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FORM 1  
REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

APPLICATION FOR A PATENT

We KERAMONT ITALIA S.p.A.

of 31 For Buonaparte, 20121 MILAN, ITALY

hereby apply for the grant of a Patent for an invention entitled:

REFRACTORY AND ELECTROCONDUCTIVE CERAMIC COMPOSITIONS AND  
PROCESS FOR THE PREPARATION THEREOF

which is described in the accompanying complete specification. This  
Application is a Convention Application and is based on the  
Application numbered: 19409 A/90 for a Patent or similar protection  
made in Italy on 19 February 1990.

Our address for service is:

GRIFFITH HACK & CO  
71 YORK STREET  
SYDNEY NSW 2000

DATED this 15th day of February 1991

KERAMONT ITALIA S.p.A.  
By their Patent Attorney

J.H. Me  
GRIFFITH HACK & CO

3017775 15/02/91  
TO: THE COMMISSIONER OF PATENTS  
COMMONWEALTH OF AUSTRALIA

1936A:rk

ASSIGNEE - APPLICANT

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

In support of an Application made by: KERAMONT ITALIA S.p.A.

for a patent for an invention entitled:  
REFRACTORY AND ELECTROCONDUCTIVE CERAMIC COMPOSITIONS AND PROCESS  
FOR THE PREPARATION THEREOF

I, Ing. Giovanni DI DRUSCO, Chief Executive Officer  
of, KERAMONT ITALIA S.p.A., 31, Foro Buonaparte, 20121 MILAN  
do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent  
to make this Declaration on its behalf.
2. The name and address of each actual inventor of the invention is  
as follows:  
  
Giovanni Giunchi; Ender Savrun; Alberto Grenni and Ching-Fong Chen  
  
of 15, Via Don Gallotti, 28100 Novara, ITALY; 5675 N. Camino  
Esplendoria Apt. 1200, Tucson AZ 85718, U.S.A.; 203, Via F. 11i  
Cervi, Residenza Fontana 20090 Segrate Milano, ITALY and 4271 W.  
Woodridge Lane, Tucson AZ 85741, U.S.A., respectively

and the fact(s) upon which the applicant is entitled to make this  
application are as follows:

- By virtue of a contract of employment between the  
inventors and the applicant.
3. The basic application(s) as defined by Section 141 of the Act was  
(were) made as follows:  
  
In Italy on 19 February 1990  
in the name(s) Keramont Italia S.p.A.
  4. The basic application(s) referred to in the preceding paragraph  
of this Declaration was (were) the first application(s) made in a  
Convention country in respect of the invention the subject of  
this application.

DECLARED at Milan

this 20th day of December 1990

Signed: KERAMONT ITALIA S.p.A.  
(Ing. Giovanni DI DRUSCO)

Position: Chief Executive Officer

GRIFFITH HACK & CO, SYDNEY, AUSTRALIA

GH&CO REF: 21321-G:RPW:RK

1936A:rk



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REFRACTORY AND ELECTROCONDUCTIVE CERAMIC COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF

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(56) Prior Art Documents  
US 4627815

(57) Claim

1. Refractory and electroconductive ceramic compositions obtained by reactive sintering of aluminium nitride with at least one oxide of a transition metal, selected from those belonging to groups IVB, VB and VIB of the Periodic Chart of the Elements, at a temperature higher than 1450°C and a pressure higher than or equal to 10 MPa wherein the ratio of aluminium nitride to said oxide is chosen to provide ceramic compositions having an oxide component content between 20 and 80% by weight and a nitride component content between 80 and 20% by weight.

6. Refractory and electroconductive ceramic compositions having melting temperatures equal to or higher than 2000°C, density higher than or equal to 4 g/cm<sup>3</sup>, densification higher than 90%, ultimate tensile strength, according to U.S. Military Standard 1942 (MR), higher than 250 MPa, Vickers microhardness, according to ASTM E-384, higher than 1000 kg/mm<sup>2</sup> and electric resistivity, according to F-43, lower than 600 microohm.cm.

