

642937

FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC CHIMIE, a French Company, of 25, Quai Paul Doumer, 92408, Courbevoie, Cedex, France, hereby apply for the grant of a Standard Patent for an invention entitled:-

"PROCESS FOR THE PREPARATION OF A COLLOIDAL DISPERSION OF A CERIUM IV COMPOUND IN AN AQUEOUS MEDIUM AND DISPERSIONS OBTAINED"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 89/16598

Country: France

Date: 15th December, 1989

Our address for service is: SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 12th Day of December, 1990
RHONE-POULENC CHIMIE

by 

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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

File: D.B. R-114

Fee: \$192.00

5018936 12/12/90

CONVENTION APPLICATION BY A COMPANY

FORM 8 - REGULATION 12 (2)

R 4132

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

(a) Here insert (in full) Name of Company. In support of the Convention Application made by.....RHONE-POULENC..CHIMIE.....

(b) Here insert Title of Invention. (hereinafter referred to as "Applicant") for a patent for an invention entitled: (b) "Process for the Preparation of a Colloidal Dispersion of a Cerium IV Compound in an Aqueous Medium and Dispersions Obtained"

(c) and (d) Here insert Full Name and Address of Company Official authorized to make declaration. I, (c).....Jean-Pierre ESSON..... of (d).....RHONE-POULENC..CHIMIE..... 25, Quai Paul Doumer, 92408 COURBEVOIE CEDEX, FRANCE

do solemnly and sincerely declare as follows:

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

(e) Here insert Basic Country followed by date of Basic Application. 2. The basic Application(s) as defined by section 141 of the Act was /were made in (e).....France..... on the.....15th day of.....December,..... 19 89

(f) Here insert Full Name(s) of Applicant(s) in Basic Country. by (f).....RHONE-POULENC..CHIMIE..... in on the day of 19 by..... in on the day of 19 by..... in on the day of 19 by.....

(g) Here insert (in full) Name and Address of actual Inventor or Inventors. 3. (g) ..Francoise PICARD-SEON, of 50 Avenue de la Dame Blanche94120 Fontenay Sous Bois, France and..... Robert ZERROUK, of Souvignet 43140 Saint Victor Malscour.France.....

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

See reverse side of this form for guidance in completing this part.

Applicant is the Assignee of the said Inventors.

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 CEDEX, FRANCE..... this..... 14th..... day of..... December..... 1990

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

(h) [Signature] Jean-Pierre ESSON (Signature of Declarant)



AU9067998

(12) PATENT ABRIDGMENT (11) Document No. AU-B-67998/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 642937

(54) Title
PROCESS FOR THE PREPARATION OF A COLLOIDAL DISPERSION OF A CERIUM IV COMPOUND
IN AN AQUEOUS MEDIUM AND DISPERSIONS OBTAINED

International Patent Classification(s)
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(71) Applicant(s)
RHONE-POULENC CHIMIE

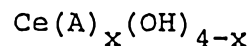
(72) Inventor(s)
FRANCOISE PICARD-SEON; ROBERT ZERROUK

(74) Attorney or Agent
SHELSTON WATERS , 55 Clarence Street, SYDNEY NSW 2000

(56) Prior Art Documents
US 4231893
AU 23500/88 B/JJ 13/00 C01F 17/00

(57) Claim

1. A process for the preparation of a weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, having the formula:



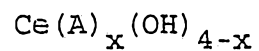
in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in an aqueous medium, said dispersion having a pH ranging from 1.5 to 5, and the colloidal particulates thereof having an average hydrodynamic diameter ranging from 8 to 15 nm, said process comprising:

- (a) acidulating a cerium (IV) hydroxide with an acid having a pKa, ranging from 2.5 to 5.0, or with a salt or mixture thereof,
- (b) next separating the resulting cerium (IV) compound that precipitates from the medium of acidulation, and then
- (c) colloiddally dispersing such cerium (IV) precipitate in an aqueous medium.

(11) AU-B-67998/90
(10) 642937

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10. A weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, having the formula:



in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in aqueous medium, said dispersion having a pH ranging from 1.5 to 5, and the colloidal particulates thereof having an average hydrodynamic diameter ranging from 8 to 15 nm.

