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We, **Jorg WILDENBURG** and **Georg WILL** of Rockumstr. 47, D 5300 BONN 1, Germany and Schlehenweg 17, D 5357 SWISTTAL-BUSCHHOVEN, Germany.

being the applicants and nominated persons in respect of Application No. **44819/89**, state the following:-

Part 1 - *We are the actual inventors.*

Parts 2 and 3 - *(Not applicable)*

Part 4 - *We are the applicants of the application listed in the declaration under Article 8 of the PCT.*

The basic application listed in the declaration made under Article 8 of the PCT was the first application made in a Convention country in respect of the invention

Parts 5, 6 and 7 - *(Not applicable)*

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GRIFFITH HACK & CO.

To: The Commissioner of Patents

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BORON NITRIDE OF HIGH HARDNESS

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(56) Prior Art Documents
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US 4361543
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(57) Claim

1. Boron nitride (aBN-2) with an amorphous structure as determined by electron beam and X-ray, and with a hardness sufficient to scratch diamond.

2. Process for the production of boron nitride of high hardness from hexagonal or turbostratic boron nitride (BN) as starting material, which is subjected to pressures above 70 Kbar and temperature of at least 1650°C, characterized in that the starting material is subjected to the pressures and temperatures for long enough for it to be completely melted, following which the thus obtained boron nitride melt is quenched and grains of amorphous boron nitride (aBN-2) with X-ray and electron beam amorphous structure and with a hardness sufficient to scratch diamond, are formed.

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(54) Title: BORON NITRIDE OF HIGH HARDNESS

(54) Bezeichnung: BORNITRID HOHER HÄRTE

(57) Abstract

The invention concerns a boron nitride with an amorphous structure, which can scratch natural diamond, and a process for producing it. According to this process high-hardness amorphous boron nitride can be obtained from hexagonal or turbostratified boron nitride by subjecting the basic material to pressures in excess of 75 kbar and temperatures of at least 1650°C, until total melting, followed by hardening. Preferably the reaction conditions are maintained in the fusion region over an interval of several minutes, and hardening is achieved by first cutting off the input of heat, which is then followed by stress relief. Preferably 3% to 20% by weight of a catalyst is added, for example Pt, Zr, H_2O, Co or C.

(57) Zusammenfassung

Die Erfindung betrifft ein Bornitrid mit amorpher Struktur, das natürlichen Diamant ritzen kann, und ein Verfahren zu seiner Herstellung. Gemäss diesem Verfahren wird amorphes Bornitrid hoher Härte aus hexagonalen oder turbostratischem Bornitrid erhalten indem das Ausgangsmaterial an Drucken von über 75Kbar und Temperaturen von mindestens 1650°C unterworfen wird, bis es vollständig aufgeschmolzen ist und nachfolgend abgeschreckt wird. Vorzugsweise hält man die Reaktionsbedingungen im Schmelzbereich über einen mehrminütigen Zeitraum aufrecht und wird zum Abschrecken zuerst die Wärmezufuhr abgestellt und dann die Druckentlastung durchgeführt. Vorzugsweise wird 3 bis 20 Gewichtsprozent eines Katalysators wie z.B. Pt, Zr, H_2O, Co oder C zugegeben.

Abstract

The invention relates to a boron nitride, of amorphous structure, which can scratch diamond, and to a process for its production.

finds a use as a cutting grain in the tool and abrasive industry. A further form of boron nitride is known under the name "turbostratic boron nitride, tBN". It is used as a starting material for pressed bodies and for the production of cubic boron nitride.

In addition to these, up to now there has only been a so-called "amorphous boron nitride", synthesized by Sumiya et al., see Materials Research Buletin, 18 pages 1203-1207, 1983, it is termed aBN-1 below, for the soft phase produced at normal atmospheric pressure. This aBN-1 is a boron structure, but consists of fragments of crystal lattice and is soft. Thus it is not established whether aBN-1 is really amorphous or whether it is only present in a finely-powdered state.

A suitable apparatus for producing the pressures and temperatures in order to produce cubic boron nitride from hexagonal boron nitride is described, for example, in U.S. Patent 2,941,243.

There is at present a great industrial need for abrasives of greater hardness. The object of the invention is to supplement or widen the palette of the known abrasives with a new one.

According to the invention, an amorphous boron nitride (aBN-2) of a structure which is amorphous by X-ray and electron beam determination, and with a hardness sufficient to scratch diamond has been found. It is characterized by an amorphous (internal) structure, i.e., non-crystalline arrangement of the atoms. Apart from this, the grains can however have a pseudomorphic form, i.e., the hexagonal or cubic form can still exist. The grains can also have a glassy external form. To distinguish it from the known boron nitride produced at normal pressure and called amorphous, termed aBN-1, the amorphous boron nitride according to the invention is termed aBN-2. The boron nitride according to the invention

is amorphous by X-rays and electron beam.
According to the invention, amorphous boron nitride of high hardness can be produced from hexagonal or turbostratic boron nitride (BN) as starting material, being treated at pressures exceeding 70 Kbar, preferably 75 Kbar or more at temperatures of at least 1650°C or higher, by subjecting the starting material to these pressures and temperatures until it is completely molten, then the thus obtained boron nitride melt is quenched and thereby grains of amorphous Boron nitride (aBN-2) of a structure which is amorphous by X-ray and electron beam and with a hardness sufficient to scratch diamond result. The crystalline components contained in the starting material are, according to the invention, completely melted and receive by quenching the consistency of a metastable, supercooled melt, so that there result grains of completely amorphous boron nitride with X-ray and electron beam amorphous structure, termed aBN-2.

In carrying out the process, after melting, the heat supply is first shut off for quenching the starting material, or if necessary a partial cooling of the melt, still under full pressure, is carried out, and relief of the pressure is then effected.

In order to carry out the process with good results, it is provided that after the heating of the starting material in the melt region, the reaction conditions of pressure and temperature are maintained for a long period. Here a period of at least several minutes should be adhered to. The period increases in dependence on increasing amounts of the charged material. In this way it is ensured that all the crystal nuclei present are destroyed, i.e. that crystal nuclei are no longer present. The heating times take, according to the amount of starting material, 5- 30 minutes with the known apparatuses.

The process according to the invention is carried out with charging of clean, i.e. pure, starting material, preferably hexagonal boron nitride, and at the given pressures and temperatures.

According to the invention, amorphous boron nitride of high hardness can be produced from hexagonal or turbostratic boron nitride (BN) as starting material, at pressures exceeding 70 Kbar, preferably 75 Kbar or more, and at temperatures of at least 1650°C or higher, by complete melting of the boron nitride charged, in that the thus obtained boron nitride melt is quenched. The crystalline componennts contained in the starting material are, according to the invention, completely melted and receive by quenching the consistency of a metastable, supercooled melt, so that there result grains of completely amorphous boron nitride with X-ray and electron beam amorphous structure, termed aBN-2.

In carrying out the process, after melting, the heat supply is first shut off for quenching the starting material, or if necessary a partial cooling of the melt, still under full pressure, is carried out, and relief of the pressure is then effected.

In order to carry out the process with good results, it is provided that after the heating of the starting material in the melt region, the reaction conditions of pressure and temperature are maintained for a long period. Here a period of at least several minutes should be adhered to. The period increases in dependence on increasing amounts of the charged material. In this way it is ensured that all the crystal nuclei present are destroyed, i.e., that crystal nuclei are no longer present. The heating times take, according to the amount of starting material, 5 - 30 minutes with the known apparatuses.

The process according to the invention is carried out with charging of clean, i.e. pure, starting material, preferably hexagonal boron nitride, and at the given pressures and temperatures.

It was found according to the invention that amorphous boron nitride of high hardness (aBN-2) can be produced without the addition of catalysts. Here active catalysts and passive catalysts are to be distinguished.

The active catalysts engage in the process as reactants themselves and require a large mass fraction to the starting substance. Hence they are present as a foreign phase in the product of the process or very strongly determine the form and size of the process product. They have to be subsequently removed. It was found according to the invention that the yield of amorphous boron nitride, aBN-2, is markedly higher without addition of catalyst to the starting material, or with the addition of passive catalysts, than it is when active catalysts are added. As active catalysts there were used Li_3N, Mg_3N_2, BCl_3, CCl_4, NH_4Cl, NH_4F, $Ca_3B_2N_4$.

According to the invention, passive catalysts were effectively used. These act favorably on the flow behavior and the heat transfer to the starting material during pressing and melting. At the end of the process for the production of aBN-2, they are either present unchanged or, with water as catalyst, no longer present. The yield of aBN-2 is increased up to nearly 100% in relation to the starting material by the use of passive catalysts. By the use of passive catalysts, larger grains of aBN-2 can be produced. Suitable passive catalysts are, e.g., Pt, Zr, H_2O, Co and C (platinum, zirconium, water, cobalt and carbon).

