

FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

593332

APPLICATION FOR A STANDARD PATENT

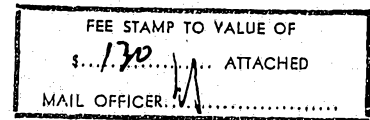
We, THANN ET MULHOUSE, of 95, rue du General de Gaulle, 68800 THANN, FRANCE, hereby apply for the grant of a Standard Patent for an invention entitled:-

"STABILISED ZIRCONIA PROCESS"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 86/03654
Country: FRANCE
Date: 14th March, 1986



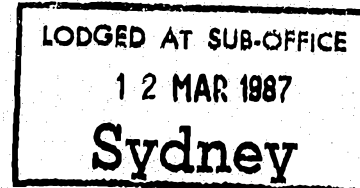
Our address for service is:

SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 12th day of March, 1987
THANN ET MULHOUSE

by *Robert J. Mulhouse*

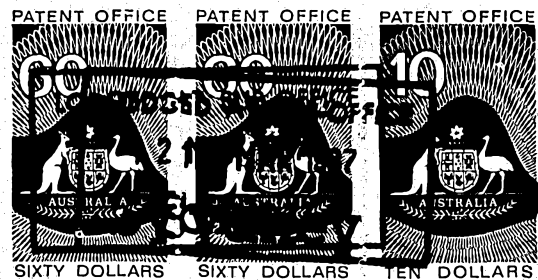
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS



To: The Commissioner of Patents
WODEN A.C.T. 2606

File: D.B.17D

Fee: \$130.00
MM



APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 23-11-89

(CONVENTION — Company)

FORM 8 — REGULATION 12 (2)

COMMONWEALTH OF AUSTRALIA PATENTS ACT, 1952-1973
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application No. made
 (a) Here Insert (In full) by (a) **THANN ET MULHOUSE**
 Name of Company.

(hereinafter referred to as "Applicant") for a patent for an invention entitled:
 (b) Here Insert Title of (b) **"STABILISED ZIRCONIA PROCESS"**
 Invention.

(c) **Jean-Marie CAZES**

(c) and (d) Here Insert
 Full Name and Address
 of Company Official
 authorised to make
 application, of (d)
 Chief of the patent department

.. 95, rue du General de Gaulle, 68800 THANN, FRANCE
 do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was/were made
 (e) in **FRANCE** on the **14th** day of **March**, **19 86**
 on the day of 19 ..

by (f) **THANN ET MULHOUSE**
 (g) **JEAN-CLAUDE GUELEN**, of 44, avenue du General Leclerc-58500-
 CLAMECY; **JEAN-FRANCOIS COLOMBET**, of 17, boulevard Richelieu-92500-RUEIL;
CLAUDE MAGNIER, of 3, rue des Chauffourniers-75019-PARIS; **JEAN-PHILIPPE**
BROWAEYS, of 22, rue de Mazarin-75009-PARIS and **ALAIN VESCO**, of 20, ...
 rue Pierre Demours-75019-PARIS, all FRANCE

are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

Applicant is the Assignee of the said Inventor(s).

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at **COURBEVOIE**
 this **21** day of **May** **19 87**.

(h) Personal Signature
 of Declarant (c) (no seal,
 witness or legalisation).

(h) **Jean-Marie CAZES**
 (Signature of Declarant)

To THE COMMISSIONER OF PATENTS.

SHELSTON WATERS

PATENT ATTORNEYS

55 CLARENCE STREET, SYDNEY

AUSTRALIA

Cables: 'Valid' Sydney Telex: 24422

(12) PATENT ABRIDGMENT (11) Document No. AU-B-69951/87
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(54) Title
STABILISED ZIRCONIA PROCESS

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(71) Applicant(s)
THANN ET MULHOUSE

(72) Inventor(s)
JEAN-CLAUDE GUELEN; JEAN-FRANCOIS COLOMBET; CLAUDE MAGNIER;
JEAN-PHILIPPE BROWAEYS; ALAIN VESCO

(74) Attorney or Agent
SHELSTON WATERS

(57) Selected for preference: a zirconium fluosulphate where x is approximately 0.5, y 0.5 and z 1.5; this can be prepared in accordance with the method described in French patent No. 1.375.076 or American patent No. 3.672.825 by attacking zirconium silicate or (zircon) with sodium carbonate, then dissolving the sodium silicozirconate obtained in hydrochloric acid, adding sodium sulphate and hydrochloric acid or sodium fluosilicate, the solution obtained is hydrolised at 60° to precipitate the zirconium fluosulphate formed and separated by filtration. The average granulation of the zirconium fluosulphate particles is usually from 3 to 10µm.

