596104

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 12-2-90

FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC SPECIALITES CHIMIQUES, a French Body Corporate, of "Les Miroirs", 18 Avenue d'Alsace 92400, Courbevoie, France, hereby apply for the grant of a Standard Patent for an invention entitled:-

"CERIUM IV COLLOIDS AND A METHOD OF MANUFACTURE"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 85 09372

Country: FRANCE

Date: 20th June, 1985

Our address for service is:

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

DATED this 18th day of June, 1986

RHONE-POULENC SPECIALITES CHIMIQUES

by Robert G. Shelston

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

LODGED AT SUB-OFFICE
19 JUN 1986
[illegible]

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

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(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. 59102/86 made

(a) Here insert (in full) Name of Company.

by [a] RHONE-POULENC SPECIALITES CHIMIQUES

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

(b) Here insert Title of Invention.

[b] "CERIUM IV COLLOIDS AND A METHOD OF MANUFACTURE"

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

I, [c] Colette TAVERNIER

of [d] RHONE-POULENC
25, quai Paul Doumer - 92408 - COURBEVOIE

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 or Countries followed by date or dates of Basic Application(s).

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

(g) Here insert (in full) Name and Address of actual Inventor or Inventors.

2. The basic Application~~(s)~~ as defined by section 141 of the Act was/~~were~~ made in [e] FRANCE on the 20th day of June, 19 85
on the ...... day of .... 19 ...
by [f] RHONE-POULENC SPECIALITES CHIMIQUES

3. [g] Jean-Yves CHANE-CHING, of 6, rue Vauvenargues-75018-PARIS, FRANCE; Jean-Yves DUMOUSSEAU, of 60, rue des Dames-75017-PARIS, FRANCE ~~or~~ and Patrick DUPUIS, of 12, rue Feutrier-75018-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:

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 18 day of July 1986.

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

[h] Colette TAVERNIER
(Signature of Declarant)

To THE COMMISSIONER OF PATENTS.

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(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-59102/86**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **596104**

(54) Title
COLLOIDAL CERIUM HYDROXIDES

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(56) Prior Art Documents
AU 563201 15715/83 C01F
AU 59000/86 C01F
AU 571929 38950/85 C01F

(57) Claim

1. An aqueous colloidal dispersion of a cerium IV compound supersaturated with OH^- ions.

9. A method of preparation of an aqueous colloidal dispersion of a cerium IV compound supersaturated with OH^- ions and described in anyone of the claims 1 to 8, comprising the step of reacting an aqueous solution of a cerium IV salt with a base so as to obtain a supersaturation ratio of from 3 to 4.

24. A mixed aqueous colloidal dispersion of a cerium IV compound and a cation of a metal M, said colloidal dispersion being supersaturated with OH- ions; said cation M being chosen from the group consisting of 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8, 3a and 4a.

COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

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Lodged:

Complete Specification Lodged:
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This document contains the amendments made under Section 49.
and is correct for printing.

596104

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Complete Specification for the Invention entitled:

"CERIUM IV COLLOIDS AND A METHOD OF MANUFACTURE"

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

CERIUM IV COLLOIDS AND A METHOD OF MANUFACTURE

The present invention concerns new aqueous colloidal dispersions of a cerium IV compound, supersaturated with OH^- ions, and one of the processes for obtaining them.

It is known from the Encyclopaedia KIRK-OTHMER, Encyclopaedia of Chemical Technology (second edition) volume 4, p.850, that one can prepare a hydrated ceric oxide expressed by formula CeO_2, xH_2O, in which x is a number lying between 0.5 and 2 and presenting itself in the form of a gelatinous precipitate, by addition of sodium or ammonium hydroxide to the solutions of ceric salts.

In accordance with French patent 2 416 867, a method of preparation of an aqueous dispersion of cerium oxide was put forward : it consists in forming a suspension of cerium IV hydroxide with water and an acid capable of provoking the desaggregation of the crystallites, in heating the suspension for a time and at a temperature such that the pH reaches a stable value, the quantity of acid present in the suspension being such that this stable value of the pH is less than 5.4, so as to produce a treated suspension into which water is incorporated to produce an aqueous dispersion of cerium oxide.

This patent mentions that the preparation of the hydrate of the cerium IV oxide can be achieved by precipitation starting from a cerium salt : for instance, cerium carbonate of high purity can be dissolved in a solution of nitric or hydrochloric acid to obtain a neutral solution of cerium nitrate or chloride which is oxidized with NH_4OH / H_2O_2 to obtain the hydrate of cerium IV oxide.

The applicant has obtained new colloidal dispersions of cerium IV compound, in aqueous medium, starting from the aqueous solution of cerium IV salt, without resorting to the steps of precipitation and separation of the ceric hydroxide and its post-treatment.