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

Form 10

SUBSTITUTE COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

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Lodged:

Complete Specification-Lodged:

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Related Art:

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TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled:

REFRACTORY AND ELECTROCONDUCTIVE CERAMIC COMPOSITIONS  
AND PROCESS FOR THE PREPARATION THEREOF

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

GH&CO REF: 21321-C:RPW:RK

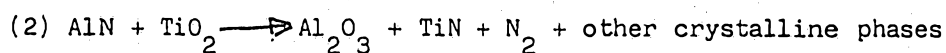
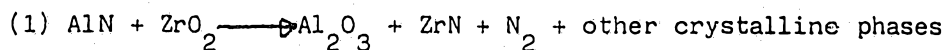
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### Field of the Invention

The present invention relates to electro-conductive ceramic compositions and to the process for the preparation thereof.

### Background of the Invention

It is known, as published in "Journal of Materials Science" 20 (1985), page 3697, in "Ceramics International" 15 (1989), page 271 or in "Journal of Material Science" 16 (1981), 2997, that at high temperatures, reactions of the type



may take place. In these above reactions, by the term "other crystalline phases" suboxides or oxynitrides, in different valency state of the corresponding metals, are intended.

It is also known that materials of the type of metal nitrides, such as for instance zirconium or titanium nitride, are good electroconductive materials and have hardness and tribologic characteristics such to be used in ceramic composite materials useful as anti-wear materials, for instance in coatings of inserts for cutting tools.

To this purpose powders of metal nitrides and alumina having suitable granulometries, can be mixed intimately and sintered at high temperature and under pressure or can be deposited on the material surfaces by techniques such as "physical vapour deposition".

On the contrary, ceramic compositions obtained by reactions (1) and (2) are not suitable for practical uses in that they have mechanical and electrical characteristics reduced and little stable or controllable.

The Applicant have now found that if reactions of the type (1) and (2) are carried out under suitable process conditions, it is possible to obtain compositions, essentially consisting of alumina and metal nitrides, with high density and showing homogeneous and isotropic scattering of components.

The thus obtained compositions are suitable for practical applications in that they are endowed with mechanical and tribologic properties higher than those of analogous compositions obtained by the above mentioned conventional sintering processes and can be worked by spark erosion techniques.

Accordingly, the present invention provides refractory and electroconductive compositions obtained by reactive sintering of aluminium nitride with at least one oxide of a transition metal, selected among those belonging to groups IVB, VB and VIB of the Periodic Chart of the Elements, at a temperature higher than 1450°C and under a pressure higher or equal to 10 Mpa wherein the ratio of aluminium nitride to said oxide is chosen to provide ceramic compositions having an oxide component content between 20 and 80% by weight and a nitride component content between 80 and 20% by weight.

At the end of the reactive sintering, the ceramic composition of the present invention essentially consists of an oxidic component, essentially represented by alumina, and of a nitride component, essentially represented by at least one nitride of at least one transition metal of groups IVB, VB and VIB.

Preferably, the ceramic compositions of the present invention are those having an oxide component content comprised between 40 and 60% by weight, and a nitride component content comprised between 60 and 40% by weight.

The compositions wherein the nitride component contains one, two or three nitrides of one, two or three transition metals are comprised in the present invention.

Transition metals used in ceramic compositions of the present invention are those belonging to groups IVB, VB and VIB of the Periodic Chart of the Elements; preferred metals are titanium, zirconium, hafnium, vanadium, niobium and tantalum.

Ceramic compositions of the present invention can be highly refractory having melting temperatures equal to or higher than 2000°C, generally between 2000 and 2500°C,



and characterized by a continuous nitride phase which makes them highly electroconductive at room temperatures; they may be endowed with superconductive properties at temperatures higher than the hydrogen liquefaction temperature.