The neutralising can successfully take place at a temperature of 20° to 100° and preferably from 20 to 40°.

CLAIM

1. A method for the preparation of zirconia particulate containing a stabilizing amount of an element selected from yttrium or cerium, which comprises the steps of:

(i) admixing an aqueous suspension of zirconium fluosulfate particles (as herein defined) containing from 5 to 35% by weight of Zr expressed as ZrO_2 , said aqueous suspension having a pH of from 0 to 3, with an aqueous solution of a salt of the stabilizing element expressed as an oxide thereof, wherein the molar ratio of the said oxide of the stabilizing element to ZrO_2 is in the range of 1/100 to 20/100,

(ii) neutralizing the resulting mixture to a pH of at least 7,

(iii) separating the mixture of hydroxides obtained from the neutralization medium,

(iv) leaching said hydroxide mixture to eliminate at least a proportion of sulfate and fluoride ions therefrom, and then

(v) calcining said mixture of hydroxides.

COMMONWEALTH OF AUSTRALIA

593332

PATENTS ACT 1952

C O M P L E T E S P E C I F I C A T I O N

FOR OFFICE USE:

Class

Int. Class

Application Number: 69951/87
Lodged:

Complete Specification Lodged:
Accepted:
Published:

This document contains the
amendments made under
Section 49 and is correct for
printing.

Priority:

Related Art:

Name of Applicant: THANN ET MULHOUSE

Address of Applicant: 95, RUE DU GENERAL DE GAULLE
68800 THANN,
FRANCE

Actual Inventor: JEAN-CLAUDE GUELEN, JEAN-FRANCOIS COLOMBET,
CLAUDE MAGNIER, JEAN-PHILIPPE BROWAEYS AND
ALAIN VESCO

Address for Service: SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

"STABILISED ZIRCONIA PROCESS"

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

METHOD FOR THE PREPARATION OF SUBMICRONIC STABILISED
ZIRCONIA FROM ZIRCONIUM FLUOSULPHATE AND APPLICATION
OF THE STABILISED ZIRCONIA OBTAINED FOR MAKING CERAMICS

The aim of this invention is to produce a method for the preparation of submicronic zirconia stabilised with yttrium or cerium using a zirconium fluosulphate and the application of the stabilised zirconia obtained in the making of ceramics.

10 The preparation of zirconia stabilised for example with yttrium by neutralising a mixture of the aqueous solution of a pure salt of zirconium (oxychloride, nitrate...) and the aqueous solution of an yttrium salt (chloride, nitrate) is already known (e.g. the non examined Japanese patent application No. 57.191234).

The applicant has found a method which makes it possible to prepare stabilised zirconia from a non water soluble zirconium salt.

20 In one aspect, the invention consists in a method for the preparation of zirconia particulate containing a stabilizing amount of an element selected from yttrium or cerium, which comprises the steps of:

(i) admixing an aqueous suspension of zirconium fluosulfate particles (as herein defined) containing from 5 to 35% by weight of Zr expressed as ZrO_2 , said aqueous suspension having a pH of from 0 to 3, with an aqueous solution of a salt of the stabilizing element expressed as an oxide thereof, wherein the molar ratio of the said oxide of the stabilizing element to ZrO_2 is in the range of 1/100 to 20/100,



(ii) neutralizing the resulting mixture to a pH of at least 7,

(iii) separating the mixture of hydroxides obtained from the neutralization medium,

(iv) leaching said hydroxide mixture to eliminate at least a proportion of sulfate and fluoride ions therefrom, and then

(v) calcining said mixture of hydroxides.

By "Zirconium fluosulphate" we mean any amorphous hydrate with an empirical formula $(ZrF_x(SO_4)_y(OH)_z)$ in which x is between 0.1 and 1, including 0.1 and 1, z is between 1 and 3.7, x and y cannot simultaneously be equal to 1. Selected for preference: a zirconium fluosulphate where x is approximately 0.5, y 0.5 and z 1.5; this can be prepared in accordance with the method described in French patent No. 1.375.076 or American patent No. 3.672.825 by attacking zirconium silicate or (zircon) with sodium carbonate, then dissolving the sodium silicozirconate obtained in hydrochloric acid, adding sodium sulphate and hydrochloric acid or sodium fluosilicate, the solution obtained is hydrolised at 60° to precipitate the zirconium fluosulphate formed and separated by filtration. The average granulation of the zirconium fluosulphate particles is usually from 3 to 10µm.