642937

COMMONWEALTH OF AUSTRALIA

FORM 10

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:

Application Number:
Lodged:

Class

Int.Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

Name of Applicant:

RHONE-POULENC CHIMIE

Address of Applicant:

25, Quai Paul Doumer, 92408, Courbevoie,
Cedex, France

Actual Inventor:

Francoise Picard-Seon and Robert Zerrouk

Address for Service:

SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

"PROCESS FOR THE PREPARATION OF A COLLOIDAL DISPERSION OF A
CERIUM IV COMPOUND IN AN AQUEOUS MEDIUM AND DISPERSIONS OBTAINED"

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

PROCESS FOR THE PREPARATION OF A COLLOIDAL DISPERSION
OF A CERIUM IV COMPOUND IN AN AQUEOUS MEDIUM AND
DISPERSIONS OBTAINED

5 The present invention relates to a process for the preparation of a colloidal dispersion of a cerium IV compound in an aqueous medium.

It relates more particularly to a process for the preparation of a colloidal dispersion of a cerium IV compound having a weakly acid character.

10 In the description of the invention which follows, the colloidal dispersion of a cerium IV compound in an aqueous medium is also denoted by the term "sol".

15 The colloidal dispersions of a cerium IV compound are used in numerous applications. However, one important application of these dispersions is heterogeneous catalysis and, in particular, the catalysis of the treatment of exhaust gases from internal combustion engines, also termed the catalysis of automobile post-combustion reactions.

20 In fact, cerium IV is an important promoter of the effect of the catalysts used, in particular because of its capacity for storing oxygen and thus creating an oxygen supersaturation in the vicinity of
25 the catalytic elements such as platinum, palladium or the like.

For this purpose, the colloidal dispersions

are used as a solution for impregnating a support with cerium, cerium oxide being produced by calcination of the impregnated support and thus decomposition of the cerium IV compound contained in the dispersion.

5 Moreover, the acid character of the colloidal dispersion influences the support-impregnating process, which must be suited to the characteristics of said support and in particular to its surface properties.

10 Thus, colloidal dispersions of a cerium IV compound, a cerium hydroxynitrate, have been proposed which have a very highly acid character with a pH generally of less than 1. These dispersions present numerous problems during impregnation when the support to be impregnated has a slightly basic character.

15 European Patent Application No. 316,205 has proposed a process for the production of colloidal dispersions having a weakly acid character and generally having a pH higher than 3.5.

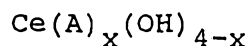
20 This process consists in destabilizing an aqueous colloidal dispersion of a cerium hydroxynitrate by an acid having a pKa lower than that of nitric acid, for example by acetic acid.

25 This process is complex because it comprises the successive production of two colloidal dispersions, a first dispersion by subjecting a hydroxide to attack by nitric acid, followed by a second dispersion by destabilization of the first suspension by acetic acid. It moreover requires a significant consumption of

reagents such as nitric acid and acetic acid.

The aim of the invention is, in particular, to overcome these disadvantages, by proposing a process for the preparation of a colloidal dispersion of a cerium IV
 5 compound having a weakly acid character which is simpler and less costly in terms of consumption of reagents.

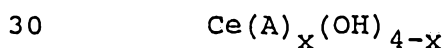
According to a first aspect, the present invention consists in a process for the preparation of a weakly acidic colloidal dispersion of particulates of a cerium
 10 (IV) compound, having the formula:



in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in an aqueous medium, said
 15 dispersion having a pH ranging from 1.5 to 5, and the colloidal particulates thereof having an average hydrodynamic diameter ranging from 8 to 15 nm, said process comprising:

- (a) acidulating a cerium (IV) hydroxide with an acid
 20 having a pKa ranging from 2.5 to 5.0, or with a salt or mixture thereof,
- (b) next separating the resulting cerium (IV) compound that precipitates from the medium of acidulation, and then
- (c) colloiddally dispersing such cerium (IV) precipitate
 25 in an aqueous medium.