The present ceramic compositions can have a density higher than or equal to  $4 \text{ g/cm}^3$ , generally between 4 and  $10 \text{ g/cm}^3$ , a densification higher than 90%, generally between 95 and 99.9%, an ultimate tensile strength, measured according to U.S. Military Standard 1942 (MR), higher than 250 MPa, generally between 300 and 600 MPa, Vickers microhardness, measured according to ASTM E-384 higher than  $1000 \text{ kg/mm}^2$ , generally comprised between 1200 and  $2500 \text{ kg/mm}^2$  and electric resistivity, measured according to ASTM F-43, lower than 600 microohm.cm, generally between 400 and 100 micro-ohm.cm.

Accordingly, the present invention also provides refractory and electroconductive ceramic compositions having melting temperatures equal to or higher than  $2000^\circ\text{C}$ , density higher than or equal to  $4 \text{ g/cm}^3$ , densification higher than 90%, ultimate tensile strength, according to U.S. Military Standard 1942 (MR), higher than 250 MPa, Vickers microhardness, according to ASTM E-384, higher than  $1000 \text{ kg/mm}^2$  and electric resistivity, according to F-43, lower than 600 microohm.cm.

Ceramic compositions of the present invention can be used in the thermotechnique as resistors for furnaces, crucibles for the evaporation of metals, etc., in mechanical processing as materials for tools, in mechanical components as anti-wear and antistatic materials, in the aerospace as coating for space apparatus, etc. or as shaped bodies.

A process for the preparation of the refractory and electroconductive ceramic compositions here described comprises:

- (a) mixing aluminium nitride with at least one oxide of a transition metal selected from those belonging to groups IVB, VB and VIB or the



Periodic Chart of the Elements; and

- (b) allowing the thus obtained mixture to react at a temperature higher than  $1450^{\circ}\text{C}$ , preferably higher than or equal to  $1500^{\circ}\text{C}$ , and under a pressure higher than or equal to 10 MPa.

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According to a preferred embodiment of the process of the present invention, in step (a) the aluminium nitride is mixed with an oxide of a transition metal or optionally with two or three oxides.

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Ratios by weight among the oxides change according to the characteristics which in the finished product are desired to be exalted.

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Both the aluminium nitride and metal oxides are preferably used in form of powders having granulometry lower than 5 micrometers, generally between 0.5 and 2 micrometers, and with AlN/oxides ratios such to obtain, in the final ceramic composite, the previously described contents of oxide component and nitride component. Molar ratios AlN/total oxides higher than or equal to  $4/3$ , preferably between  $4/3$  and  $2/1$ , are those which can be

20

3  
7  
2  
6  
8  
1  
9



used.

The mixing of powders can be performed either in dry or in wet according to techniques well known to those skilled in the art.

If the mixture is carried out in wet, as dispersing agent organic liquids can be used, such as acetone, alcohols, aliphatic hydrocarbons containing a low number of carbon atoms, such as hexane, etc.

It is also possible to use optional binding agents able to solubilize or disperse in the liquid base and to degrade during the reaction/sintering step.

Examples of binding agents are those used for ceramic powders, such as polyvinylbutyral.

The mixture, after evaporation of the solvent, can be directly introduced into the sintering die as powder or as pre-shaped body.

Alternatively, for objects having a complicate shape or wide sizes, the mixture can be pre-stiffed according to the different techniques used for forming ceramic materials and then sintered, after having removed the organic components, under inert gas pressure (Hot isostatic press).

The shaped article is sintered according to the step (b), at a temperature preferably comprised between 1450 and 1950 °C, or in an atmosphere controlled by inert gases, such as nitrogen, argon, etc., at high pressure, preferably comprised between 15 and 300 MPa, or under vacuum and with a mechanical

pressure preferably comprised between 10 and 50 MPa.

Sintering times are usually higher than 30 minutes and are generally comprised between 45 and 120 minutes.

Powders, which make up the reaction mixture, can have a purity degree generally higher than 96% and are easily available on the market.

To better understand the present invention and to practically perform it, some illustrative but not limitative examples are given hereinafter.

