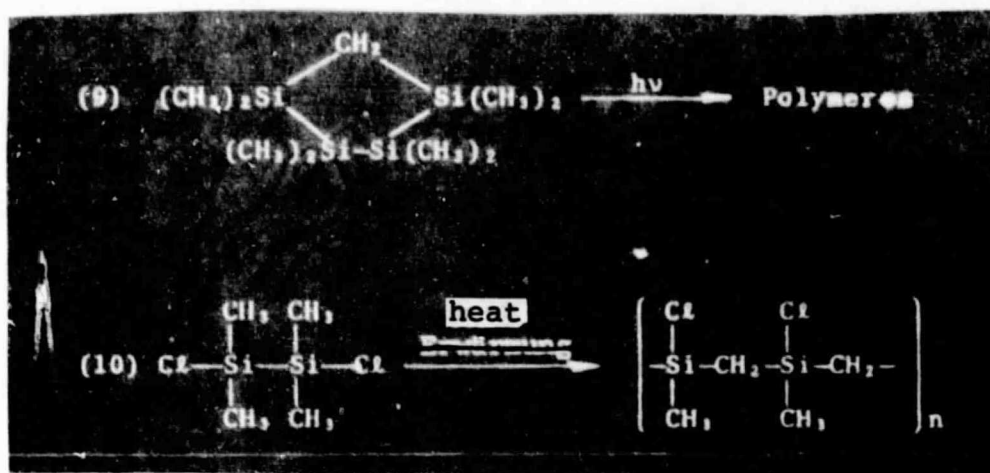
The production of high molecular weight organosilicon compounds in which silicon and carbon are the main structural components, starting from initial organosilicon compounds belonging to the above named groups (1) to (5) and (7) to (11), can take place by polycondensation reaction in which the organosilicon compound is subjected to radiation, heat, or addition of a polycondensation catalyst.

Examples of several known reactions for the production of the named high molecular weight organosilicon compounds from the initial materials of groups (1) to (5) and (7) to (11) by catalyst addition, radiation and/or heating are given in the following:



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Apart from the above named processes for the production of high / 16
molecular weight organosilicon compounds, at least one organosilicon
compound from groups (1) to (5) and (7) to (11) is polymerized within
a temperature range of 200 to 1500°C under vacuum, inert gas, CO gas /17
or hydrogen gas under pressure, if necessary, to form the high mole-
cular weight organosilicon compounds in which silicon and carbon are
the main structural components.

The reason for carrying out the above reaction within a temperature
range of 200 to 1500 °C is the following: If the temperature is below
200°C, the synthesis reaction does not proceed satisfactorily, while
at temperatures above 1500°C the decomposition reaction is intense and
the yield of high molecular weight organosilicon compound is low; there-
fore, the temperature must be in the range 200 to 1500°C and the best
results can be achieved within the range 300 to 1200°C.

The above synthesis reaction can be carried out in a pressure vessel
and in this case the optimal temperature range is 350 to 500°C; since
the thermal decomposition reaction during polycondensation of the
organosilicon compounds builds up pressure, it is not always necessary
to apply (external) pressure. The polycondensation reaction described
above can be performed in a continuously operating device. The
following describes one such process employing a continuously operating
device as shown in Fig. 4: The organosilicon compound is fed into
a heated reaction column 2 through a valve 1 and is heated in the
column to a temperature of 300 to 1500°C, preferably 500 to 1200°C. A
portion of the reaction product consisting of high molecular weight
organosilicon compound is removed from the system through a valve 3,

while low molecular weight compounds formed in the reaction column 2 are fed into a fractionating column 5 through a valve 4, distilled and separated. The gas formed in the fractionating column 5 is removed /18 through a valve 6 and the high molecular weight compound through a valve 7. The low molecular weight compounds separated in the fractionating column 5 are recycled to the reaction column 2 through a valve 8. The molecular structure of the resulting high molecular weight organo-silicon compounds was examined by means of nuclear magnetic resonance spectroscopy and infrared spectroscopy, confirming the presence of Si-C bonds and the fact that the main structural components of the compounds were based on silicon and carbon.

The following describes a process which employs polycarbosilane as a binding agent. Among the binding agents named earlier, polycarbosilane is easily produced and exhibits the lowest weight loss following heat treatment,

Polycarbosilane is liquid or solid and can be used directly or in viscous solution of the solid in a solvent such as benzene, toluene, xylene, hexane, ether, tetrahydrofuran, dioxane, chloroform, methylene chloride, petroleum ether, gasoline, ligroin, DMSO, DMF and other solvents which dissolve polycarbosilane, as a binding agent in the production of metal nitride sintered products. Binding agents other than polycarbosilane can be used according to the above data by employing the polycarbosilane process.

The binding agent is added in amounts corresponding to 0.3 to 45% by weight with respect to the metal nitride powder. The amount added can be an amount which is necessary for the sintering of metal nitrides, and can be determined by the shaping and sintering process as described in the following. The resulting mixture is shaped into the prescribed form. Alternatively, a hot-press process can be used, in which the mixture is heated in a mold and pressing takes place during the sintering process.

Sintering of the above briquettes is achieved by heating to a temperature of 800 to 2200°C in vacuum, inert gas, CO gas and/or hydrogen gas.