According to a second aspect, the present invention consists in a weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, having the formula:



in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in aqueous medium, said dispersion having a pH ranging from 1.5 to 5, and the



colloidal particulates thereof having an average hydrodynamic diameter ranging from 8 to 15 nm.

Compounds which may be mentioned as cerium IV hydroxide are the hydroxides obtained, in particular, by precipitation in a basic and oxidizing medium.

Acids suitable for the invention are, in particular, chosen from the group comprising acetic acid, formic acid, propionic acid and chloroacetic acid. Acetic acid is the preferred compound for the invention.

It is also possible to use the salts of these acids or a salt/acid mixture. Amongst the suitable salts, those which may be mentioned are the alkali metal salts or the ammonium salts. The latter are those preferred. In fact, ammonia is generally not a compound which is troublesome in catalysis reactions and, on the other hand, will be decomposed during the calcination of the sol in the case where it is desired to obtain an oxide, the most general case in catalysis.

The acid solutions used for attack can be either a concentrated acid or an aqueous solution. Preferably, the total acid plus acid salt concentration is between 1 mole/l and 3 moles/l.

According to another characteristic of the invention, the amount of acid added is such that the molar ratio (acid + salt)/cerium IV is between about 0.5 and about 1.3, preferably between 0.7 and 1.0.

Acid is understood to be an acid, a mixture of acids, a salt, a mixture of salts or an acids/salts mixture.

The attack on the cerium hydroxide is effected by simple mixing of this hydroxide with the acid, at a temperature which is not critical. This temperature can be close to ambient temperature (15°C - 25°C). This attack can also be carried out under hot conditions, up to a temperature of the order of 100°C.



The precipitate obtained is then separated from the reaction mixture by any means, for example filtration, centrifuging or settling.

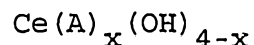
5 The precipitate is then dispersed in an aqueous medium.

The concentration of cerium IV contained in the dispersion is preferably between 1 mole/l and 3 moles/l.

10 The amount of cerium IV in colloidal state contained in the dispersion is typically between 50% and 100% of the total amount of cerium, more preferably between 95% and 100%.

The colloidal dispersion of the cerium IV compound, which is also a subject of the invention, has a pH of between 1.5 and 5, preferably of between 2.5 and 5.

15 The compound forming the colloids has the following chemical formula:



20 in which A represents the anion of an acid or of a salt of this acid having a pKa of between 2.5 and 5.0, and x is a number higher than or equal to 0.01 and lower than or equal to 0.7.

25 This compound may also contain other anions in a small proportion, these anions originating from the hydroxide used as starting material.

Thus, the compound may contain nitrate anions in a molar proportion, relative to cerium, of less than 0.15, preferably less than 0.10.

30 The dispersed particles have colloidal dimensions, the average hydrodynamic diameter of which varies between 8 and 15 nm.

This size is determined by quasi-elastic diffusion of light in accordance with the method described by Michael L. MacComwell in "Analytical" -----



Chemistry, Vol. No. 53, No. 8, 1007 (1981)".

The average hydrodynamic diameter of the particles depends on the pH of the dispersion. Thus, the colloids are the larger the higher the pH of the sol.

The sols of the invention are stable under customary storage conditions and are used, in particular, to produce catalyst, for example by impregnation of a support such as an alumina with this sol, followed by calcination to generate a cerium oxide.

The invention will be illustrated by the examples given below solely by way of illustration.

Example 1

94 ml of 17 N acetic acid and 90 ml of distilled water are added to 340 g of cerium hydroxide.

Magnetic stirring is applied until a homogeneous suspension is obtained. The pH of the suspension is 1.6. After filtering, the mass of moist hydroxyacetate recovered is 380 g. This precipitate is redispersed in 760 ml of distilled water. The sol obtained is stable and has a pH of 1.5. It contains 240 g/l of CeO_2 . This sol can be concentrated to 500 g/l by evaporation.

Example 2

A solution containing 64.7 ml of 17 N acetic acid and 38.5 g of ammonium acetate is added to 340 g of cerium hydroxide. The solution is made up to 1 litre

with distilled water. Magnetic stirring is applied until a homogeneous suspension is obtained. The pH of the suspension is 4.1. After filtering, the mass of moist hydroxyacetate recovered is 380 g. This precipitate is redispersed in 760 ml of distilled water. The sol obtained is stable and has a pH of 4.1. It contains 260 g/l of CeO_2 .