#### EXAMPLE 1

A mixture consisting of 57.15% molar AlN and 42.85% molar  $\text{TiO}_2$ , both components having purities higher than 99.5% and average granulometry equal to 1.5 micrometers, is prepared by wet milling in acetone using  $\text{Al}_2\text{O}_3$  marbles and polyethylene jar.

After having evaporated the solvent under reduced pressure, the powder is stiffed in a graphite die, coated with boron nitride powder, by an uniaxial compression equal to 6 MPa. By mechanical pressing of 20 MPa and under vacuum at 1550°C for 60 minutes, a composite is obtained having a density of  $4.35 \text{ g/cm}^3$ , with a 95.4% densification, and electroconductive, with a resistivity of 360 microhm.cm.

The bending stress resistance at 4 points is 436 MPa and the Vickers microhardness is  $1963 \text{ kg/mm}^2$ .

Crystalline phases in the thus obtained composite are identified by X ray diffraction which shows only the presence of



$\alpha$ - $\text{Al}_2\text{O}_3$  and TiN as illustrated in Fig.1

#### EXAMPLE 2

A mixture consisting of 57.15% molar AlN, 31.07% molar  $\text{TiO}_2$  and 11.78% molar  $\text{ZrO}_2$ , the three components having all purity degrees higher than 99.5% and average granulometries of about 1.5 micrometers, is prepared by wet milling in acetone, using  $\text{Al}_2\text{O}_3$  marbles and polyethylene jar. After having evaporated the solvent under reduced pressure, the powder is pressed in a graphite die by an uniaxial compression of 6 MPa. By mechanical pressing at 40 MPa and under vacuum, at 1550°C for 1 hour, an electroconductive composite is obtained having a density equal to 4.34 g/cm<sup>3</sup>.

The bending stress resistance at 4 points is 341 MPa; the Vickers microhardness is 1260 kg/mm<sup>2</sup>. Crystalline phases in the thus obtained composite are identified by X ray diffraction as illustrated by the diagram of Fig. 2.

#### EXAMPLE 3

A mixture consisting of 57.15% molar AlN and 42.85% molar  $\text{ZrO}_2$ , both having a purity degree higher than 99% and an average granulometry of about 2 micrometers, is prepared by wet milling in acetone using  $\text{Al}_2\text{O}_3$  marbles and polyethylene jar. After having evaporated the solvent under reduced pressure, the powder is pressed in a graphite die by an uniaxial compression at 6 MPa.

By mechanical pressing at 40 MPa and under vacuum at 1700°C for

1 hour, a composite is obtained having a density of  $4.88 \text{ g/cm}^3$ ; the electric resistivity is  $590 \text{ microhm.cm}$  and the Vickers microhardness is  $1530 \text{ kg/mm}^2$ . In the obtained product, both the oxide component and the nitride component are intimately mixed to give only one oxinitride crystalline phase of the cubic type, as shown by the X-ray diffraction diagram of Fig. 3.

#### EXAMPLE 4

A mixture consisting of 57.15% molar AlN, 35.41% molar  $\text{TiO}_2$  and 7.44% molar  $\text{Nb}_2\text{O}_5$ , all the three components having purity degrees higher than 99% and granulometries of about 1.5 micrometers, is prepared as described in the preceding examples and is pressed under vacuum at the pressure of 40 MPa, at the temperature of  $1550^\circ\text{C}$  for 1 hour.

A composite is obtained having a density of  $4.66 \text{ g/cm}^3$ , electric resistivity of  $574 \text{ microhm.cm}$  and Vickers microhardness of  $1420 \text{ kg/mm}^2$ , said composite consisting of  $\alpha\text{-Al}_2\text{O}_3$  and of a mixture of nitride phases of the cubic type as shown by the X-ray diffraction diagram of Fig. 4.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Refractory and electroconductive ceramic compositions obtained by reactive sintering of aluminium nitride with at least one oxide of a transition metal, selected from those belonging to groups IVB, VB and VIB of the Periodic Chart of the Elements, at a temperature higher than 1450°C and a pressure higher than or equal to 10 MPa wherein the ratio of aluminium nitride to said oxide is chosen to provide ceramic compositions having an oxide component content between 20 and 80% by weight and a nitride component content between 80 and 20% by weight.