The neutralising can successfully take place at a temperature of 20 to 100° and preferably from 20 to 40°.

In order to obtain stabilised zirconia with



particularly desirable mechanical properties, a molar ratio of Y_2O_3/ZrO_2 of 1/100 to 20/100 (preferably 2/100 to 6/100) is used when the stabilising element is yttrium and a molar ratio CeO_2/ZrO_2 of 5/100 to 20/100 (preferably 8/100 to 15/100) when the stabilising element is cerium.

Among the salts of stabilising elements which can be used is yttrium nitrate.

Among the neutralising bases which may be used, ammonium hydroxide and soda are preferred; the neutralisation is done preferably at a pH of at least 10 when the neutralising base is ammonium hydroxide and a pH of 13 when the base is soda.

The subsequent leaching is desirably carried out at a temperature of 20 to 100°C (preferably 20 to 40°C), at the same pH as that at the end of the neutralisation so as to eliminate the ion sulphates and a part of the fluoride ions desorbed during the neutralisation.

The optional leaching step with nitric or hydrochloric acid is intended to eliminate the alkaline or ammonium ions adsorbed by the mixture of hydroxides. This may be done at a temperature of 20 to 100°C, usually approximately 20°C.

The pH is dependent on the nature of the stabilising element. The pH of the suspension must be higher than the conditions of pH existing upon dissolution of the hydroxide of the stabilizing element, but not exceeding 8. If the latter is yttrium, a pH of 7 to 8 is preferred;



if it is cerium the pH can be from 3 to 8.

A particularly useful method in accordance with the invention is to neutralise with ammonium hydroxide at a pH close to 10.5, the subsequent leaching is done at the same pH with a solution of ammonium hydroxide; after filtration the mixture of hydroxides obtained is leached to a pH close to 7.5 with nitric or hydrochloric acid.

10 The mixture of hydroxides obtained after neutralisation, basic leaching and leaching with an acid is then calcined after filtration at a temperature of preferably 6000 to 1300°C, and most preferably 900 to 1200°C, the temperature being a function of the pH of neutralisation; thus for a pH of neutralisation of less than, or equal to 10, a temperature of at least 1150°C is preferred; for a higher pH, it may vary between 900 to 1100°C.

This operation may take from 15 minutes to 12 hours; but usually from 1 to 6 hours.

20 The stabilising zirconia powder obtained in this way has an average granulation of 3 to 10µm.

Whatever the stabilising element, the radio-crystallography shows that the product obtained is a solid solution.

It is then crushed in a wet medium according to proven methods, for example in a ball mill with very small balls having a diameter of approximately 1mm, so as to obtain after drying and sifting a powder with an average granulation_____



of 0.15 to 1 μm composed of elementary crystallites of 200 to 1200 $\text{\AA}$, and generally of 300 to 600 $\text{\AA}$. The specific surface varies between 50 and 3 m^2/g .

The given properties of the stabilised powder are determined in the following manner:

The stabilised zirconia powder is mixed with a binding agent at a weight ratio of 2%, this agent is selected from those well known for this type of technique, i.e. polyvinyl alcohol (RHODOVIOL 4/20 marketed by Rhone-Poulenc).

10 Density: The mixture is pelletised under pressure of 1 to 4 T/cm^2 . It is then sintered, the rate of increase in temperature is $5^\circ\text{C}/\text{mn}$; when the sintering temperature, which is between 1300 and 1600°C is reached it is maintained for 3 hours, then left to cool. A stabilised zirconia ceramic is obtained, the density of which reaches at least 97% of the theoretical density of the stabilised zirconia under consideration.

20 Bending strength: The piece which has been fired is cut with a diamond tipped saw to obtain parallelepiped samples of 40 mm x 3 mm x 4 mm.

The 3-point bending strength test is carried out on about 10 samples (the distance between the end supports is 30 mm, the speed of displacement of the press is $0.5\text{mm}/\text{mn}$).

The figures obtained depend on the type and quantity of stabiliser present.

For a stabilised zirconia powder stabilised with 3% molar Y_2O_3 the bending strength is between 600 and 800 MPa.

30 The zirconia powder stabilised in accordance with the invention can be used for making ceramics having good mechanical, thermodynamic and electrical properties, ceramics for use in making carriers and crucibles to be used at high temperatures, oxygen probes, parts exposed to hard wear or adiabatic thermal engines, tools for particular processes and other well known uses in this area.