If the heat treatment is done in air, the binding agent oxidizes to form SiO₂; therefore, heat treatment is preferably carried out in at least one of the named atmospheres, i.e. vacuum, inert gas, CO gas or hydrogen gas.

If the combustion procedure according to the hot-press process above is carried out under a pressure of 70 to 20,000 kg/cm² in vacuum, inert gas, CO gas and/or hydrogen gas, conversion of the binding agent into SiC can be increased and a metal nitride sintered product of higher strength can be obtained. Furthermore, if the combustion process takes place in vacuum, conversion of the binding agent to SiC is increased if the heating temperature is raised for a sufficient period of time, resulting in dense sintered products of considerably greater strength.

The hot-press process according to the invention is a process for /19 sintering high temperature-resistant powders which are not shaped beforehand, but rather heated in a mold and pressed during the sintering process, resulting in more densely packed products.

In industrial hot-press procedures, the temperature is generally 1500 to 2200°C and the pressure 100 to 700 kg/cm². Furnace heating is generally electric by means of resistance heating or a high frequency induction heating process.

In resistance heating, the voltage is continuously increased from 0 V to 30 V and an induction regulator of 15,000 A is generally used, as well as a graphite resistance tube as the heating element, with thickness 1.3 cm, outside diameter 20 cm and length 150 cm. In the high frequency induction method, frequencies of 1000 to 40,000 Hz can be used. In a small scale hot-press process for the production of briquettes of diameter 2.5 cm and length 2.5 cm, 15 kVA at 30,000 Hz is recommended, and for large briquettes of diameter 35 cm and length 25 cm, 300 kVA at 1000 Hz is required.

The simplest pressing method is the lever type, which is not, however, suitable for pressure adjustment. An impact or die press type with oil pressure or air pressure is generally used.

If the mold is electrically conductive at temperatures of 1500 to /20 2200°C, which is the pressing temperature, heating can take place directly by means of resistance heating or an induction process, and generally employs graphite. There are many types of graphite, but for hot pressing dense graphite of the highest possible strength and machinability is most suitable.

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The following describes in detail the sintering procedure for metal nitrides in the production of metal nitride sintered products. The organosilicon compounds and high molecular weight organosilicon compounds used as binding agents are thermally decomposed during heat treatment and excess carbon and hydrogen volatilizes; the remaining carbon and silicon react to form essentially SiC, which bonds with the metal nitride powders. During the course of this treatment, the organosilicon compound or high molecular weight organosilicon compound, if the temperature is gradually increased over a sufficient period of time, fills the interstices between the metal nitride powder grains and as combustion proceeds, the volatile components gradually vaporize and the remaining components react to form SiC, and self-sintering of the metal nitrides, whose self-diffusion is slow, is accelerated. In this case, the organosilicon compounds and high molecular weight organosilicon compounds added as binding agent decompose at a relatively low temperature, as shown in Fig. 1. Hydrogen, chlorine, and a portion of the carbon volatilize, while the remaining carbon and silicon react and at a temperature above about 1250°C are completely converted to SiC. Even if the metal nitride sintering temperature is lower than that in conventional sintering processes, high strength sintered products can be obtained with high oxidation and corrosion resistance as well as high thermal shock resistance. /21
This is a characteristic feature of the invention. If the binding agent according to the invention is converted to SiC, microcrystalline SiC is formed with a grain size of 30 to 70 Å, which is much smaller than in previously known SiC sintered products. The specific surface area is considerably larger and the effective self-diffusion coefficient of SiC is very high. The sinterability of the metal nitride products according to the invention is increased, resulting in sintered products of high strength.

Another feature of the invention is the fact that the binding agent used ultimately is converted to SiC, which has high oxidation resistance, corrosion resistance and the additional favorable property of hardly ever reacting with metals. SiC is industrially more preferable as a binding agent than oxides such as MgO, Al₂O₃, Y₂O₃ and similar compounds which have previously been used as binding agents for the metal nitrides.

It is possible to obtain sintered products of high strength by subjecting the products obtained above at least once to the following

secondary treatment: the sintered products are impregnated with a liquid form of the above organosilicon compounds or high molecular weight organosilicon compounds under reduced pressure of 1 torr and then heated to a temperature of 800 to 2200°C in vacuum, inert gas, hydrogen gas and/or CO gas. The above organosilicon compounds or high molecular weight organosilicon compounds must be used in liquid form, i.e. organosilicon compounds or high molecular weight organosilicon compounds which exist or which can be obtained in liquid form can be used directly or, if necessary, can be dissolved in a small amount of benzene, toluene, xylene, hexane, ether, tetrahydrofuran, dioxane, chloroform, methylene chloride, petroleum ether, gasoline, ligroin, DMSO, DMF or other solvents which dissolve the compounds, in order to reduce the viscosity. If the organosilicon compounds or high molecular weight organosilicon compounds used do not have /22 satisfactory flow properties, it is advisable to use these compounds in solution form, i.e., dissolved in the solvents named above. As mentioned earlier, the organosilicon compounds include low molecular weight compounds as well as high molecular weight compounds formed by polycondensation of same; however, the latter are preferred as impregnating agents. Furthermore, by carrying out or repeating the secondary treatment described above at least once, sintered products of very high strength can be produced, even if sintering takes place at a relatively lower temperature than that in conventional sintering.