2. Compositions according to claim 1, essentially consisting of an oxide component, essentially represented by alumina, and of a nitride component, essentially represented by at least one nitride of at least one transition metal of groups IVB, VB and VIB.

3. Compositions according to claim 1 or claim 2 wherein the nitride component contains one, two or three nitrides of one, two or three transition metals.

4. Compositions according to anyone of the preceding claims, wherein the transition metals are selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum.

5. Compositions according to claim 4, wherein the transition metal is titanium.

6. Refractory and electroconductive ceramic compositions having melting temperatures equal to or higher than 2000°C, density higher than or equal to 4 g/cm<sup>3</sup>, densification higher than 90%, ultimate tensile strength, according to U.S. Military Standard 1942 (MR), higher than 250 MPa, Vickers microhardness, according to ASTM E-384, higher than 1000 kg/mm<sup>2</sup> and electric resistivity, according to F-43, lower than 600 microhm.cm.

7. Compositions according to claim 6 having density between 4 and 10 g/cm<sup>3</sup>, densification between 95 and 99.9%, ultimate tensile strength between 300 and 600 MPa, Vickers microhardness between 1200 and 2500 kg/mm<sup>2</sup>,



electric resistivity between 400 and 100 microhm.cm.

8. Process for the preparation of electroconductive refractory ceramic compositions which comprises:

- 5 (a) mixing aluminium nitride with at least one oxide of a transition metal selected from those belonging to groups IVB, VB and VIB of the Periodic Chart of the Elements; the ratio of aluminium nitride to oxide being chosen to provide final ceramic compositions having an  
10 oxide component content between 20 and 80% by weight and a nitride component content between 80 to 20% by weight; and
- 15 (b) allowing the mixture thus obtained to react at temperature higher than 1450°C, preferably higher than or equal to 1500°C, and at a pressure higher than or equal to 10 MPa.

9. Process according to claim 8, wherein the aluminium nitride is mixed with an oxide of a transition metal or optionally with two or three oxides.

20 10. Process according to claim 8 or 9, wherein the aluminium nitride and the metal oxides are used in form of powders having granulometries lower than 5 micrometers, generally between 0.5 and 2 micrometers.

25 11. Process according to anyone of claims 8 to 10, wherein the molar ratios  $AlN$ /total oxides are higher than or equal to 4/3.

12. Process according to anyone of claims 8 to 11, wherein the mixing is carried out in dry or in wet.

30 13. Process according to anyone of claims from 8 to 12, wherein the sintering of step (b) is carried out between 1450 and 1950°C under atmosphere controlled by inert gases at high pressure comprised between 15 and 300 MPa.

35 14. Process according to anyone of claims 8 to 12, wherein the sintering of step (b) is carried out under vacuum and with a mechanical pressure comprised between 10 and 50 MPa.

15. Process according to anyone of claims 8 to 14,



wherein sintering times are higher than 30 minutes and generally comprised between 45 and 120 minutes.

16. Process according to anyone of claims 8 to 15, wherein reagents are used with a purity degree higher than 96%.

17. Use of the electroconductive ceramic compositions of anyone of claims 1 to 7 in thermotechnique, in mechanical processing, in mechanical component industry, in space field.

18. Shaped bodies of ceramic compositions as defined in anyone of claims 1 to 7.

19. Refractive and electroconductive ceramic compositions substantially as herein described with reference to any one of the Examples.

20. Process for the preparation of refractive and electroconductive ceramic compositions substantially as herein described with reference to any one of the Examples.