It has been found to be advantageous to add passive catalysts in small amounts, such as about 3 - 20 wt.% in relation to the amount of the starting material.

The direct production of amorphous boron nitride aBN-2 without catalysts takes place with good yield already from pressures of 75 - 78 Kbar at temperatures of 1800 - 2000°C, preferably from 1900°C. As long as the reaction conditions of temperature and pressure are high enough and a sufficiently long period is maintained, so that according to the invention a melt completely free from crystal nuclei is obtained, the starting material is completely converted into amorphous boron nitride aBN-2. If on the contrary the reaction conditions of temperature and pressure are left insufficiently high and do not act for long enough on the starting material (BN), then cubic boron nitride is formed, among others.

Further developments of the invention are explained below in an example of an embodiment and with reference to the drawings.

Figures 1 - 8	show electron microscope pictures of different kinds of boron nitride
Figure 9	shows a phase diagram of the different boron nitrides [KEY: Ordinate, Pressure (Kbar); abscissa, Temperature °C; "Schmelze" = Melt.]
Figure 10	shows a picture of a scratched diamond (001)
Figure 11	shows a picture of polished aBN-2 grains
Figure 12	shows a schematic view of a high pressure press
Figure 13	shows a schematic assembly drawing of a press tool
Figure 14	shows a schematic cross section through a

externally. The outer closure is then formed by a thick-walled tube 303 of pyrophyllite, if necessary in a soft setting. The thus insulated heatable platinum capsule is then covered top and bottom with steel or molybdenum plates 301b, which contact the graphite tube 304 and act as current leads. The covers 300 form the closure; they have cover plates 302 of sintered corundum, Al_2O_3, which are mounted in steel rings 301 and act as abutment faces for the press punch. The platinum skin of the capsule acts as a protective cover for the boron nitride and is temperature-stable up to about 1680°C. Molten platinum is thus an indication that this temperature was exceeded in the production of aBN-2.

This high pressure insert 30 makes it possible to supply pressure and temperature in a suitable manner and of the required magnitude to the boron nitride in the capsule interior. The completed high pressure insert 30 is inserted into the press tool, see Figure 13. This consists in principle of three rotationally symmetrical parts:

- The upper press plate 20 with water cooling and plunger mount with plunger 27 of tungsten carbide hard material,
- The middle press collar 22 with water cooling and the inner annular press die 223 of tungsten carbide hard material,
- The lower press plate 21, which is fitted mirror imagewise symmetrically of the upper press plate and likewise has water cooling, plunger mount and plunger 28 of tungsten carbide hard material.

The press plates 20, 21 and also the press collar 22 are respectively assembled from several rings 201, 202, 203 or 211, 212, 213, or 221, 222, 223 of which the two outer ones are made of steel or the like and the respective innermost ring consists of hard material. Thus the inner rings of the press plates form the plunger mounts for the plungers 27 or 28 and are likewise made of tungsten carbide hard material. The plungers are conically shaped at the head and are introduced into corresponding conical apertures 224, 225 at the top and bottom of the press die 223.

Figure 13 shows the press tool in the retracted position of the parts. The press die 223 has a cylindrical cavity 220 in the center, which will be termed "the belt" and into which the high pressure insert is inserted, so that it projects, however, upwards and downwards into the conical-shaped enlargements 224. When the plungers 27, 28 are advanced, the high pressure insert is pressed together in the direction of the narrowest place 220, the belt. All the metal parts of the press tool including the plungers are heated by electric current and hence very strongly heated. For this reason, the tool parts 20, 21, 22 are cooled. For this purpose, they are provided with through-flow cooling channels 24, which are shown here only schematically, and which are connected via inlets 240, 241, 242 to each press tool and via outlets 250, 251, 252 to a cooling water system. The cooling water circuit is designed such that the cooling water is first introduced at an inlet 240 into the upper press plate in the direction of the arrow E, then from the upper press plate into the lower press plate via the duct 25 and via the inlet 241, then out of the lower press plate via the duct 26 into the press collar via the inlet 242, and out of this is fed back again into the cooling water supply at the outlet A.

The described three-part press tool is connected, during the synthesis of aBN-2, to a cooling water circuit and also to a source for the heating current. The cooling water reduces the material loading on the steel and hard material. The current feed is arranged such that a high current (40 - 20 A) can flow at low voltage (2 - 10 V) into the interior of the assembly and can there heat the graphite hollow cylinder due to its inherent resistance. This miniature furnace is insulated by the pyrophyllite cylinder 306b as a sheath around the platinium capsule 306.

The heatable water-cooled press tool is placed in a hydraulic 630 t press and acted on by a press force of a maximum of 110 t: see the schematic representation of a press 100 in Figure 12.

- The middle press collar 22 with water cooling and the inner annular press die 223 of tungsten carbide hard material,
- The lower press plate 21, which is fitted mirror imagewise symmetrically of the upper press plate and likewise has water cooling, plunger mount and plunger 28 of tungsten carbide hard material.

The press plates 20, 21 and also the press collar 22 are respectively assembled from several rings 201, 202, 203 or 211, 212, 213 or 221, 222, 223 of which the two outer ones are made of steel or the like and the respective innermost ring consists of hard material. Thus the inner rings of the press plates form the plunger mounts for the plungers 27 or 28 and are likewise made of tungsten carbide hard material. The plungers are conically shaped at the head and are introduced into corresponding conical apertures 224, 225 at the top and bottom of the press die 223.

Figure 13 shows the press tool in the retracted position of the parts. The press die 223 has a cylindrical cavity 20 [sic - 220?] in the center, which will be termed "the belt" and into which the high pressure insert is inserted, so that it projects, however, upwards and downwards into the conical-shaped enlargements 224. When the plungers 27, 28 are advanced, the high presssure insert is pressed together in the direction of the narrowest place 224 [sic], the belt. All the metal parts of the press tool including the plungers are heated by electric current and hence very strongly heated. For this reason, the tool parts 20, 21, 22 are cooled. For this purpose, they are provided with through-flow cooling channels 24, which are shown here only schematically, and which are connected via inlets 240, 241, 242 to each press tool and via outlets 250, 251, 252 to a cooling water system. The cooling water circuit is designed such that the cooling water is first introduced at an inlet

240 into the upper press plate in the direction of the arrow E, then from the upper press plate into the lower press plate via the duct 25 and via the inlet 241, then out of the lower press plate via the duct 26 into the press collar via the inlet 242, and out of this is fed back again into the cooling water supply at the outlet A.

The described three-part press tool is connected, during the synthesis of aBN-2, to a cooling water circuit and also to a source for the heating current. The cooling water reduces the material loading on the steel and hard material. The current feed is arranged such that a high current (40 - 20 A) can flow at low voltage (2 - 10 V) into the interior of the assembly and can there heat the graphite hollow cylinder due to its inherent resistance. This miniature furnace is insulated by the pyrophyllite cylinder 306b as a sheath around the platinum capsule 306.

The heatable water-cooled press tool is placed in a hydraulic 630 t press and acted on by a press force of a maximum of 110 t: see the schematic representation of a press 100 in Figure 12.

The reaction times are 15 - 30 minutes. The crystalline components contained in the starting substance are completely melted by the pressure and temperature conditions.

After this time the high pressure insert or the capsule is quenched by cessation of the heating current, followed by pressure relief in a matter of seconds. After quenching, the starting material has been converted and possesses the consistency of a metastable supercooled melt, i.e., glass-like material - BN-glass - termed aBN-2. Since the mass of the inserted capsule is small, the capsule can cool down (from melt temperature to about room temperature) in a matter of seconds after the heating current is switched off, due to which crystallization is prevented. As against this, the decompression takes several minutes.

For preparation of the initial mixture, 46 mg of hBN and 4 mg of water were used. About 1kW heating load was used for the temperature production. For water cooling during the synthesis, about 500 l of water circulated through the cooling system. The most rapid heating-up time from 20°C to 1700°C took about 3 minutes, and the pressure loading took on average 5 minutes to reach the maximum value provided by the press used, about 78 Kbar.

Setting and regulation of temperature was carried out by measurements on calibration assemblies and extrapolation of the load curve. The synthesis assembly was measured with Ni-NiCr thermoelements up to 1200°C and plotted against the heating load, The measurement curve obtained was extrapolated to 2000°C.

The heating load was manually controlled on the basis of the data thus obtained. For further temperature monitoring, thermochromic pigments were used instead of the sample. These oxide pigments show a characteristic color change on reaching a minimum temperature. The finest temperature gradients in the sample space could thus be measured by microscopic evaluation. Further, a temperature estimation was carried out based on the melting of the crucible material. The maximum temperature reached was accordingly 2000°C.