If, for example, Si_3N_4 sintered bodies are subjected five times to the impregnation procedure described above, the resulting flexural strength attains values of 20 to 40 kg/mm², even at the low sintering temperature of 1100°C. The effective density is low, 2.5 to 2.9 g/cm³, and the weight is low, but the flexural strength is high. This is one of the features of the invention. Using known procedures, it is generally impossible to obtain Si_3N_4 sintered products at a temperature below 1500°C. Sintered products having the properties indicated above can be obtained at temperatures below 1500°C only with the process according to the invention. In addition, the size and/or dimensions of the Si_3N_4 sintered products obtained according to the invention do not change appreciably before and after combustion, signifying high dimensional accuracy. Even if shaped pieces of complex form are sintered, the dimensional accuracy of the sintered product is essentially the same before and after combustion, which is a note-

worthy characteristic of the invention compared to conventional procedures for the production of Si_3N_4 sintered bodies.

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The metal nitride sintered bodies described above may contain free carbon, which can be removed by burning the sintered product at a temperature of 800 to 1400°C in an oxidizing atmosphere. If this combustion takes place at temperatures below 800°C, carbon cannot be removed, while at temperatures above 1400°C the oxidation reaction of the metal nitride becomes excessive, so such high temperatures are not recommended. The time required for this combustion in oxidizing atmosphere varies depending on the combustion temperature, the size of the pieces and the structure of the furnace. If the combustion temperature is low, long times are required, while at high combustion temperatures the required times can be short; if, however, combustion takes place at a lower temperature for a relatively long period of time, low quantities of metal oxide are formed and good results can be obtained. For example, the combustion time for a crucible produced according to the invention in air at a temperature of 1000°C for removal of free carbon is 1 to 3 hours.

In the metal nitride sintered bodies formed as described above, the binding agent is ultimately converted into SiC , so that the products do not contain impurities such as MgO , Al_2O_3 , Y_2O_3 , etc., which are commonly found in the products of conventional processes. The metal nitride sintered products according to the invention, compared to those of conventional processes, have greater oxidation and corrosion resistance and thermal shock resistance, as well as high strength even at lower densities.

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As previously mentioned, the amount of binding agent added, according to the invention, is 0.3 to 45% by weight. With less than 0.3 wt.-%, it is difficult to obtain metal nitride sintered products of high strength, while more than 45% results in low effective density, lower strength and decreased oxidation resistance when used at high temperatures; therefore, the amount of binding agent added must be between 0.3 and 45% by weight. When using the hot-press method, the amount added is preferably 1 to 10 wt.-%, and in the procedure in which the mixture of metal nitride powder and binding agent is pressed and the formed mixture combusted, amounts of 3 to 15 wt.-% are preferred.

Si_3N_4 sintered products obtained according to the invention have flexural strength values of not less than 5 kg/mm^2 , effective densities of not more than 3.05 g/cm^3 , high dimensional accuracy and high purity.

AlN sintered products obtained according to the invention have flexural strengths of not less than 3 kg/mm^2 , effective densities of not more than 3.0 g/cm^3 , high dimensional accuracy and high purity.

In the following, the invention is described in more detail, with reference to the attached drawings. The drawings show:

Fig. 1: a plot illustrating the relationship between the heating temperature in vacuum and polycarbosilane residual weight;

Figs. 2 and 3: plots illustrating the dependence of flexural strength on sintering temperature for Si_3N_4 and AlN sintered products according to the invention;

Fig. 4: a schematic for a device for polycondensation of organosilicon compounds in the formation of high molecular weight organosilicon compounds;

Figs. 5 and 6: plots illustrating the relationship between the number of impregnation treatments and flexural strength as well as effective density for Si_3N_4 and AlN sintered products according to the invention.

In the following examples, the data given are percentages by weight or parts by weight, unless specified otherwise.

Example 1

Dodecamethylcyclohexasilane was heat treated for 36 hours in an autoclave at 400°C in an argon atmosphere to obtain a resinous polycarbosilane with an average molecular weight of 800. Si_3N_4 powder with a grain size of less than 45μ was worked up or ground together with 10 wt.-% (with respect to the Si_3N_4 powder) of the above polycarbosilane and a suitable amount of n-hexane. The mixture was pressed into prisms of $10 \text{ mm} \times 10 \text{ mm} \times 30 \text{ mm}$ under a pressure of approximately 2000 kg/cm^2 and the prisms were heated in argon atmosphere at a temperature increase of $100^\circ\text{C}/\text{hour}$ in such a way that the temperature at various stages in the range 800 to 1400°C was held constant for one hour. The dependence of flexural strength of the Si_3N_4 sintered products obtained at individual heating temperatures on sintering

temperature is shown in Fig. 2. As the figure shows, Si_3N_4 sintered products of sufficient strength can already be obtained at the relatively low temperature of 1000°C .