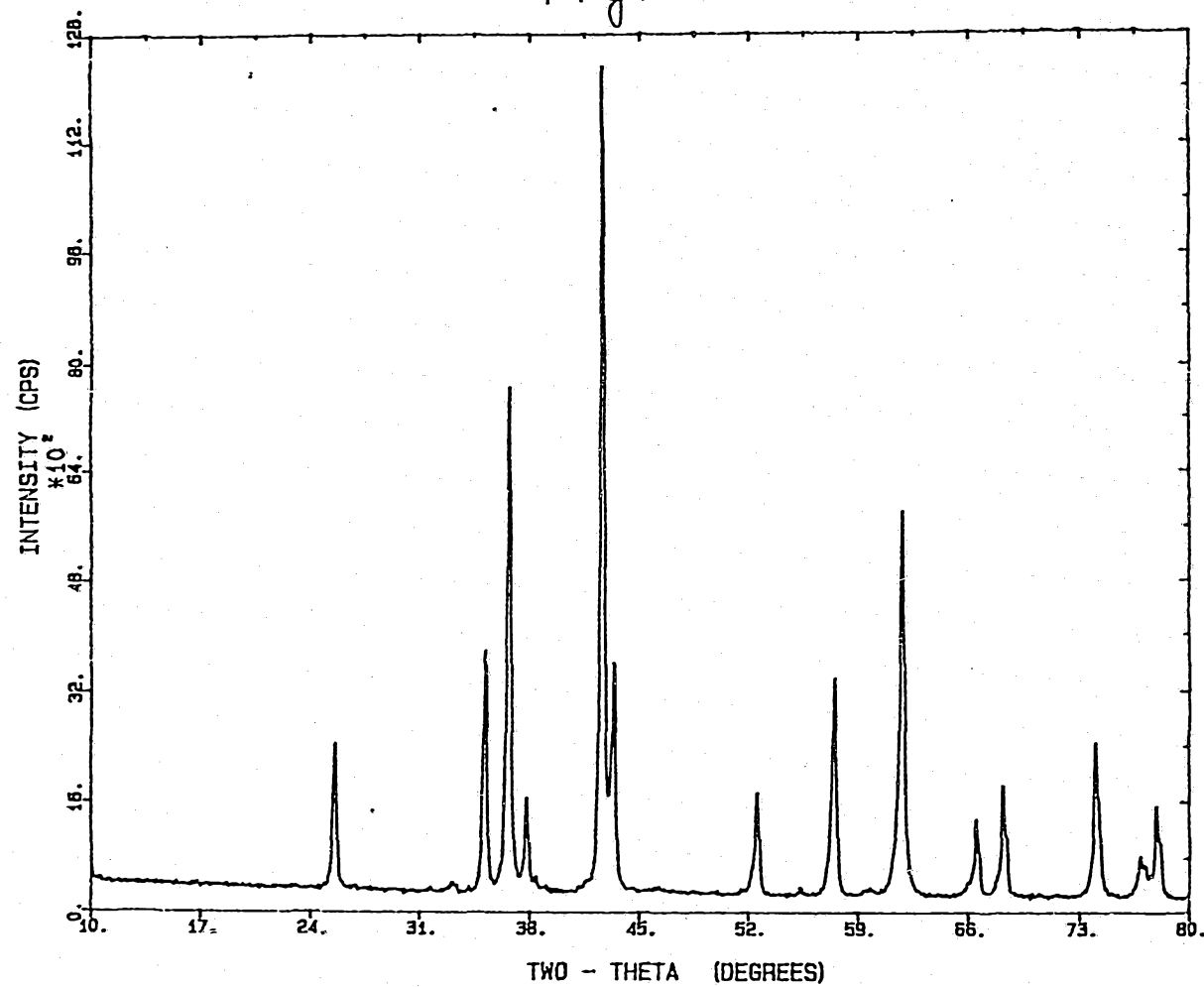
Dated this 10th day of August 1993

20 KERAMONT ITALIA S.p.A.  
By their Patent Attorney  