A temperature distribution on heating the high pressure insert in the press tool is shown schematically in Figure 15. It can be seen how the high temperatures produced by the graphite tube 304 spread out and simultaneously there occurs on the outside a screening by the cover parts 302 and the pyrophyllite tube 303. The momentary temperature picture on reaching 1600°C in the graphite tube is shown, where a temperature of about 1400°C is present in the adjacent zone t, a temperature of 1100°C in the adjoining zone z, a temperature of about 700°C in the center y, and externally a temperature of about 740°C is present in the regions x.

The pressure reached in the interior of the capsule was calculated from calibration pressure curves of bismuth strips (with known transition pressures) and by computer methods. At most 80 Kbar was attained here.

The product obtained consists of water-clear to amber-colored grains of 1/100 mm to 1 mm diameter, which in a compact mass appear white to brownish-black. Because of the small dimensions of the sample space used, the yield of large grains (0.5 - 1 mm) is low, i.e., 3 volumes %. The largest proportion, at 50 volume %, is of grains of about 1/50 mm size. The residual fraction consists of grains with diverse sizes. The grains are amorphous by X-ray and electron beam, and scratch diamond on all faces: see Figure 10. They show strains in polarized light, have insulating properties, and conduct heat well. Scanning electron microscope pictures show a glass-like grain form, but pseudomorphic forms are also possible. The individual grains have a somewhat irregular ameba-like shape.

The amorphous boron nitride aBN-2 according to the invcention is a tough material which can be used advantageously in grinding wheels, since it shows little tendency to shatter. This is also an advantage over diamond and cubic boron nitride, which can be split along the different fracture surfaces of the crystal lattice. As a grinding material, it has a substantially higher working life than, e.g., cBN or diamond, since these are more likely to shatter because of the crystal structure. The new amorphous and tough boron nitride aBN-2, as against this, cannot be fractured in an oriented manner.

When a passive catalyst, e.g., platinum or cobalt, is added, a greater yield of large grains is obtained.

The product according to the invention - amorphous boron nitride aBN-2 - is compared with the different known varieties of boron nitride by means of electron microscope pictures.

Figure 1	shows hexagonal boron nitride (hBN) in a scanning electron microscope picture, enlarged about x 10600. Six-cornered platelets can be clearly seen.
Figure 2	shows hexagonal boron nitride (hBN) in a transmission electron microscope diffraction exposure (0001). Many fine reflection points can be seen on concentric circles. hBN is a starting material for the production of aBN-2.
Figure 3	shows "turbostratic" boron nitride (tBN) in a scanning electron microscope exposure, enlarged about x 10600. Starting material for the production of aBN-2.
Figure 4	shows "Turbostratic" boron nitride (tBN) in a transmission electron microscope diffraction exposure (0001). Many reflection points can be seen, some double.
Figure 5	shows cubic boron nitride (cBN) in a scanning electron microscope exposure, enlarged about x 570. Up to now the hardest BN modification

in cubic habit, according to U.S. Patent 2,947,617.

Figure 6 shows cubic boron nitride (cBN) in a transmission electron microscope diffraction exposure (111). A few strong reflection points are seen in a 6-angled grid arrangement with a view in the direction of a 3-fold space axis.

Figure 7 shows the new kind of boron nitride (aBN-2) in a scanning electron microscope exposure, enlarged about x 800. Melt particles without symmetry or faces can be seen, in a finer matrix.

Figure 8 shows the new kind of boron nitride (aBN-2) in a transmission electron microscope diffraction exposure without orientation. No (!) reflection points can be seen, but only diffuse rings. A true amorphous material is concerned.

Figure 9 shows the phase diagram of hexagonal boron nitride (hBN), cubic boron nitride (cBN) and amorphous boron nitride (aBN-s) in dependence on pressure and temperature, as ascertained by research on direct synthesis of amorphous aBN-2. hBN is represented by O, cBN by □, and aBN-2 by ▽ . The broken lines indicate the assumed phase boundaries between the physically different substances. The identification of the phases resulted after quenching and decompression. It is conceivable that the phase boundaries are displaced in an in-situ process.

Figure 10	shows a photograph, enlarged 50 times, of a flat surface (001 face) of a brilliant-cut diamond, scratched by amorphous aBN-2 grains.
Figure 11	shows a sectional picture of aBN-2 grains, enlarged, showing the ameba-like external shape. The white spots represent molten platinum droplets.

The diagram and the production processes, which have been compared with each other, for cBN and aBN-2 confirm that aBN-2 is obtained when the reaction conditions are chosen such that the pressure for the production of aBN-2 is markedly higher than for the production of cBN at altogether higher temperatures.

For confirmation of the hardness of the aBN-2 according to the invention, a hardess measurement was performed according to the setup schematically shown in Figure 16. A diamond 41 was tightly clamped in a plate 42. A drill 40 was equipped at the tip with grains 45 of amorphous aBN-2. The drill 40 was then pressed perpendicularly onto the diamond at a speed of 30,000 r.p.m. and a pressing force of 250 g. Here a force of 8 t was reached at the tip of the aBN-2 material loaded on the tightly clamped diamond 41. This test was continued for several hours, and in the course of time an erosion of diamond by the drill tip was effected, and can then be measured as penetration into the diamond as path length.

The hardness measurements of aBN-2 against diamond carried out according to Figure 16 are shown in Figure 17, and in fact for three trials V1, V2 and V3; the average curve from these, Vsum, is likewise indicated. The penetration depth into the diamond 41 was measured against the time in hours.

The confirmation was thus derived that the aBN-2 according to the invention, which is amorphous by electron beam and X-rays, is able to scratch diamond and has a hardness comparable to that of diamond. In addition, aBN-2 and cBN were subjected to hard X-rays (synchrotron radiation) and the diagrams were sketched.

The sketched curve of cBN is shown in Figure 18; the angular dispersion with hard X-ray irradiation was measured with a diffractometer. The single peaks are clearly visible, and provide the confirmation of the crystal structure of cBN.

The measured diagram for amorphous aBN-2 is shown in Figure 19, and in fact the energy dispersion, measured in the diffractometer, but with a substantially higher resolution, since the aBN-2 has no crystal structure and to this extent there could not be a recognizable measurement curve in a representation according to Figure 18. The smaller, upward-directed peaks, shown in Figure 19 and recognizable from the measurement curve, are caused by the means of attachment of the aBN-2 grains to a measurement head and hence excluded from consideration relating to aBN-2. The amorphous structure of aBN-2 is likewise established with this measurement result according to Figure 19.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Boron nitride (aBN-2) with an amorphous structure as determined by electron beam and X-ray, and with a hardness sufficient to scratch diamond.

2. Process for the production of boron nitride of high hardness from hexagonal or turbostratic boron nitride (BN) as starting material, which is subjected to pressures above 70 Kbar and temperature of at least 1650°C, characterized in that the starting material is subjected to the pressures and temperatures for long enough for it to be completely melted, following which the thus obtained boron nitride melt is quenched and grains of amorphous boron nitride (aBN-2) with X-ray and electron beam amorphous structure and with a hardness sufficient to scratch diamond, are formed.

3. Process according to Claim 2 in which the pressure is 75Kbar or more.

4. Process according to Claim 2 or Claim 3, characterized in that to quench the boron nitride melt the heat supply is first stopped and after this, pressure relief is performed.

5. Process according to any one of Claims 2 to 4, characterized in that the starting material (BN) is subjected to the desired reaction conditions of temperature and pressure for a long period of several minutes.

6. Process according to any one of Claims 2 to 5, characterized in that the starting material (BN) is subjected to pressures of at least 75 Kbar and temperatures of at least 1900°C.

7. Process according to any one of Claims 2 - 6, characterized in that a passive catalyst such as water (H_2O), carbon (C), platinum (Pt), zirconium (Zr) or cobalt (Co) is added to the starting material (BN).

8. Process according to Claim 7, characterized in that the passive catalyst is added in amounts of 3 - 20 wt.%, based on the amount of the starting material (BN).

