FORM 1 623087

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

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

"PROCEDURE FOR OBTAINING A COLLOIDAL DISPERSON OF A COMPOUND OF RARE EARTH IN AN AQUEOUS MEDIUM AND PRODUCT OBTAINED"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 87/12669

Country: France

Date: 14th September, 1987

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

DATED this 13th Day of September, 1988
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: R-5

Fee: $235.00

CONVENTION APPLICATION BY A COMPANY

FORM 8 – REGULATION 12 (2)

R 3717

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by

(a) Here Insert (In full) Name of Company.

(a) RHONE-POULENC CHIMIE

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here Insert Title of Invention.

(b) "PROCEDURE FOR OBTAINING A COLLOIDAL DISPERSION OF A COMPOUND OF RARE EARTH IN AN AQUEOUS MEDIUM AND PRODUCT OBTAINED"

(c) and (d) Here Insert Full Name and Address of Company Official authorised to make declaration.

I, (c) Marie-Claude DUTRUC-ROSSET

of (d) RHONE-POULENC CHIMIE, 25, Quai Paul Doumer, 92408 Courbevoie, Cedex

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) Here Insert Basic Country followed by date of Basic Application.

(f) Here Insert Full Name(s) of Applicant(s) in Basic Country.

In (e) FRANCE on the 14th day of September, 19 87

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) CLAIRE DAVID, of 14 Bis, rue Friant - 75014 - PARIS, FRANCE

..... is/~~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 inventor.

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, France

this 17 day of November 19 88

(12) PATENT ABRIDGMENT (11) Document No. AU-B-22180/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 623087

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PROCEDURE FOR OBTAINING A COLLOIDAL DISPERSION OF A COMPOUND OF RARE EARTH IN AN AQUEOUS MEDIUM AND PRODUCT OBTAINED

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(56) Prior Art Documents
AU 46759/89 C01F 017/00
AU 23500/88 C01F 017/00
US 3082103

(57) Claim

1. A procedure for preparing a colloidal dispersion of a compound of rare earth in an aqueous medium characterised by the fact that it consists of reacting a rare earth oxide with a water soluble monovalent acid having a pK_a between 2.5 and 5.0 in a molar ratio of the acid to the rare earth oxide expressed in metallic cation of smaller than 2.5 and greater than 1 and then heating the reaction medium obtained.

623087

COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

Class Int.Class

Application Number:
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Complete Specification Lodged:
Accepted:
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Priority:

Related Art:

Name of Applicant: RHONE-POULENC CHIMIE

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Actual Inventor: Claire David

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

Complete Specification for the Invention entitled:

"PROCEDURE FOR OBTAINING A COLLOIDAL DISPERSON OF A COMPOUND OF RARE EARTH IN AN AQUEOUS MEDIUM AND PRODUCT OBTAINED"

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

PROCEDURE FOR OBTAINING A COLLOIDAL DISPERSION OF A COMPOUND OF RARE EARTH IN AN AQUEOUS MEDIUM AND PRODUCT OBTAINED

The present invention is related to a procedure for obtaining a colloidal dispersion of a compound of rare earth in an aqueous medium. More precisely, the invention is related to a procedure for preparing a colloidal dispersion of a compound of yttric rare earth. It also pertains to a novel industrial product: the product obtained.

In the following description of the invention, "yttric rare earth" will apply to the heaviest elements of rare earths, according to the atomic number, beginning with samarium and finishing with lutecium, and including yttrium.

In US-A 3,024,199 has been proposed a procedure for preparing hydrated aqueous sols of rare earth oxides which consists of:

combining an aqueous solution of a monovalent rare earth salt with ammonia so as to precipitate the corresponding hydrated rare earth oxide;

eliminating most of the ammonium salts with ammonia; the pH being maintained between 9.5 and 10.5;

separating the hydrated rare earth oxide then "digesting" it by heating at a temperature between 60°C and 100°C.

The hydrated rare earth sols obtained have a concentration, expressed in rare earth oxides, between 10 and 50% by weight, particle size varying from 5 to 200 millimicrons with a ratio length/diameter of approximately 1:1 to 5:1, they have a pH of 7.0 to 8.3, and they contain a stabilising monovalent anion: the molar ratio of rare earth oxide/stabilising monovalent anion being 6.6:1 to 165:1.

These hydrated sols of rare earth oxides therefore have a formula close to that of the true hydroxides of rare earths.

In contrast to the procedure of this previous technique which includes numerous stages and involves a freshly prepared hydrated rare earth oxide that is difficult to handle, and the use of large quantities of ammonia, the invention proposes a much simpler procedure for preparing a colloidal dispersion, in aqueous media, of a compound of rare earth, later referred to by the word "sol".