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Example 2

Dodecamethylcyclohexasilane was heat treated for 36 hours in an autoclave at 400°C in an argon atmosphere to obtain a resinous polycarbosilane with an average molecular weight of 800. AlN powder with a grain size of less than $45\ \mu$ was worked up or ground together with 10 wt.-% (with respect to the AlN powder) of the above polycarbosilane and a suitable amount of n-hexane. The mixture was pressed into prisms of 10 mm x 10 mm x 30 mm under a pressure of approximately $2000\ \text{kg/cm}^2$ and the prisms were heated in a nitrogen atmosphere at a temperature increase of $100^\circ\text{C}/\text{hour}$ in such a way that the temperature at various stages in the range 800 to 1400°C was held constant for one hour. The relationship between the flexural strength of the resulting AlN sintered products and the sintering temperature is shown in Fig. 3. As the figure shows, sintered products of sufficient strength can be obtained at a temperature as low as 1100°C , according to the invention.

Example 3

Linear dimethylpolysilane produced from dimethyldichlorosilane was placed in an autoclave and heated for 32 hours in an argon atmosphere at 30 atm. to a temperature of 410°C to obtain polycarbosilane with an average molecular weight of 1600. Si_3N_4 powder with an average grain size of $2\ \mu$ was worked up or ground together with 10 wt.-% (with respect to the Si_3N_4 powder) of the above polycarbosilane as binding agent. The mixture was placed in a graphite mold to form prisms of 10 mm x 10 mm x 30 mm and heated by means of high frequency induction heating at a temperature increase of $300^\circ\text{C}/\text{hour}$ in argon atmosphere under a pressure of $300\ \text{kg/cm}^2$ with the use of a hot-press. The temperature at various stages in the range 600 to 1600°C was held constant for 0.5 hours. Properties of the Si_3N_4 sintered product obtained at 1500°C are shown in Table 1.

TABLE 1

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Sample properties	Si ₃ N ₄ -10%MgO* (1850°C hot pressed) conventional product	Si ₃ N ₄ -SiC hot-pressed example 3	Si ₃ N ₄ -SiC sintered product example 5
effective density (g/cm ³)	3.17	2.7 - 3.05	2.5 - 2.9
growth due to oxidation (mg/cm ²)			
1000°C	7.3 (50 Std)	2.0 (50 Std)	4.0 (50 Std)
1200°C	5.2 (50 Std)	2.0 (50 Std)	4.0 (50 Std)
flexural strength (Kg/mm ²)	60-85	40-130	30-60 impregnation treatment 5 times
Young's modulus (Kg/mm ²)	2.8x10 ⁴	4.1x10 ⁴	3.1x10 ⁴
thermal shock resistance rapid heating, quenched (25°C ± 1000°C)	good	>1000 cycles	>1000 cycles
corrosion resistance in molten Al	good	very good	good
alkali resistance developed amount NH ₃ in 25% NaOH	low	very low	low
hardness (Mohs)	9	9	9

* published values

Example 4

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Linear dimethylpolysilane produced from dimethyldichlorosilane was placed in an autoclave and heated to 400°C for 30 hours under 30 atm. argon to produce polycarbosilane with an average molecular weight of 1500. AlN powder with an average grain size of 2 μ was worked up or ground with 10 wt.-% (with respect to the AlN powder) of the above polycarbosilane as binding agent. The resulting mixture was placed in a graphite mold to form prisms of 10 mm x 10 mm x 30 mm and heated by means of a hot-press with a temperature increase of 300°C/hours under a pressure of 300 kg/cm² in an argon atmosphere. The temperature at various stages in the range 600 to 1700°C was held constant for 0.5 hours. Properties of the AlN sintered product obtained at 1500°C are listed in Table 2.

TABLE 2

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Sample properties	AlN-20%Y ₂ O ₃ (1700°C conven- tional sintered product)	AlN-SiC (hot-pressed) example 4	AlN-SiC molded sin- tered product example 6
effective density (g/cm ³)	3.26-3.50	2.75-3.10	2.6-2.9
growth due to oxidation (mg/cm ²) 1000°C	0.20 (72 Std)	0.5 (50 Std)	1.0 (50 Std)
1100°C	0.50 (72 Std)	1.0 (50 Std)	2.0 (50 Std)
flexural strength (Kg/mm ²)	30-70	15-80	30-50 impregnation treatment five times
Young's modulus (Kg/mm ²)	3.1x10 ⁴	4.0x10 ⁴	3.5x10 ⁴
coefficient of thermal expansion (x10 ⁶ /°C) 25-1000°C	5.70	4.86	5.54
thermal shock resist- ance rapid heating, quenched (25°C±1000°C)	good	>1000 cycles	>1000 cycles
corrosion resistance in molten Al	good	very good	good
hardness (Mohs)	7	7-8	7-8

* published values

As can be seen from Table 2, sintered products having a density practically equal to the theoretical density can be obtained at temperatures as low as 1500°C according to the invention.

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Example 5

The Si_3N_4 sintered product obtained by sintering at 1100°C according to Example 1, with an effective density of 2.31 g/cm³, was treated with a solution of 20 ml liquid polycarbosilane in 10 ml toluene under reduced pressure to impregnate the sintered product. The impregnated sintered product was heated to 1100°C in 8 hours in an argon atmosphere, resulting in a new or treated sintered product. The effective density of this Si_3N_4 sintered product was 2.41 g/cm³. This product was subjected to consecutive impregnation treatments and heating stages under the same conditions as described above. The effective density of the resultant sintered product increased to 2.48 g/cm³. When the sintered product formed in this way was again subjected to the subsequent treatment under the same conditions as described above, the effective density of the product attained a value of 2.54 g/cm³. By repeating the impregnation and heating procedures as described above, sintered products of high strength can be obtained even at low sintering temperatures. The relationship between the number of impregnations and flexural strength or effective density of products obtained according to this example is shown in Fig. 5.