DATED THIS 3RD DAY OF MARCH 1992
Jorg WILDENBURG and Georg WILL
By its Patent Attorneys:
GRIFFITH HACK & CO
Fellows Institute of Patent
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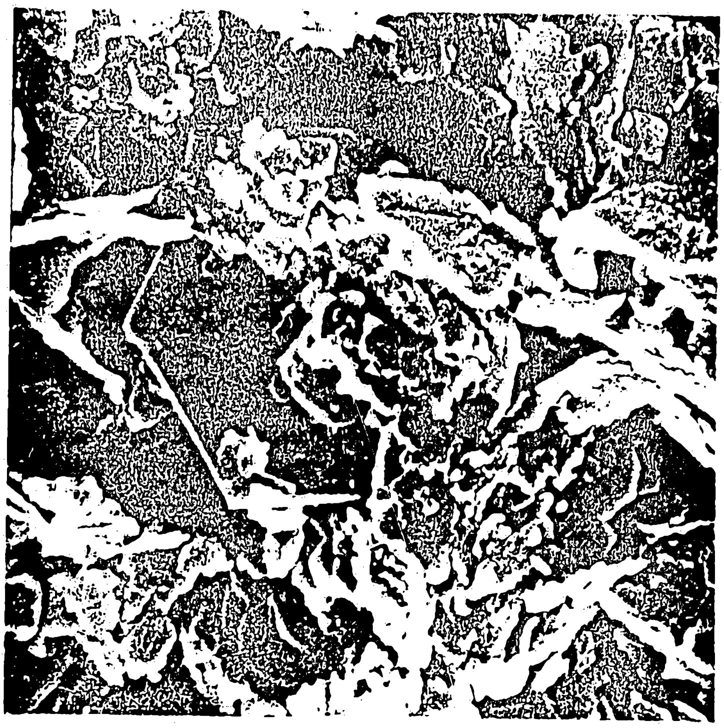