The following examples are given as an indication only and should not be considered as placing limits on the concept or areas of use of the invention.



Example 1 :

40 g of an aqueous solution of yttrium nitrate containing 13.5 % by weight of yttrium expressed as Y_2O_3 is mixed with 530 g of an aqueous suspension with a pH of 2 of zirconium fluosulphate with the empiric formula $ZrF_{0.5} (SO_4)_{0.5} (OH)_{1.5}$ this suspension contains 17.8 by weight of zirconium in the form of ZrO_2 .

The acid mixture obtained is stirred vigorously and neutralised in 15 mn with an aqueous solution of ammonium hydroxide 10N until a pH of 10.5 is reached.

The mixture is then filtered and again placed in suspension in 1000 cm³ of an aqueous solution of ammonium hydroxide with a pH of 10.5

This filtration/re-suspension in ammonium hydroxide with a pH of 10.5 is repeated several times until the sulphate ions disappear completely from the water.

When the ion sulphates have been desorbed, the filtered gel is placed in suspension in 1000 cm³ of demineralised water, refiltered and placed in suspension again in 1000 cm³ of water, to which nitric acid N2 has been added until a pH of 7.5 is obtained.

The suspension is then filtered, leached with 1000 cm³ of demineralised water and filtered again.

250 g of a mixture of damp zirconium hydroxide and yttrium hydroxide is obtained, this is calcined at 1150°C for 5 hours, the temperature increase being 10°C per minute.

100 g of yttriated zirconia is obtained entirely crystallised in quadratic form, it is characteristic of the solid solution $ZrO_2 - 3\% Y_2O_3$.

This powder is placed in suspension in demineralised water containing 0.5% by weight of isopropanol ; this suspension containing 600 g/l of oxide is crushed in a mini-ball mill until a powder is obtained with an average granulation of 0.5 µm, the specific surface then being 8 m² /g.

The powder is mixed at 2% by weight with polyvinyl alcohol, flash dried and compacted under pressure of 3T/cm². The unfired density of the compacted piece is 54% of the

theoretical density.

After sintering at 1450°C for 3 hours, the density of the ceramic obtained is 5.95, i.e. 97.5 % of the theoretical density.

The bending strength of this material measured on about 10 samples shows an average of 750 MPa.

Example 2 :

The same process is followed as that described in example 1 ; the only difference being that the calcination is done at 1050°C for 5 hours instead of at 1150°C, the powder obtained after crushing has an average granulation of 0.5 μm and a specific surface of 12 m^2/g .

Characteristics of the product :

- . unfired density : 52 % of the theoretical density
- . density after sintering : 97.2 of the theoretical density.
- . average bending strength : 720 MPa.

Example 3 :

An acid mixture solution of yttrium nitrate - suspension of zirconium fluosulphate is prepared as in example 1, it is neutralised with an aqueous solution of ammonium hydroxide 10 N until a pH of 10.5 is obtained.

The mixture is filtered and re-placed in suspension in 1000 cm^3 of demineralised water.

This process of filtration - replacing in suspension in water is repeated several times until the sulphate ions are washed away.

250 g of a mixture of damp zirconium hydroxide and yttrium hydroxide obtained by filtration is calcined at 1150°C for 5 hours.

The resulting powder is crushed (average granulation 0.5 μm , specific surface 7 m^2/g), compacted and sintered as in example 1.

Characteristics of the product :

- . unfired density : 56 % of the theoretical density
- . density after sintering : 97 % of the theoretical density.
- . average bending strength : 700 MPa.

Example 4 :

An acid mixture, yttrium nitrate solution - zirconium fluosulphate suspension is prepared as in example 1, neutralised with an aqueous soda 3.5 N solution to a pH of 13.5.

After filtration it is placed in suspension in 1000 cm³ of an aqueous soda solution with a pH of 13.5

The mixture is filtered, replaced in suspension in 1000 cm³ of demineralised water.

10 This process of filtration - suspension in water is repeated twice.

After filtration the cake is placed in suspension in 1000 cm³ of water to which nitric acid 2 N is added until a pH of 7.5 is obtained.

The mixture is then filtered, replaced in suspension in water at a pH of 7.5 ; this process of filtration - suspension in water is repeated until total desorption (< 50 ppm of Na₂O) of the sodium ions adsorbed during neutralisation.

20 After filtration 250 g of a wet mixture of zirconium hydroxide and yttrium hydroxide is obtained, this mixture is calcined at 1000°C for 3 hours.