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Example 6

AlN sintered products obtained by sintering at 1100°C according to Example 2 were placed in an autoclave together with the polycarbosilane and the pressure in the autoclave was reduced. The temperature was increased to 400°C to impregnate the sintered product with the polycarbosilane, and pressure was simultaneously applied using nitrogen gas. The impregnated sintered product was then heated to 1100°C in 8 hours in the nitrogen atmosphere to obtain a new sintered product. The above impregnation and heating procedures were repeated. The relationship between number of impregnations and flexural strength or effective density for the products obtained according to this example is shown in Fig. 6.

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Example 7

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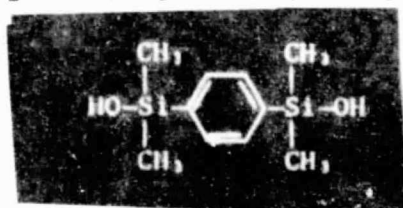
A solution of 3 g octaphenyltrisilane ($(C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_3$) in benzene and 30 g Si_3N_4 powder of grain size 45μ was thoroughly worked up or ground and the resulting mixture was pressed into a prism $10 \text{ mm} \times 10 \text{ mm} \times 30 \text{ mm}$ under a pressure of 1000 kg/cm^2 . The formed prism was heated in a nitrogen atmosphere to 1300°C at a temperature increase of $100^\circ\text{C}/\text{hour}$ to obtain a sintered product with an effective density of 2.25 g/cm^3 . The resulting product was heated in air for 3 hours to 900°C . The Si_3N_4 sintered product obtained in this way had a free carbon content of less than 0.2% and an effective density of 2.27 g/cm^3 . The flexural strength of the product was 6.3 kg/mm^2 . /36

Example 8

A solution of 4 g p-bis(dimethylvinylsilyl)benzene ($CH_2=CHSi(CH_3)_2-C_6H_4-Si(CH_3)_2CH=CH_2$) in xylene and 30 g AlN powder with a grain size less than 45μ was thoroughly ground and the resulting mixture was pressed to form a prism $10 \text{ mm} \times 10 \text{ mm} \times 30 \text{ mm}$ under a pressure of 700 kg/cm^2 . The prism was heated to 1200°C in a nitrogen atmosphere in 12 hours. The final sintered product had an effective density of 2.30 g/cm^3 and a flexural strength of 6.4 kg/mm^2 . /37

Example 9

p-bis(oxydimethylsilyl)benzene



was heated and polymerized in the presence of a potassium hydroxide catalyst to form high molecular weight organosilicon compounds with an average molecular weight of 5000. A solution of 4 g of the high molecular weight organosilicon compound in benzene and 500 g Si_3N_4 powder with a grain size less than 45μ was thoroughly worked up or ground and the resulting mixture was pressed to form a prism $10 \text{ mm} \times 10 \text{ mm} \times 30 \text{ mm}$ under a pressure of 700 kg/cm^2 . The prism was then heated to 1400°C in an argon atmosphere at a temperature increase of $100^\circ\text{C}/\text{hour}$ to obtain a sintered product with an effective density of 2.20 g/cm^3 .

The Si_3N_4 sintered product, together with the above high molecular weight organosilicon compound, was placed in an autoclave and the pressure was reduced. The temperature was increased to 400°C to impregnate the sintered product with the high molecular weight organosilicon compound (until a pressure of 15 atm. was attained). The impregnated sintered product was then heated to 1400°C in an argon atmosphere at a temperature increase of $100^\circ\text{C}/\text{hour}$. The resulting sintered product had an effective density of $2.35 \text{ g}/\text{cm}^3$ and a flexural strength of $11 \text{ kg}/\text{mm}^2$.

Example 10

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A mixture of about 78% dimethyldichlorosilane, 8% methyltrichlorosilane, 3% trimethylchlorosilane and 2% methyldichlorosilane, synthesized directly from methylene chloride and metallic silicon, was polycondensated using the apparatus shown in Fig. 4.

The mixture described above, together with argon, was fed into a reaction column 2 heated at 750°C at a rate of 1 l/hour. In the reaction column 2, the starting materials were subjected to a decomposition and polycondensation reaction to form a high molecular weight compound and a low molecular weight compound. A portion of the high molecular weight polymer can be removed from the reaction column 2, but the majority of the high molecular weight compound was fed into a fractionating column 5 together with the low molecular weight compound, where the high molecular weight compound was separated from gas and the low molecular weight compound. The low molecular weight compound was recycled into the reaction column 2 and used again as a starting material. The yield of high molecular weight compound was 19% and the average molecular weight was 1800. The high molecular weight compound obtained in liquid form was thoroughly worked up or ground with Si_3N_4 powder of grain size less than 45μ in a nitrogen atmosphere, in an amount corresponding to 10% by weight liquid high molecular weight compound. The resulting mixture was pressed to form a prism $10 \text{ mm} \times 10 \text{ mm} \times 30 \text{ mm}$ under a pressure of $1000 \text{ kg}/\text{cm}^2$. The prism was heated to 1400°C at a rate of $100^\circ\text{C}/\text{hour}$ to obtain a sintered product with an effective density of $2.25 \text{ g}/\text{cm}^3$ and a flexural strength of $8 \text{ kg}/\text{mm}^2$.