Fig. 1

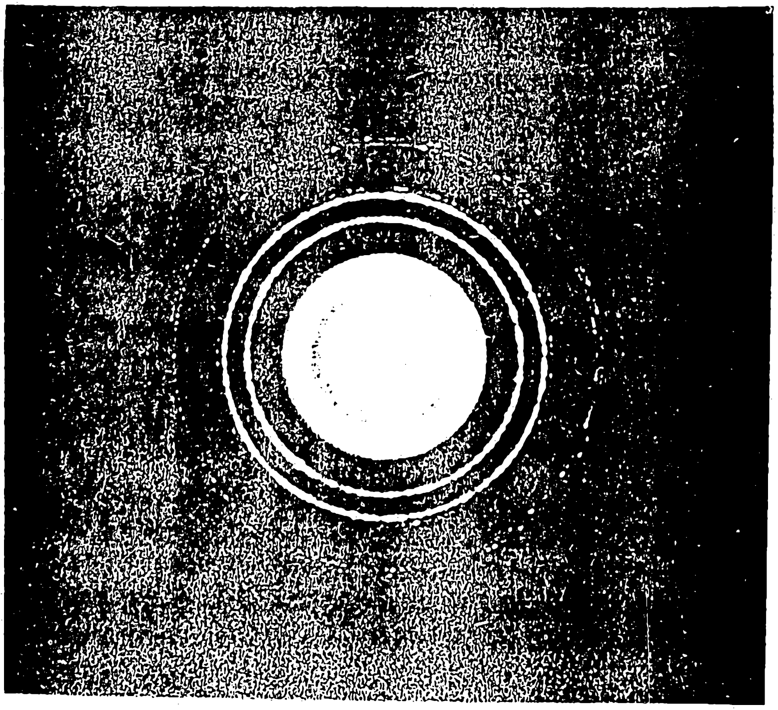


Fig. 2

Fig. 3

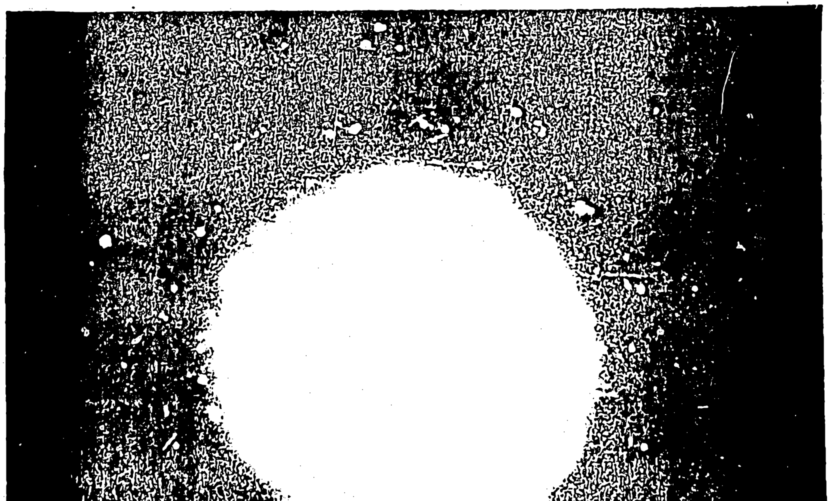


Fig. 4

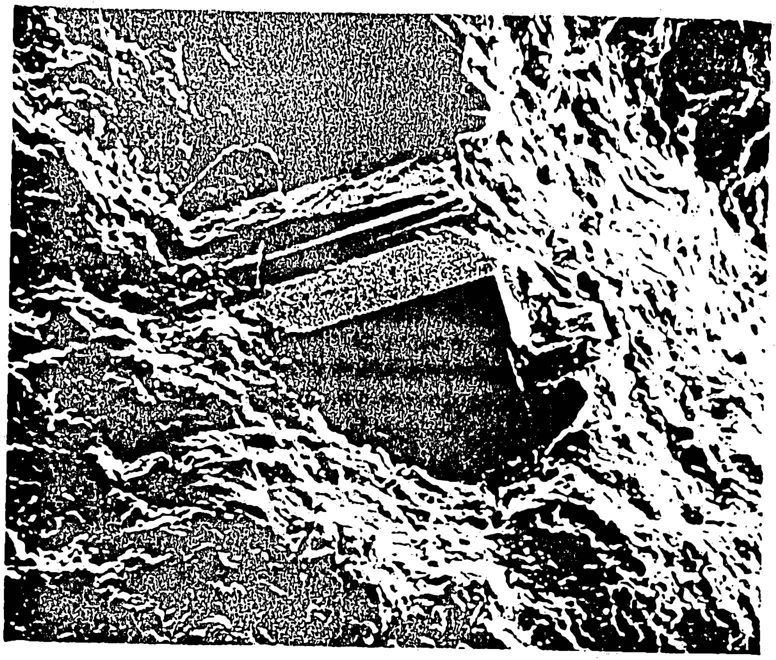


Fig. 5

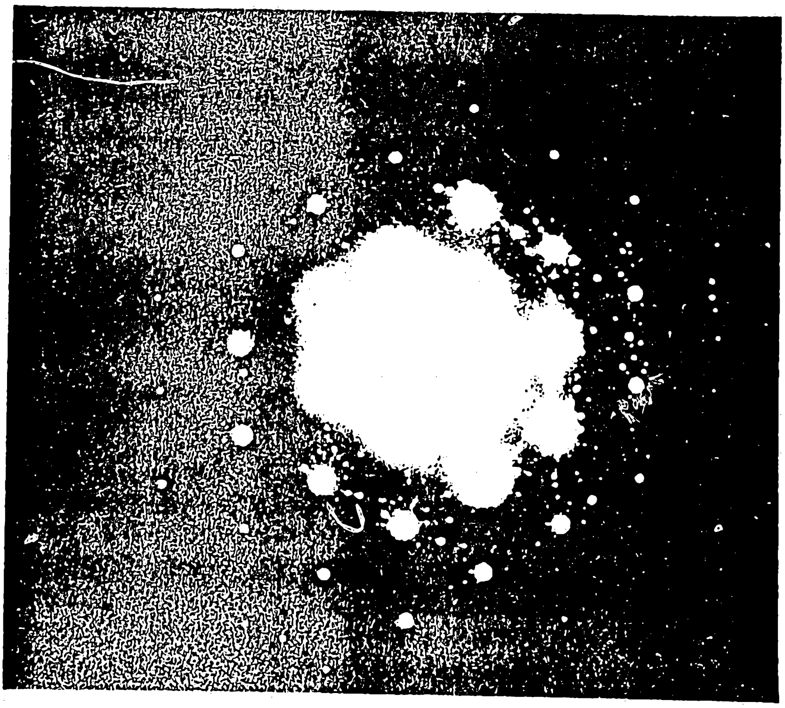


Fig. 6

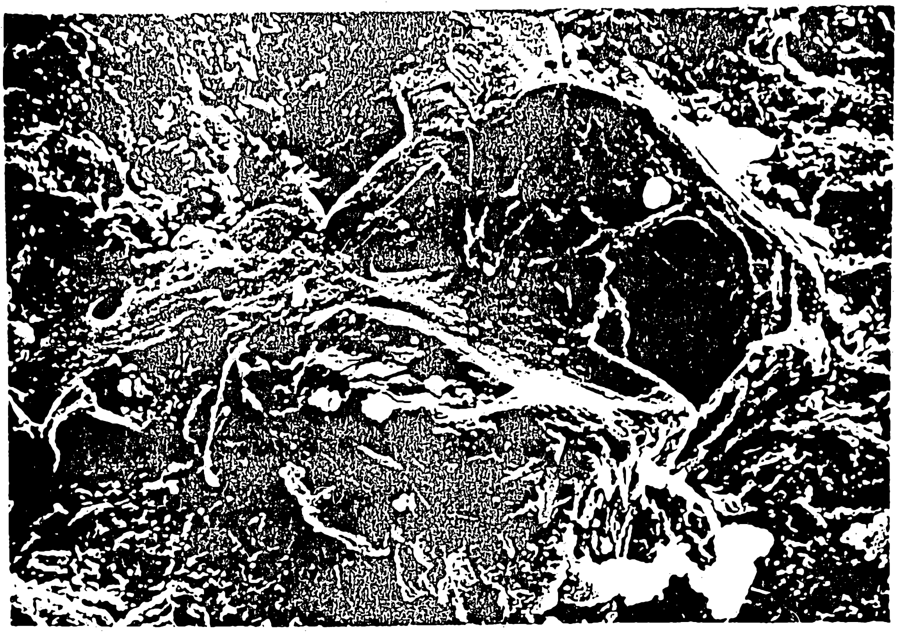


Fig. 7

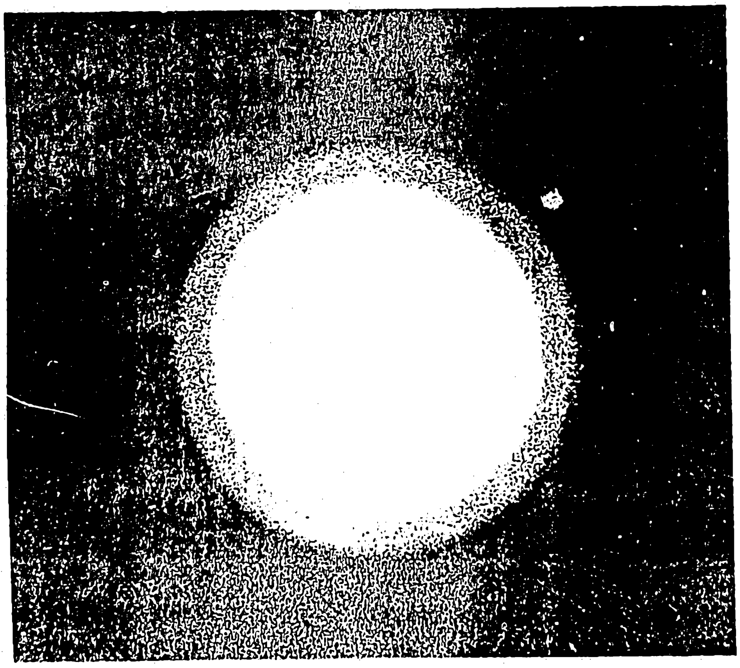


Fig. 8

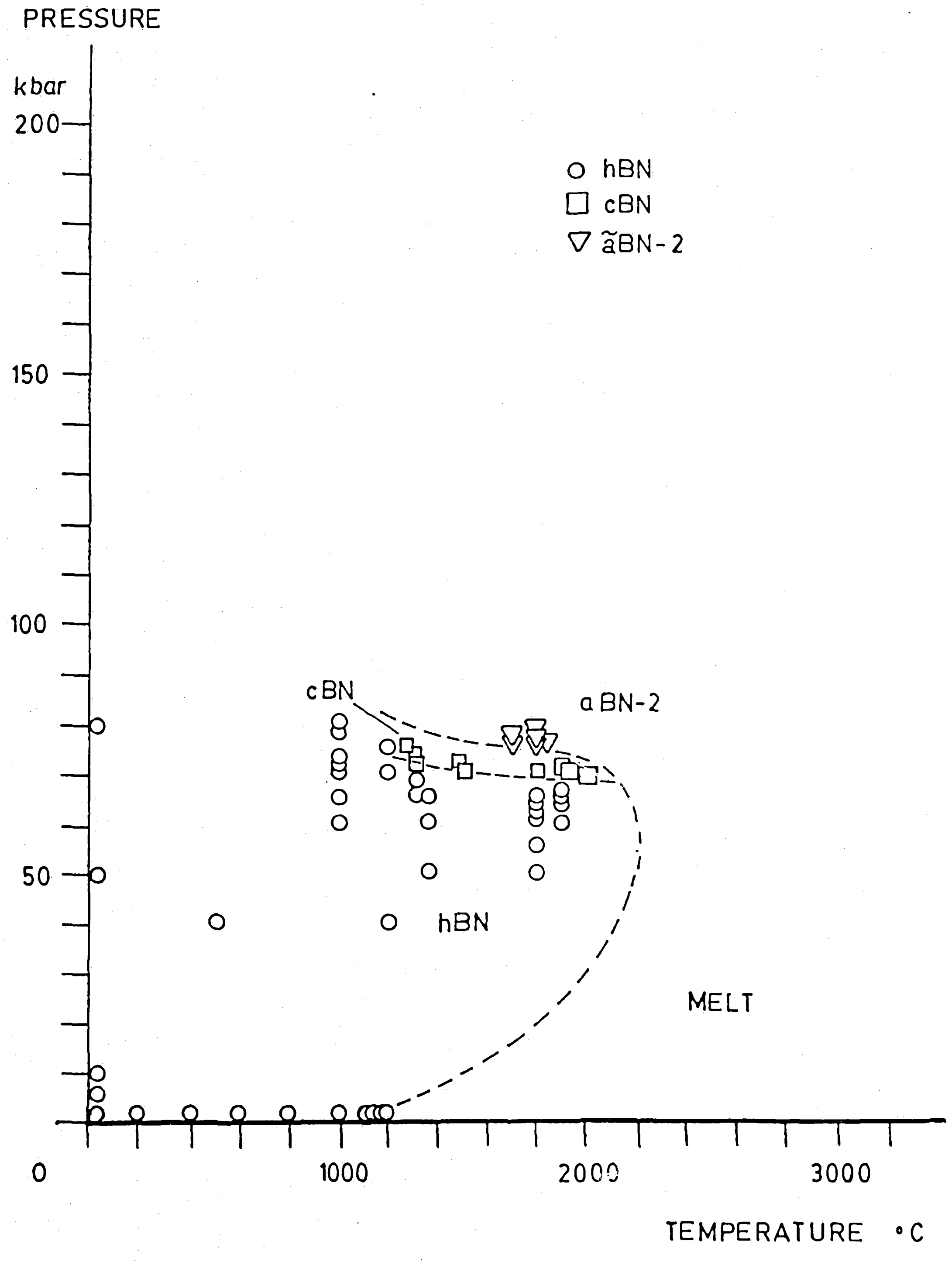

PRESSURE
kbar
200
150
100
50
0
1000
2000
3000
TEMPERATURE °C
○ hBN
□ cBN
▽ ãBN-2
cBN
a BN-2
hBN
MELT