The invention preparation procedure is characterised by a procedure for preparing a colloidal dispersion of a compound of rare earth in an aqueous medium characterised by the fact that it consists of reacting a rare earth oxide with a water soluble monovalent acid having a pK_a between 2.5 and 5.0 in a molar ratio of the acid to the rare earth oxide expressed in metallic cation of smaller than 2.5 and greater than 1 and then heating the reaction medium obtained.

The invention procedure permits the direct preparation of a sol, the characteristics of which are described hereafter.

An oxide of rare earth, usually in the form of a sesquioxide, is used in the invention procedure.

An oxide of yttric rare earth is preferably used, and even more so, yttrium oxide Y_2O_3 or holmium oxide, Ho_2O_3.

It is desirable that the purity of the oxide used should be high, preferably greater than or equal to 99 %, and an oxide of 99,99 % purity is most preferred.

The rare earth oxide is in the form of a fine powder, the particle size of which is a few microns and the mean diameter most often between 1 and 5 µm. The mean diameter is defined as a diameter such that 50 %, by weight, of the particles have a diameter greater than or smaller than the mean diameter.

A preferred variation of the invention procedure consists of using a rare earth oxide which has undergone a calcination at a temperature between 850°C and 1050°C, preferably around 950°C.

The duration of the said calcination is preferably between 2 and 4 hours.

The choice of the acid, on the other hand, is directed by the fact that it has to be soluble in water, monovalent and of a pKa between 2,5 and 5,0.

Acetic acid is very well suited to the operation of the invention procedure.

An acid free of impurities is preferably used. Its initial concentration is not critical, hence it may be used diluted, for example 1 N, or concentrated up to 17 N. The concentration of the solution of the said acid is usually chosen between 1 and 4 N, since constituting the dispersion medium of the rare earth oxide, it has to provide a liquid phase sufficient to allow its reaction under good conditions.

The quantity of acid used is an important aspect of the invention procedure. It must be less than the stochiometric amount i.e. the molar ratio of the acid used to the rare earth oxide, expressed in metallic cation, is smaller than 2,5 and greater than 1.

The upper limit is defined according to the economic constraints of good productivity and kinetics.

The said molar ratio is usually chosen between 1,1 and 2,2, and preferably between 1,2 and 1,8.

According to a pratical mode of achievement of the invention, the rare earth oxide is added to the acid solution, the concentration of which is adjusted so that it conforms to the previous specifications.

According to another method, the rare earth oxide is suspended in water, then the acid, in suitable quantity, is added.

In both cases, the operation may be performed while stirring and at room temperature, the latter most often between 15°C and 25°C.

The second step of the invention procedure consists of treating the reaction medium thermally at a temperature between 50°C and the reaction medium reflux temperature. The thermal treatment is preferentially performed between 70°C and 100°C.

The duration of the said treatment is very variable and the more elevated the temperature, the shorter it will be.

Once the reaction temperature reached, it is maintained for 1 to 4 hours, preferably 3 to 4 hours.

The formation of a sol of a compound of rare earth is observed, and when the rare earth oxide has been treated at a temperature below 70°C, the eventual presence of a deposit constituted mainly of unreacted rare earth oxide is seen.

A preferred variation of the invention is to separate this deposit according to solid-liquid separation techniques: filtration, decantation or centrifugation.

The separation is performed, preferably by centrifugation, and a colloidal dispersion of a compound of rare earth in an aqueous medium is obtained.

According to the present invention, the compound of rare earth is in the form of a water colloidal dispersion i.e. the said compound has particles of colloidal size but this does not exclude the presence of rare earth in ionic form.

The amount of rare earth in the colloidal form is preferably between 85 and 100 %.

The said dispersion may show a rare earth compound concentration, expressed in rare earth oxide, possibly reaching 1 mole/liter.

Its pH is close to neutral and is, more precisely, between 6,0 and 7,5.

The chemical composition of the colloids is determined on the basis of the residue obtained after ultracentrifugation of the dispersion, by titration of the rare earth with a chelating method using EDTA and by acidimetric titration of the monovalent anion originating from the acid.

It corresponds to the following chemical formula (I):

$$TR\ (A)_x\ (OH)_{3-x} \qquad (I)$$

where:

- TR symbolises the rare earth, preferably yttric, cation
- A represents the anion of a water soluble monovalent acid of pK_a between 2,5 and 5.
- x is a number smaller than 2,5 and greater than 1, preferably between 1,1 and 2,2 and even more so between 1,2 and 1,8.