The resulting powder is crushed (average granulation 0.5 µm, specific surface 14 m²/g,) compacted and sintered as in example 1.

Characteristics of the product :

- . unfired density : 55 % of the theoretic density
- . density after sintering : 97.5 % of the theoretic density.
- . average bending strength : 650 MPa.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for the preparation of zirconia particulate containing a stabilizing amount of an element selected from yttrium or cerium, which comprises the steps of:

(i) admixing an aqueous suspension of zirconium fluosulfate particles (as herein defined) containing from 5 to 35% by weight of Zr expressed as ZrO_2 , said aqueous suspension having a pH of from 0 to 3, with an aqueous solution of a salt of the stabilizing element expressed as an oxide thereof, wherein the molar ratio of the said oxide of the stabilizing element to ZrO_2 is in the range of 1/100 to 20/100,

(ii) neutralizing the resulting mixture to a pH of at least 7,

(iii) separating the mixture of hydroxides obtained from the neutralization medium,

(iv) leaching said hydroxide mixture to eliminate at least a proportion of sulfate and fluoride ions therefrom, and then

(v) calcining said mixture of hydroxides.

2. A method according to claim 1, wherein said aqueous solution comprises from 5 to 20% by weight of yttrium or cerium, expressed as the oxide thereof.

3. A method according to claim 1 or 2 wherein said neutralization (ii) is accomplished with ammonia, or an alkali metal hydroxide.



4. A method according to claim 3 wherein said neutralization (ii) is accomplished with ammonia, at a pH of at least 10.

5. A method according to claim 3 wherein said neutralization (ii) is accomplished with an alkali metal hydroxide, at a pH of about 13.

6. A method according to any one of the preceding claims wherein said zirconium fluosulfate particles (as herein defined) have, at the neutralization stage, an average granulation size of 3 to 10 μm .

7. A method according to any one of the preceding claims, wherein at the neutralization stage the zirconium fluosulfate suspension contains from 20 to 30% by weight of Zr expressed as ZrO_2 , and that the salt solution of the stabilising element contains from 10 to 15% by weight of yttrium or cerium expressed as the oxide thereof.

8. A method according to any one of the preceding claims, said aqueous solution comprising a salt of yttrium, and the molar ratio $\text{Y}_2\text{O}_3/\text{ZrO}_2$ ranging from about 1/100 to 10/100.

9. A method according to claim 8 wherein said molar ratio $\text{Y}_2\text{O}_3/\text{ZrO}_2$ ranges from about 2/100 to 6/100.

10. A method according to any one of the preceding claims wherein said aqueous solution comprises a salt of cerium, the molar ratio $\text{CeO}_2/\text{ZrO}_2$ ranging from about 5/100 to 20/100.

11. A method according to claim 10, said molar ratio $\text{CeO}_2/\text{ZrO}_2$ ranging from about 8/100 to 15/100.



12. A method according to any one of the preceding claims, said aqueous solution comprising yttrium nitrate.

13. A method according to any one of the preceding claims wherein said leaching (iv) is accomplished with water containing either ammonia or an alkali metal hydroxide.

14. A method according to any one of the preceding claims, further comprising, prior to the calcination (v), releaching the mixture of hydroxides at least once, by suspending same in an aqueous acid solution, the suspension which results having a pH of up to 8.

15. A method according to claim 13 the suspension which results having a pH of from 7 to 8.

16. A method according to claim 14, the suspension which results having a pH of from 3 to 8.

17. A method according to claim 14 wherein said acid solution is a solution of hydrochloric or nitric acid.

18. A method according to any one of the preceding claims which further comprises (vi) crushing the stabilized zirconia particulates thus produced.

19. A method according to claim 18, which further comprises (vii) sifting the stabilized zirconia obtained.

20. A method according to claims 18 or 19, said ground particulates having an average grain size of from 3 to 10 μm in diameter.

21. A method according to any one of the preceding claims, characterised by using for the neutralising stage



ammonium hydroxide at a pH of 10.5, the washing stage being done at the same pH with an ammonium hydroxide solution and the leaching with acid stage being done at a pH of 7.5.

22. A method according to any one of the preceding claims, characterised by a neutralising stage, a washing stage, and a leaching with acid stage, wherein each stage is carried out at a temperature of 20 to 100°C.

23. The application of the stabilised zirconia obtained in accordance with the method of any one of the previous claims in the preparation of ceramics.

DATED this 1st day of NOVEMBER, 1989.

THANN ET MULHOUSE

Attorney: IAN T. ERNST

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