FIG. 9

Fig. 10

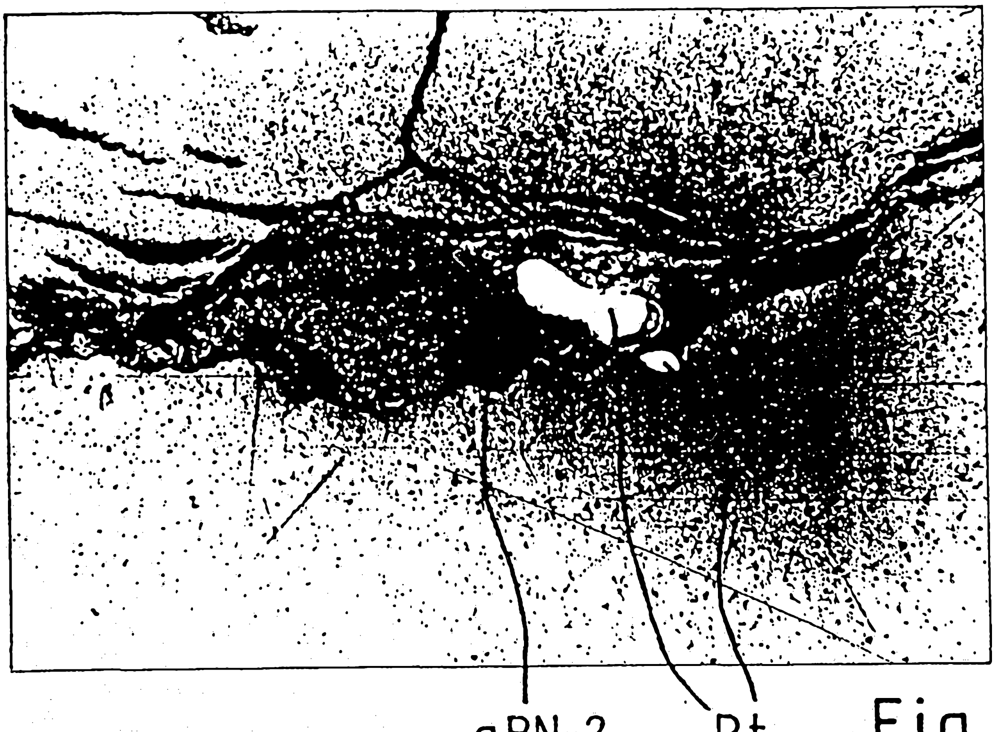


Fig. 11

Fig. 12

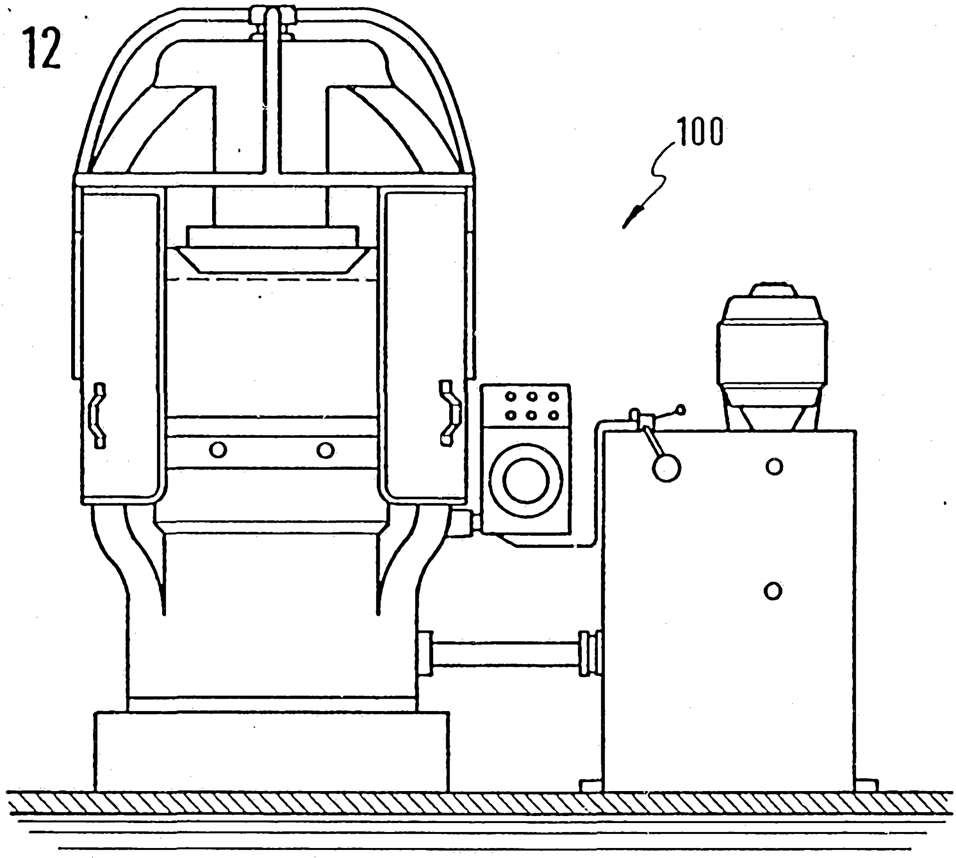

100

Fig. 13

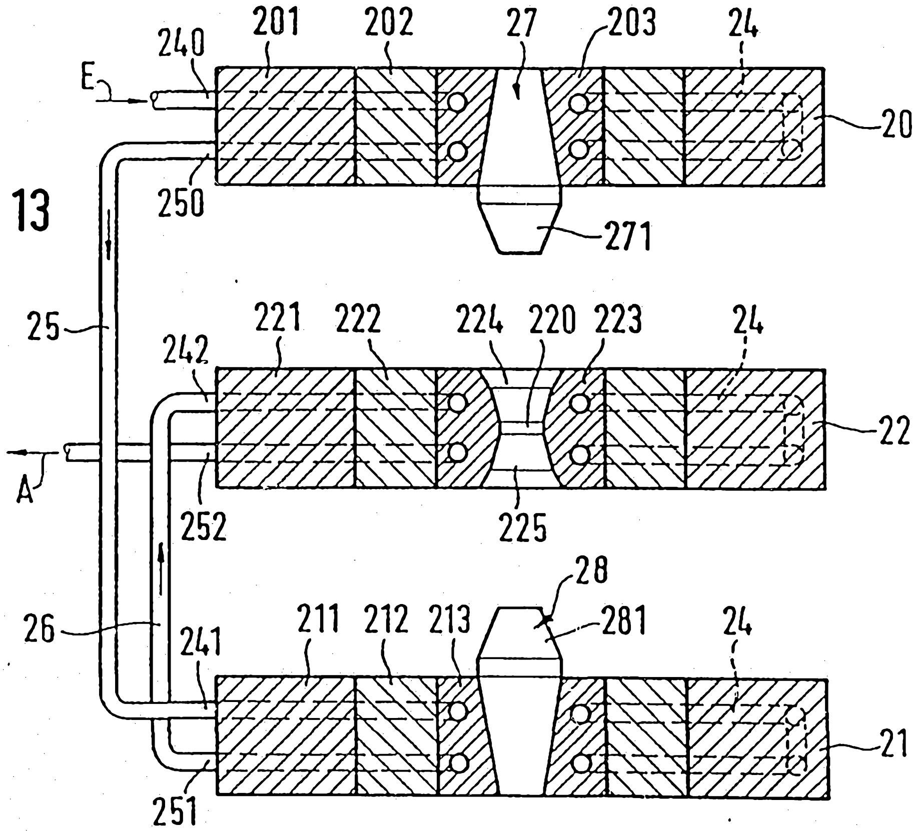
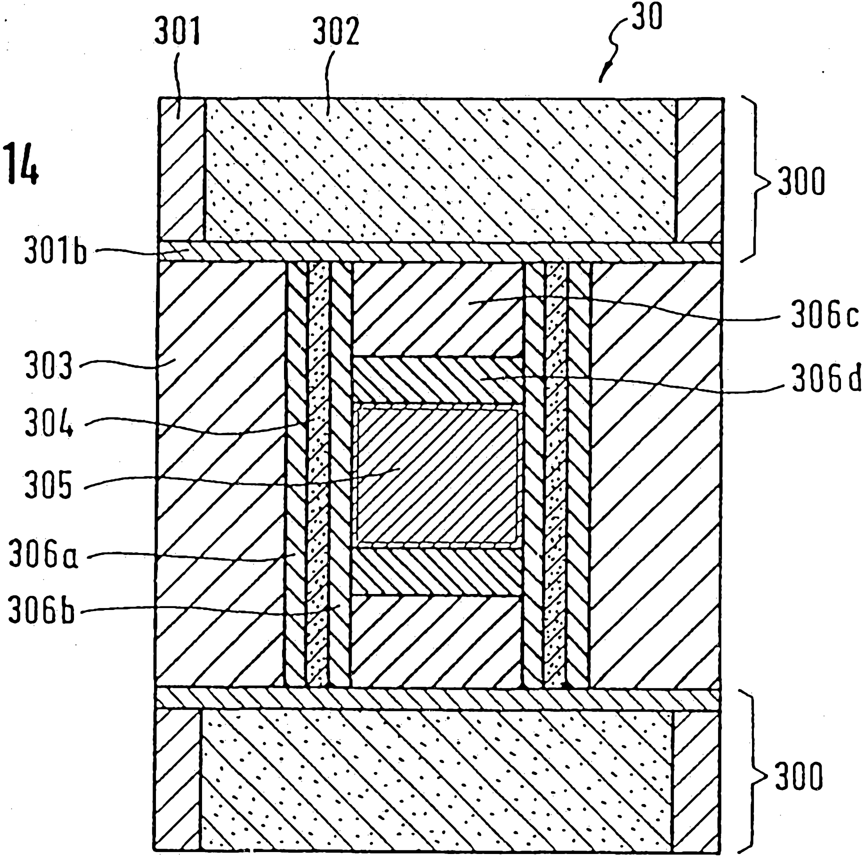
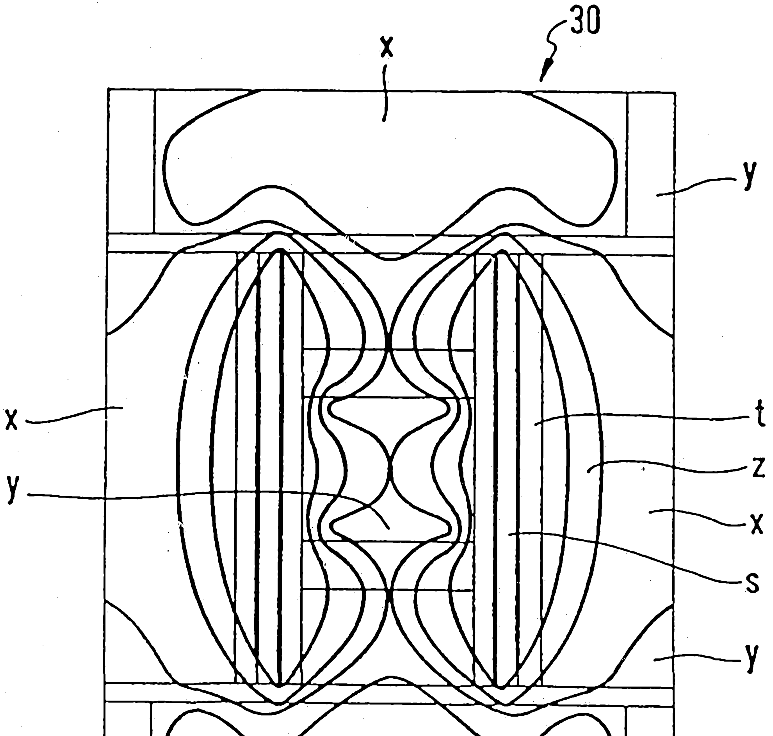