Example 3

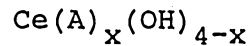
340 g of cerium hydroxide are added to a solution containing 82.3 ml of 17 N acetic acid and 15.4 g of ammonium acetate in 1 litre of water.

After stirring, a suspension is obtained and after filtering and redispersing the precipitate a sol is obtained which has a pH of 3, containing 255 g/l of CeO_2 .

This sol can be concentrated by evaporation to a concentration of 500 g/l of CeO_2 . All of the cerium is in colloidal cerium IV form.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for the preparation of a weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, having the formula:



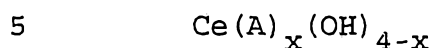
- 5 in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in an aqueous medium, said dispersion having a pH ranging from 1.5 to 5, and the colloidal particulates thereof having an average
- 10 hydrodynamic diameter ranging from 8 to 15 nm, said process comprising:
- (a) acidulating a cerium (IV) hydroxide with an acid having a pKa, ranging from 2.5 to 5.0, or with a salt or mixture thereof,
- 15 (b) next separating the resulting cerium (IV) compound that precipitates from the medium of acidulation, and then
- (c) colloiddally dispersing such cerium (IV) precipitate in an aqueous medium.
2. The process according to claim 1, said acid comprising acetic acid, propionic acid, chloroacetic acid or formic acid.
3. The process according to claim 2, said acid comprising acetic acid.
4. The process according to any one of claims 1 to 3, comprising acidulating the cerium (IV) hydroxide with an alkali metal or ammonium salt of said acid.
5. The process according to any one of the preceding claims, comprising acidulating the cerium (IV) hydroxide with an aqueous solution of said acid or salt or mixture thereof, said solution having a total (acid + salt) concentration ranging from 1 mole/l to 3 moles/l.
6. The process according to any one of the preceding claims, wherein the molar ratio (acid + salt)/cerium (IV) ranges from 0.5 to 1.3 in said acidulating step (a).
7. The process according to claim 6, said molar ratio ranging from 0.7 to 1.0.



8. The process according to any one of the preceding claims, comprising acidulating at a temperature ranging from ambient to 100°C.

9. The process according to any one of the preceding claims, further comprising concentrating the colloidal dispersion thus produced.

10. A weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, having the formula:



10 in which A is an anion of an acid having a pKa ranging from 2.5 to 5.0, or salt thereof, and x is a number ranging from 0.01 to 0.7 in aqueous medium, said dispersion having a pH ranging from 1.5 to 5, and the colloidal particulates thereof having an average hydrodynamic diameter ranging from 8 to 15 nm.

11. The colloidal dispersion according to claim 10, having a pH ranging from 2.5 to 5.

12. The colloidal dispersion according to claim 10 or 11, the cerium concentration therein ranging from 1 mole/l to 3 moles/l.

13. The colloidal dispersion according to any one of claims 10 to 12, wherein the proportion of cerium (IV) compound in colloidal state ranges from 50% to 100% of the total amount of cerium values contained therein.

14. The colloidal dispersion according to claim 13, such proportion ranging from 95% to 100%.

15. The colloidal dispersion according to any one of claims 10 to 14, wherein the molar ratio (acid + salt)/cerium (IV) ranges from 0.5 to 1.3.

16. The colloidal dispersion according to claim 15, said molar ratio ranging from 0.7 to 1.0.

17. The colloidal dispersion according to any one of claims 10 to 16, further comprising nitrate anions, in a



molar proportion relative to cerium, of less than 0.15.

18. A colloidal dispersion according to claim 17, said molar proportion being less than 0.10.

19. A process for preparation of a weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, substantially as herein described with reference to any one of the Examples.

20. A weakly acidic colloidal dispersion of particulates of a cerium (IV) compound, substantially as herein described with reference to any one of the Examples.

DATED this 20th day of July 1993

RHONE-POULENC CHIMIE

Attorney: IAN T. ERNST

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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