The preferred sols of the invention are those of a rare earth compound of formula (I) where TR represents yttrium or holmium and A the acetate anion: x being between 1,1 and 2,2, preferably between 1,2 and 1,8.

The colloids obtained according to the invention are of spherical form.

The size of the colloids is defined by the measure of the colloids hydrodynamic diameter, determined by quasi elastic scattering of light according to the method described by Michael L. McConnell in "Analytical Chemistry, Vol 53, n°8. 1007 A

(1981)". It varies between 10 and 2000 Å and the colloids mean hydrodynamic diameter is between 30 and 100 Å.

It should be noted that the sols obtained according to the invention procedure are perfectly stable under normal storage conditions: this storage is done at a temperature preferably below room temperature, preferentially between 5 and 10° C.

The properties of the sols obtained are highlighted in the following examples:

Example 1

In a 2 liter reactor equipped with a thermometer, a stirrer, a system for introducing the reagents, a reflux condensor as well as with a heating device and a pH meter, are introduced:

- 1 000 cm^3 of a 2 N acetic acid solution.

In the said medium are dispersed under mechanical stirring 173 g of yttrium oxide of 99,99 % purity, commercialised by Rhone-Poulenc Society under the name "luminophore quality".

Heating then begins and is maintained for 3 hours and 30 minutes once the temperature of 70°C is reached.

The formation of an yttrium compound sol is observed and the presence of a deposit made of unreacted yttrium oxide, which may be separated as described thereafter and possibly recycled at the step of attack, is seen.

The reaction medium is subjected to centrifugation, by means of a .IOUAN centrifuge, at 3500 rotations/minute for 20 minutes.

The supernatant is collected.

The large particles borne along are eliminated by filtration on millipore paper, the pore size of which is greater than 1 µm.

An attack reaction yield of 99 % is determined.

An yttrium compound sol of the following chemical formula : $Y(OH)_{1,7}(CH_3COO)_{1,3}$, with a concentration, expressed in Y_2O_3, of 182 g/l and a pH of 6,8 is obtained.

The percentage of yttrium in the colloidal form is determined by quantifying total yttrium in the supernatant solution obtained following centrifugation (45 000 rpm - 1 hour) by titrated chelation with a titrated solution of EDTA. The quantification of yttrium in the supernatant permits the determination of a percentage of yttrium in the colloidal form of 95 %.

The size of the colloids is characterised by quasi elastic scattering of light according to the method described by Michael L. McConnell in Analytical Chemistry, Vol 53, n°8, 1007 A (1981). The colloid mean hydrodynamic diameter is of the order of 41 Å.

The sol obtained is stable to storage at 5°C for at least one month.

Example 2

In a reactor such as that described in example 1 are introduced:

- 1 000 cm^3 of a 2N acetic acid solution.

In this medium are dispersed under mechanical stirring 173 g of yttrium oxide of 99,99 % purity, commercialised by Rhone-Poulenc Society under the name luminophore quality.

Heating then begins and is maintained for 1 hour once the temperature of 100° C is reached.

The formation of an yttrium compound sol is observed.

An attack reaction yield of 99 % is determined.

An yttrium compound sol of the following chemical formula : $Y(OH)_{1,7}(CH_3COO)_{1,3}$, with a concentration, expressed in Y_2O_3, of 182 g/l and a pH of 6,7 is obtained.

The percentage of yttrium in the colloidal form is 95 %.

The mean hydrodynamic diameter of the colloids is 43 Å.

The sol obtained is stable to storage at 5°C for at least one month.

Example 3

In a reactor such as that described in example 1 are introduced:

- 1 000 cm^3 of a 2 N acetic acid solution.

In the said medium are dispersed under mechanical stirring 290 g of holmium oxide of 99,99 % purity, also commercialised by Rhone-Poulenc Society.

Heating then begins and is maintained for 3 hours and 30 minutes once the temperature of 70°C is reached.

The formation of a holmium compound sol is observed and the presence of a deposit made of unreacted holmium oxide, which may be separated as described thereafter and possibly recycled at the step of attack, is seen.

The reaction medium is subjected to centrifugation, by means of a JOUAN centrifuge, at 8500 rotations/minute for 20 minutes.

The supernatant is collected.

The large particles borne along are eliminated by filtration on millipore paper, the pore size of which is greater than 1 µm.

An attack reaction yield of 99 % is determined.

A holmium compound sol of the following chemical formula : $Ho(OH)_{1,7}(CH_3COO)_{1,3}$, with a concentration, expressed in Ho_2O_3, of 290 g/l and a pH of 7,1 is obtained.