240
201
202
27
203
24
E
20
250
271
25
221
222
224
220
223
24
242
22
A
252
225
28
26
241
211
212
213
281
24
21
251

Fig. 14



301
302
30
300
301b
303
304
305
306a
306b
306c
306d
300

Fig. 15



30
x
y
x
y
t
z
x
s
y
x
y

Fig. 16

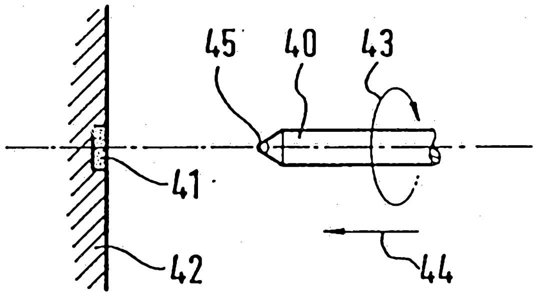
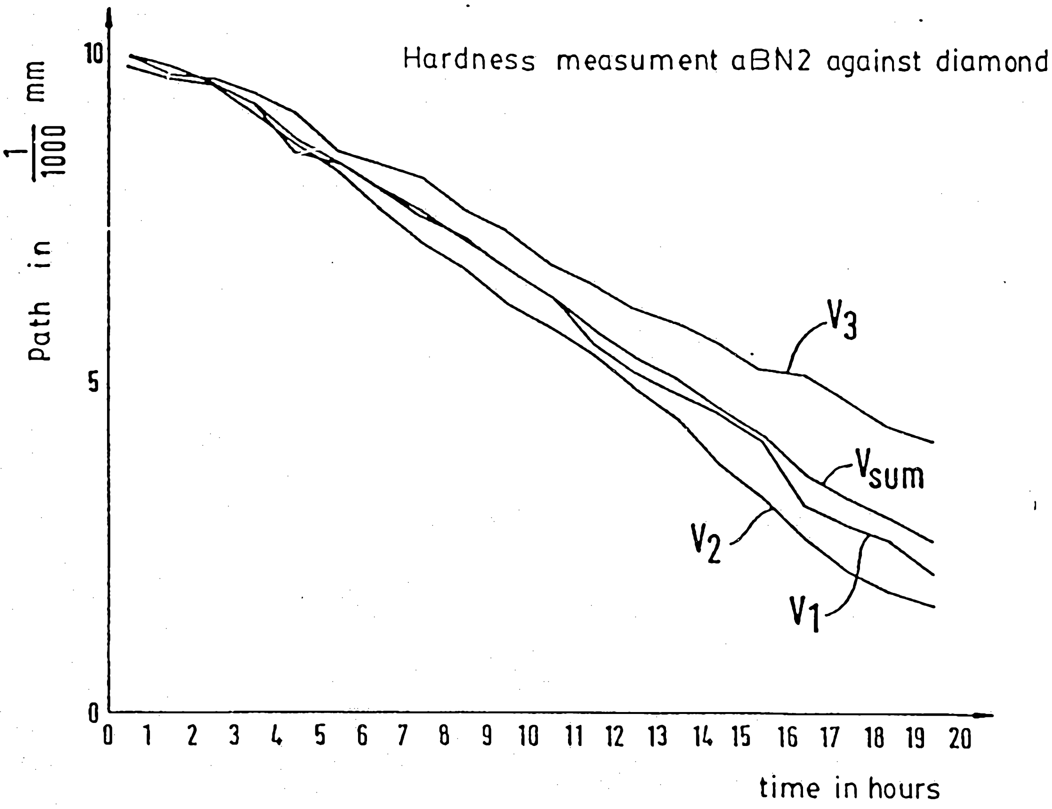

45
40
43
41
42
44

Fig. 17


Hardness measument aBN2 against diamond
Path in $\frac{1}{1000}$ mm
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
time in hours
V3
Vsum
V2
V1