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Even though the invention has been described above using Si_3N_4 and AlN as typical examples of the well known nitrides, other metal nitrides

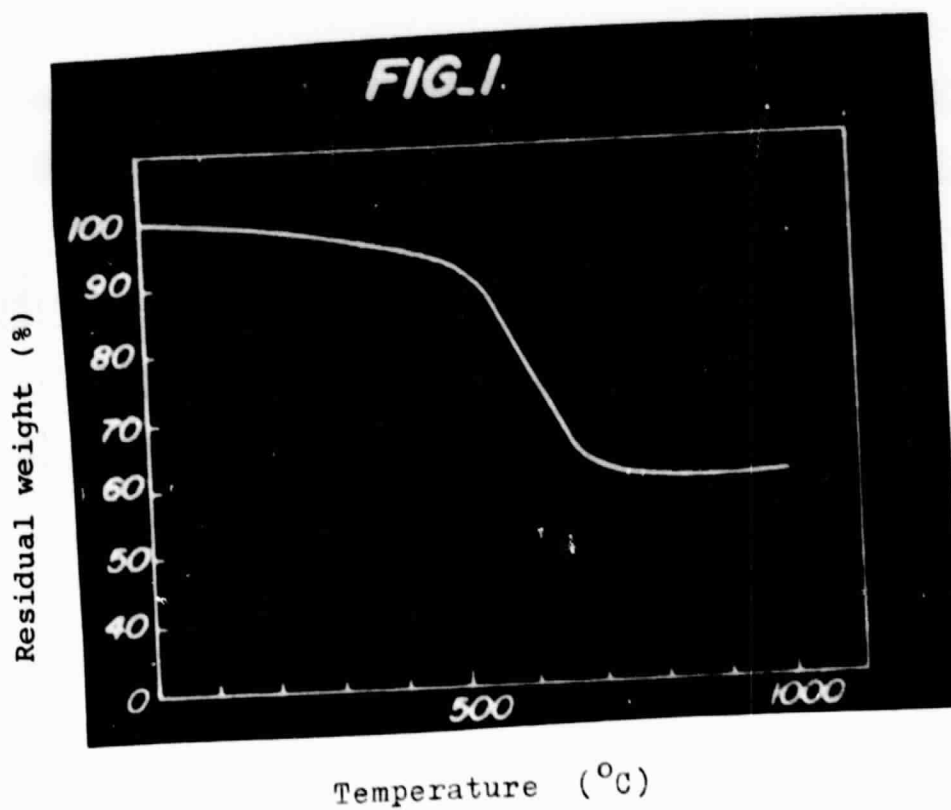
can also be used, according to the invention, to obtain sintered products with equally excellent properties.

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According to the invention, a process is presented for the production of sintered products with excellent mechanical strength, thermal resistance, oxidation resistance, corrosion resistance and thermal shock resistance at lower sintering temperatures than those used in conventional processes by using organosilicon compounds or high molecular weight organosilicon compounds as binding agents for the nitrides. The nitride sintered products obtained according to the invention can be used to exhibit these excellent properties in many areas which require high thermal stability, oxidation resistance, corrosion resistance and mechanical strength, as well as in all applications where nitride sintered products have already been used, such as, for example, melting crucibles, blast furnace materials, tubes, nozzles, turbine blades, diverse engine parts, coating materials, nuclear reactor materials, etc.