GRIFFITH HACK & CO



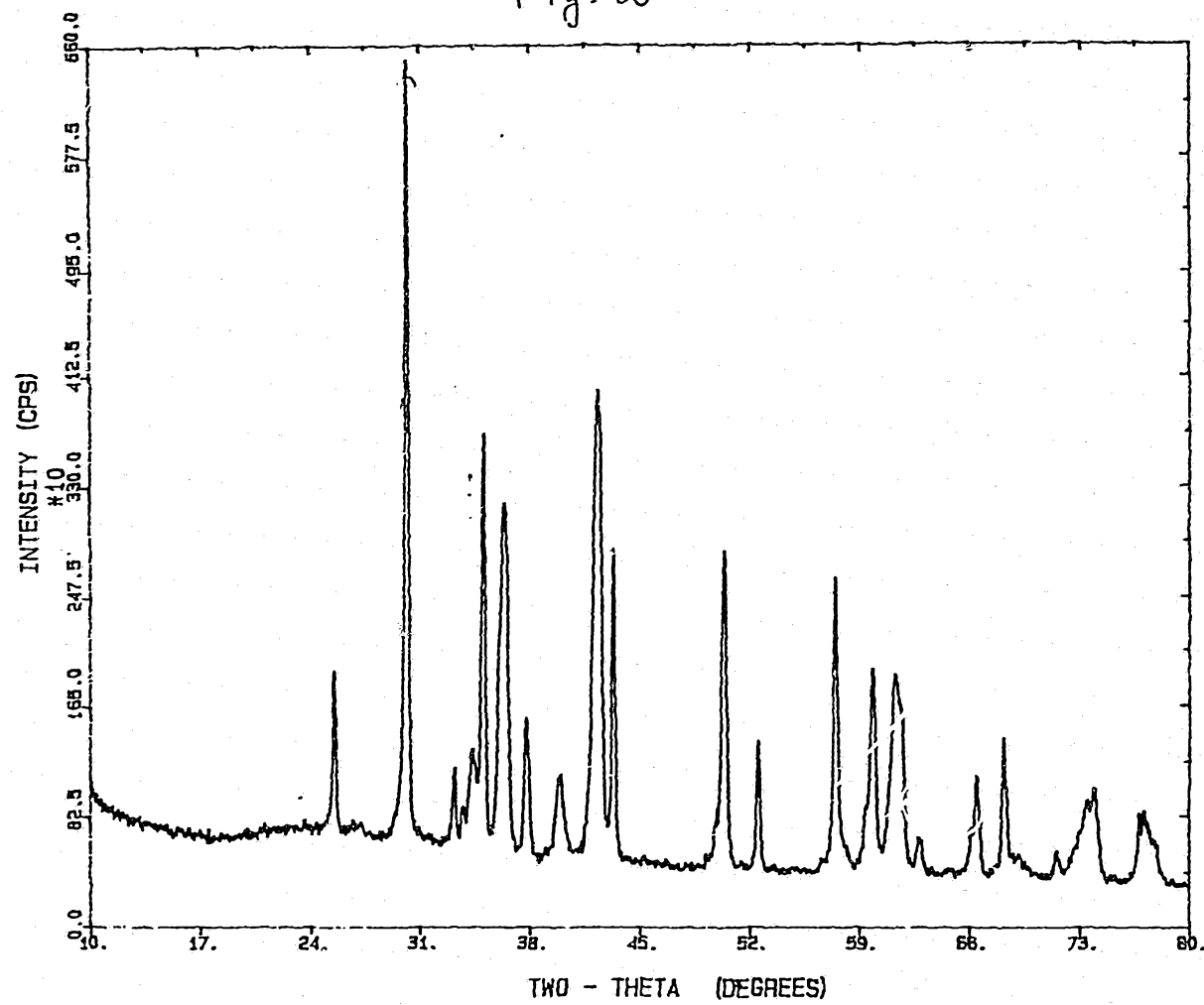
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Fig. 1