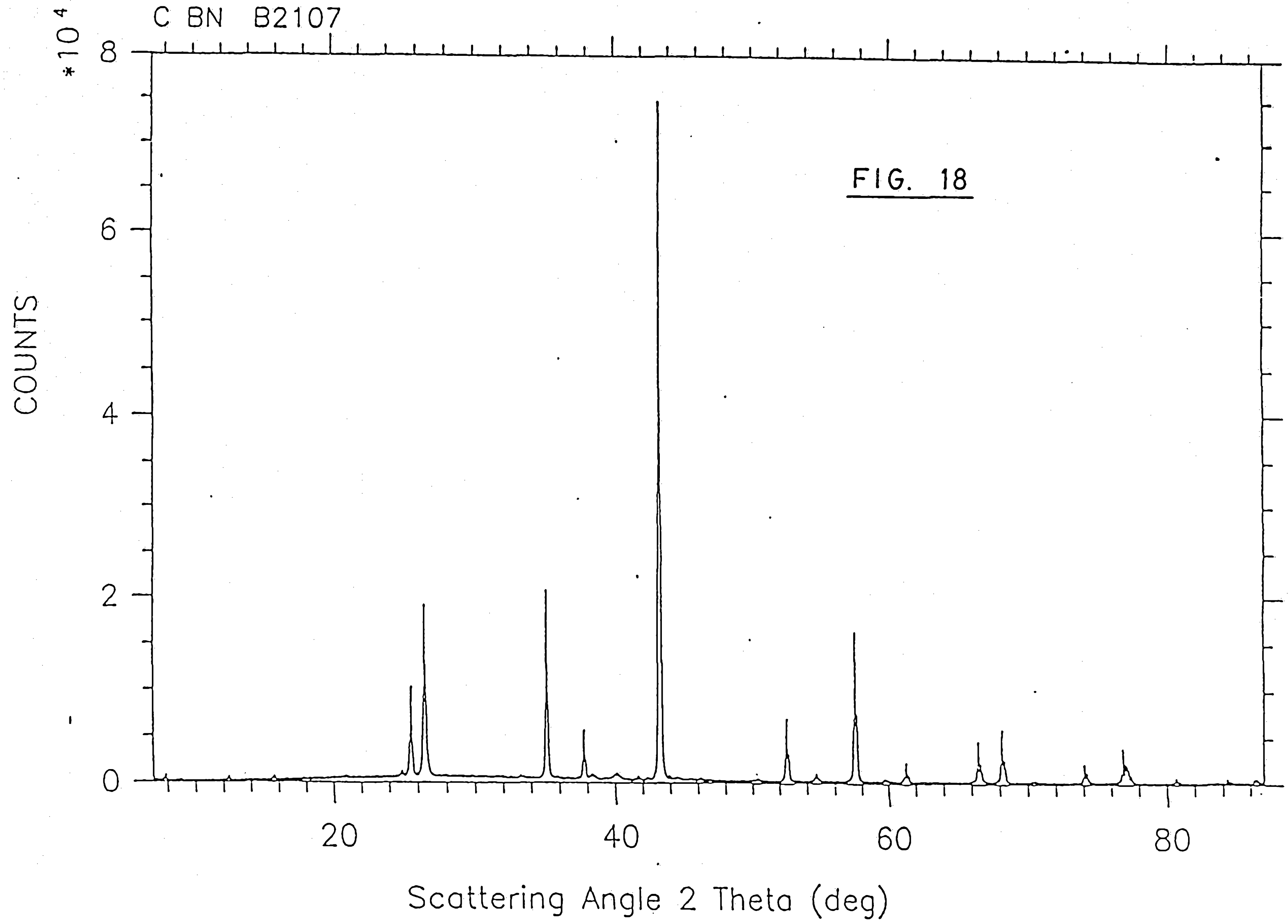
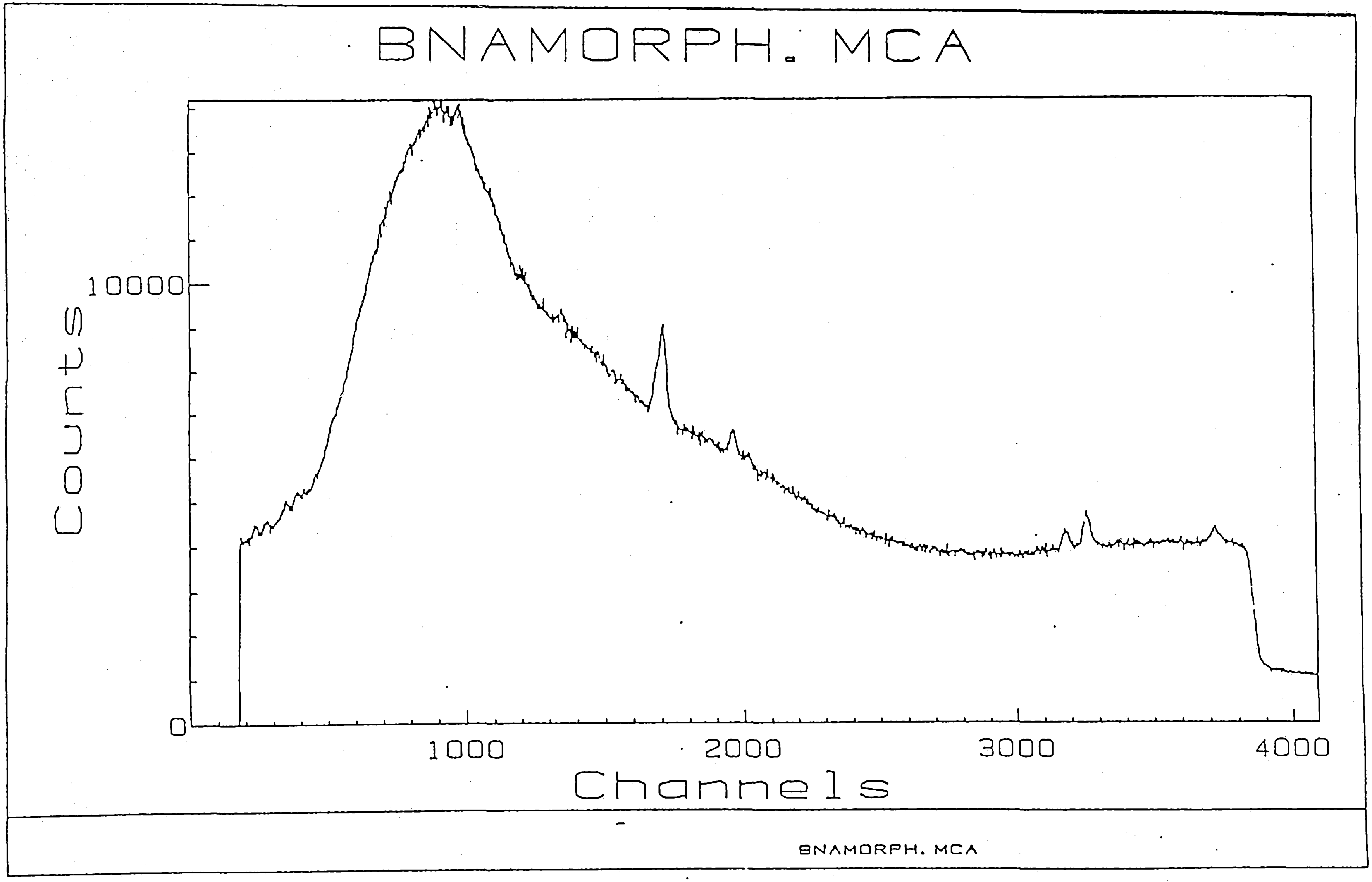

C BN B2107
*10^4
COUNTS
8
6
4
2
0
20
40
60
80
Scattering Angle 2 Theta (deg)

FIG. 18

11/01

FIG. 19


BNAMORPH. MCA
Counts
10000
0
1000
2000
3000
4000
Channels
BNAMORPH. MCA

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/1049

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 C01B 21/064 ; C04B 35/58 ; B01J 3/06

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
Int.Cl.5	C01B ; C04B ; B01J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4361543 (ZHDANOVICH) 30 November 1982 see claims 1-5	3,6-8
Y	see example 2, lines 63-67 ---	4,5
Y	CHEMICAL ABSTRACTS, vol. 93, no. 10, September 1980 Columbus, Ohio, USA page 153; right hand column; ref. no. 97824 C & JP-A-8060008 (NAT. INST. FOR RES. IN INORG. Mat.) (6/5/1980) see abstract ---	3-8
Y	US, A, 3233988 (WENTDORF) 8 February 1966 see claim 3 ---	7,8
	./.	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 23 January 1990 (23.01.90)	Date of Mailing of this International Search Report 22 February 1990 (22.02.90)
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer

International Application No. PCT/EP 89/01049

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	PATENT ABSTRACTS OF JAPAN vol.11, no. 322 (C-453)(2769) 20 October 1987, & JP-A-60 108713 (DENKI KAGAKU KOKOYO K.K.) 20 May 1987, see the whole document --	7,8
A	US, A, 4150098 (SIROTA) 17 April 1979 see abstract; example 1; lines 13-15; example 2; lines 40.50 -----------	3-6

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 89/01049
SA 31883

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 23/01/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4361543	30-11-82	DE-A- 3217556 FR-A,B 2526413	10-11-83 10-11-83
Ma-.-		None	
US-A-3233988		None	
US-A-4150098	17-04-79	None	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen PCT/EP 89/01049

I. KLASSIFIKATION DES ANMELDUNGSGEGENSTANDS (bei mehreren Klassifikationssymbolen sind alle anzugeben)[6]

Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC

Int.Kl. 5 C01B21/064 ; C04B35/58 ; B01J3/06

II. RECHERCHIERTE SACHGEBIETE

Recherchierter Mindestprüfstoff[7]

Klassifikationssytem	Klassifikationssymbole
Int.Kl. 5	C01B ; C04B ; B01J

Recherchierte nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Sachgebiete fallen[8]

III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN[9]

Art.°	Kennzeichnung der Veröffentlichung[11], soweit erforderlich unter Angabe der maßgeblichen Teile[12]	Betr. Anspruch Nr.[13]
Y	US,A,4361543 (ZHDANOVICH) 30 November 1982 siehe Ansprüche 1-5	3, 6-8
Y	siehe Beispiel 2, Zeile 63-67 ---	4, 5
Y	CHEMICAL ABSTRACTS, vol. 93, no. 10, September 1980 Columbus, Ohio, USA Seite 153; rechte Spalte; ref. no. 97824 C &JP-A-8060008 (NAT. INST. FOR RES. IN INORG. Mat.)(6/5/1980) siehe Zusammenfassung ---	3-8
Y	US,A,3233988 (WENTDORF) 8 Februar 1966 siehe Anspruch 3 --- -/--	7, 8

° Besondere Kategorien von angegebenen Veröffentlichungen[10] :

"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

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"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)

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"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist

"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist

"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

IV. BESCHEINIGUNG

1

Datum des Abschlusses der internationalen Recherche 23.JANUAR 1990	Absendedatum des internationalen Recherchenberichts 22.02.90
Internationale Recherchenbehörde EUROPÄISCHES PATENTAMT	Unterschrift des bevollmächtigten Bediensteten ZALM W.E.

Internationales Aktenzeichen PCT/EP 89/01049

III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2)

Art °	Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der maßgeblichen Teile	Betr. Anspruch Nr.
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 322 (C-453)(2769) 20 Oktober 1987, & JP-A-60 108713 (DENKI KAGAKU KOKOYO K.K.) 20 Mai 1987, siehe das ganze Dokument ---	7, 8
A	US,A,4150098 (SIROTA) 17 April 1979 siehe Zusammenfassung; Beispiel 1; Zeile 13-15; Beispiel 2; Zeile 40-50 ---	3-6

ANHANG ZUM INTERNATIONALEN RECHERCHENBERICHT ÜBER DIE INTERNATIONALE PATENTANMELDUNG NR.

PCT/EP 89/01049

SA 31883

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am 23/01/90
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
US-A-4361543	30-11-82	DE-A- 3217556 FR-A,B 2526413	10-11-83 10-11-83
Ma-.-		Keine	
US-A-3233988		Keine	
US-A-4150098	17-04-79	Keine	

EPO FORM P0473

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82