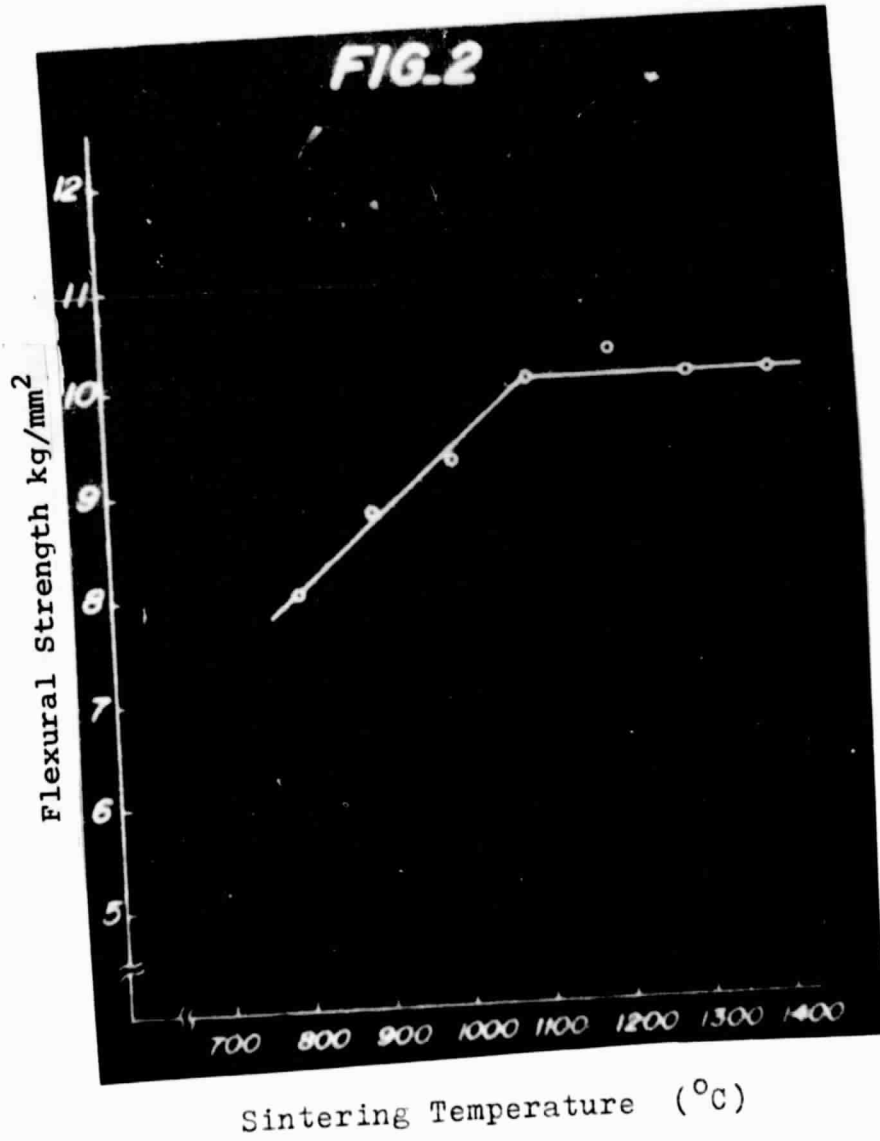
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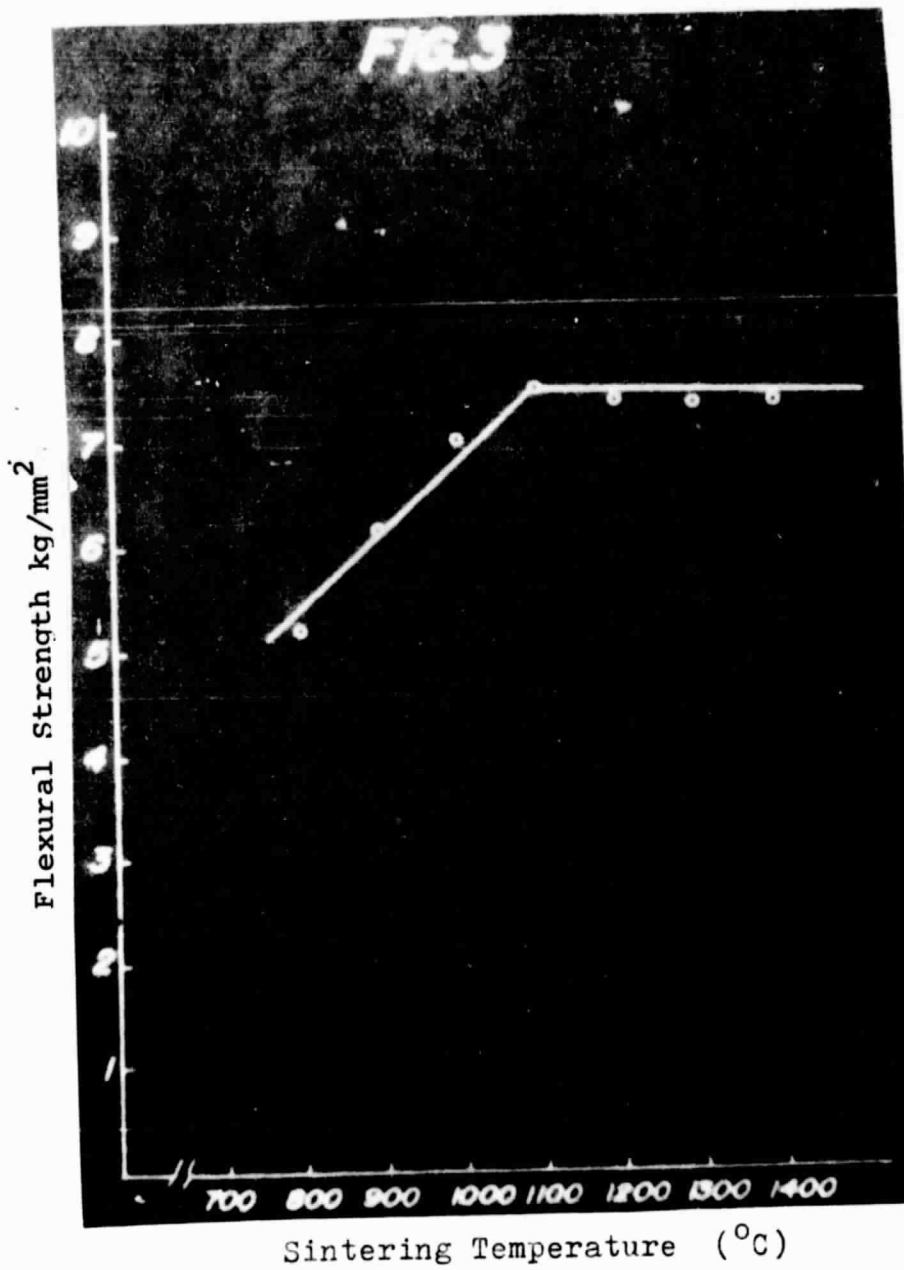