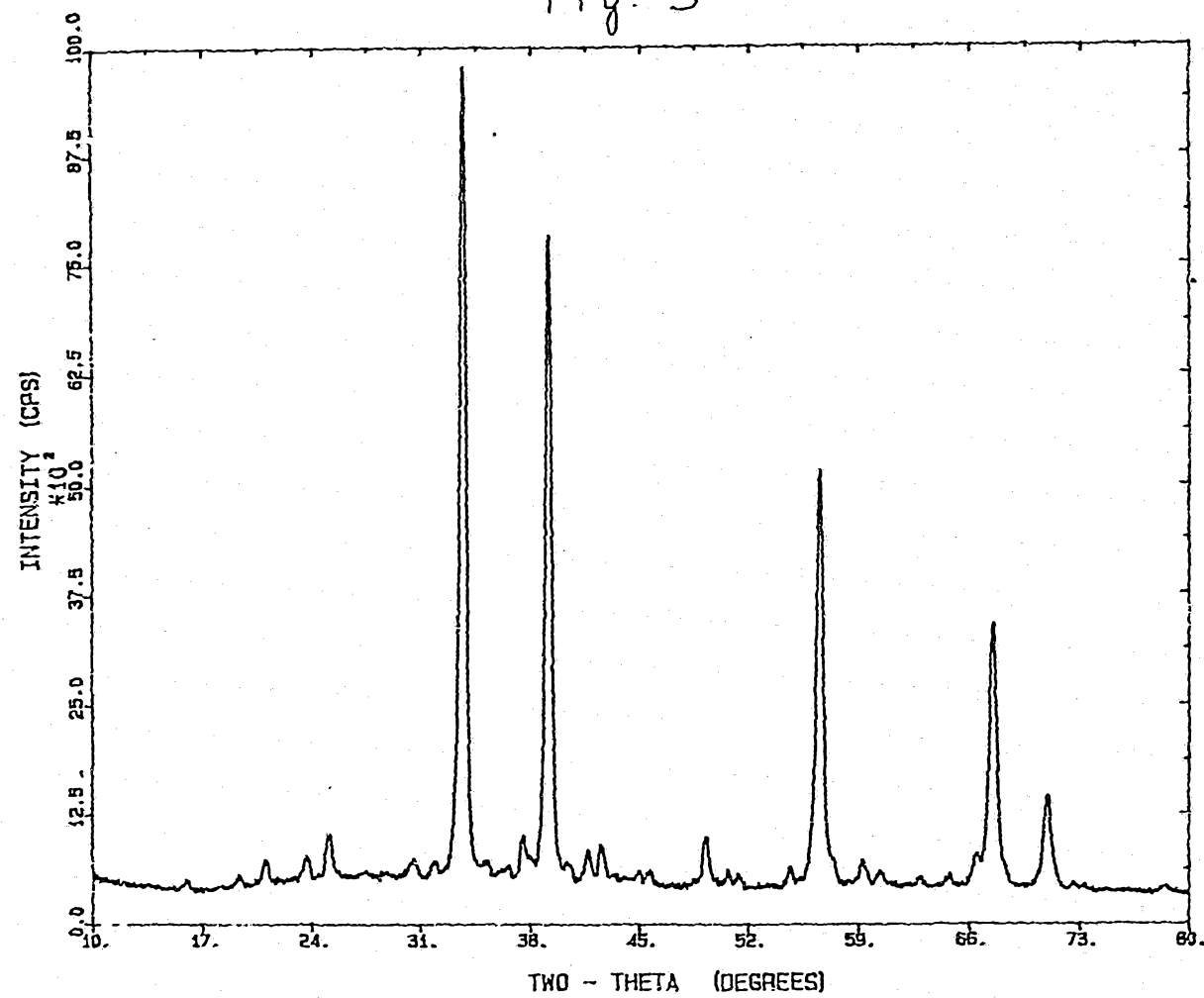
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Fig. 2



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Fig. 3



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Fig. 4