The percentage of holmium in the colloidal form is 82 %.

The colloid mean hydrodynamic diameter is 45 Å.

The sol obtained is stable to storage at 5°C for at least one month.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A procedure for preparing a colloidal dispersion of a compound of rare earth in an aqueous medium characterised by the fact that it consists of reacting a rare earth oxide with a water soluble monovalent acid having a pK_a between 2.5 and 5.0 in a molar ratio of the acid to the rare earth oxide expressed in metallic cation of smaller than 2.5 and greater than 1 and then heating the reaction medium obtained.

2. Procedure according to claim 1 characterised by the fact that the oxide of rare earth is an oxide of yttric rare earth.

3. Procedure according to claim 2 characterised by the fact that the oxide of rare earth is yttrium oxide or holmium oxide.

4. Procedure according to any one of claims 1 to 3 characterised by the fact that the purity of the rare earth oxide is between 99 and 99.99%.

5. Procedure according to any one of claims 1 to 4 characterised by the fact that the rare earth oxide is subjected to calcination at a temperature between 850°C and 1050°C.

6. Procedure according to claim 5 characterised in that the said calcination temperature is 950°C.

7. Procedure according to claim 5 or 6 characterised in that the duration of the calcination varies between 2 and 4 hours.

8. Procedure according to any one of claims 1 to 7 characterised by the fact that the acid used is acetic acid.

9. Procedure according to any one of claims 1 to 8 characterised by the fact that the concentration of the said acid solution is chosen between 1 and 4 N.

10. Procedure according to any one of claims 1 to 9 characterised by the fact that the said molar ratio is between 1.1 and 2.2.

11. Procedure according to any one of claims 1 to 10 characterised by the fact that the said molar ratio is between 1.2 and 1.8.

12. Procedure according to any one of claims 1 to 11 characterised by the fact the rare earth oxide is added to the monovalent acid aqueous solution at its desired concentration.

13. Procedure according to any one of claims 1 to 11 characterised by the fact that the rare earth oxide is suspended in water and the acid, in adequate quantity, is then added.

14. Procedure according to any one of claims 1 to 13 characterised by the fact that the reaction medium is thermally treated at a temperature between 50°C and the reaction medium reflux temperature.

15. Procedure according to claim 14 characterised by the fact that the said temperature is between 70°C and 100°C.

16. Procedure according to claim 14 or 15 characterised by the fact that the reaction temperature is maintained for 1 to 4 hours.

17. Procedure according to claim 16 characterised by the fact that the reaction temperature is maintained for 3 to 4 hours.

18. Procedure according to any one of claims 1 to 17 characterised by the fact that the deposit is separated by filtration, decantation or centrifugation.

19. Colloidal dispersion, in aqueous medium, of a rare earth compound of the following chemical formula (1):

$$TR\ (A)_x\ (OH)_{3-x} \qquad (1)$$

TR symbolises the rare earth cation;
A represents the anion of the water soluble monovalent acid of a pK_a between 2.5 and 5.0;
x is a number smaller than 2.5 and greater than 1.

20. Colloidal dispersion according to claim 19 characterised by the fact that TR represents an yttric rare earth.

21. Colloidal dispersion according to claim 20 characterised by the fact that TR represents yttrium or holmium.

22. Colloidal dispersion according to any one of claims 19 to 21 characterised by the fact that A represents the acetate anion.

23. Colloidal dispersion according to any one of claims 19 to 22 characterised by the fact that x is between 1.1 and 2.2.

24. Colloidal dispersion according to claim 23 characterised by the fact that x is between 1.2 and 1.8.

25. Colloidal dispersion according to any one of claims 19 to 24 characterised by the fact that the colloids are of spherical form.

26. Colloidal dispersion according to any one of claims 19 to 25 characterised by the fact that the colloid mean hydrodynamic diameter is between 30 and 100Å.

27. Colloidal dispersion according to any one of claims 19 to 26 characterised by the fact that it contains an mount of rare earth in the colloidal form between 85 and 100%.

28. Colloidal dispersion according to any one of claims 19 to 27 characterised by the fact that its pH is between 6.0 and 7.5.

29. Procedure for preparing a colloidal dispersion of a compound of rare earth in an aqueous medium, substantially as herein described with reference to any one of Examples 1 to 3.

30. Colloidal dispersion, in aqueous medium, of a rare earth compound substantially as herein described with reference to any one of Examples 1 to 3.

DATED this 6th day of February 1992

RHONE-POULENC CHIMIE

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Fellow Institute of Patent Attorneys of Australia

of SHELSTON WATERS