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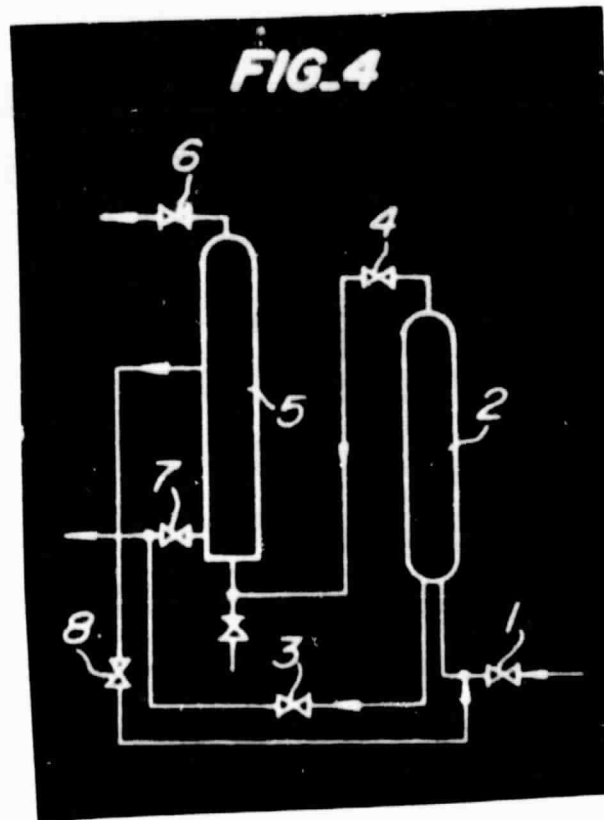
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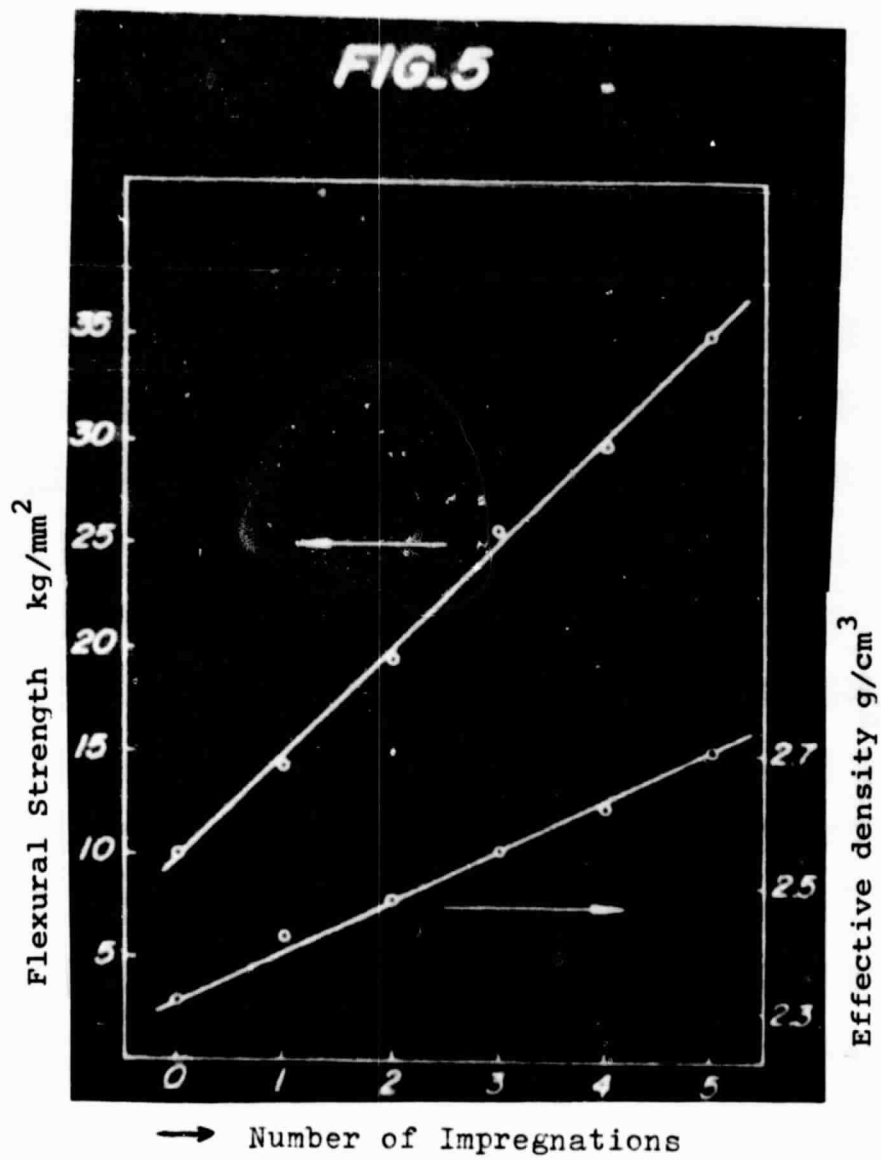
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