One of the purposes of the present invention concerns new aqueous colloidal dispersions of a cerium IV compound, supersaturated with OH^- ions.

Knowing the solubility product of the ceric hydroxide to be equal to 10^{-50}, one can define, in relation to the concentration, a pH range in which the ceric hydroxide is stable in the form of a solid precipitate.

Now the applicant has found that one can obtain the cerium IV in the form of a colloidal dispersion in a pH range in which one should have expected to obtain the cerium IV in the form of a precipitate of ceric hydroxide.

One advantage of the invention is that the aqueous colloidal dispersions of a cerium IV compound of the invention have a very high proportion of cerium in colloidal form which can reach 100 %.

One advantage of the invention is that said dispersions are stable at ambient temperature and when they are subjected to a temperature increase which can reach 100°C.

Yet another advantage is that said dispersions exhibit a low acidity (pH less than about 3).

Dispersions have been obtained, which have the predefined characteristics, according to a process which consists in making an aqueous solution of a cerium IV salt react with a base in order to obtain a supersaturation rate greater than 3 and less than 4.

Before defining the rate of supersaturation, we shall specify the nature of the reagents involved in the process of the invention.

The solution of a cerium salt used according to the process of the invention can be an aqueous solution of ceric nitrate or an aqueous solution of ammoniacal-cerium nitrate. Said solution can safely contain cerium in the cerous state but it is desirable it should contain at least 85 % cerium IV.

The solution of cerium salt is chosen so that it does not contain impurities which could find their way into the final product. In particular, it is preferable it should be free of covalent anions of a coagulating nature such as sulphates, etc. However, small quantities can be tolerated. For instance, these anions can represent up to 5 % by weight of the cerium salt expressed as CeO_2.

The concentration of the solution of cerium salt is not a critical factor, as the invention has shown. When expressed as cerium IV, it can range between 0.1 and 3 moles per litre. A concentration lying between 0.1 and 1.5 moles per litre being preferred.

The aqueous solution of cerium IV salt generally exhibits a certain initial acidity and can have a normality ranging from 0.1 N to 4 N. The concentration of H^+ ions is not critical. It is desirable it should lie between 0.1 N and 1 N.

The solution of ceric nitrate obtained by the process of electrolytic oxidation of a solution of cerous nitrate and which is described in the application for French patent FR-A 2 570 087 (n° 84 13641) is a choice starting material.

The basic solution used according to the process of the invention can be an aqueous solution of ammonium hydroxide, of soda or of potash. One can also use ammonia. According to the invention, one prefers a solution of ammonium hydroxide.

The normality of the basic solution used is not a critical factor, according to the invention. It can vary within wide limits, for instance, between 0.1 and 11 N but it is preferable, to obtain concentrated solutions of cerium IV, to first use a solution the concentration of which ranges between 5 and 11 N, then a more diluted solution, for instance from 0.1 to 5 N.

The proportion between the basic solution and the solution of cerium IV salt must be such that the rate of supersaturation is greater than 3 and less than 4.

The rate of supersaturation r is defined by the following equation :

$$r = \frac{n3 - n2}{n1}$$

in which :

- n1 represents the number of moles of Ce IV present in the final colloidal dispersion
- n2 represents the number of OH^- moles necessary to neutralize the acidity contributed by the aqueous solution of the cerium IV salt
- n3 represents the total number of OH^- moles contributed by the addition of the base.

The rate of supersaturation reflects the colloidal state of the cerium IV

- with $r = 4$, the cerium IV precipitates in gelatinous form
- with $r = 0$, the cerium IV is in ionic form
- with $0 < r < 4.0$, the cerium IV is in ionic and/or colloidal form.

The applicant has found that obtaining a colloidal dispersion of a cerium IV compound from the two above-mentioned reagents was bound to two parameters, namely the rate of supersaturation and the final concentration of cerium IV of said dispersion.

According to the invention, one chooses a rate of supersaturation greater than 3 and less than or equal to 3.8 for a final concentration of cerium IV of the colloidal dispersion obtained ranging from 0.1 M (that is to say 17 g/l of CeO_2) and 2 M (that is to say 344 g/l of CeO_2). One prefers the rate of supersaturation to be greater than or equal to 3.4 and less than or equal to 3.8 for a final concentration of cerium IV of said dispersion ranging from 0.5 M (that is to say 86 g/l of CeO_2) and 1.2 M (that is to say 206 g/l.

In practice, to obtain a desired rate of supersaturation r, chosen in the abovementioned range for a given concentration of Ce IV in the final colloidal dispersion, the concentration of the basic solution is adjusted so that it complies with the following equation :

$$(OH^-) = \frac{(n_1 . r + n_2)\,[\text{Ce IV}]_f\,[\text{Ce IV}]_i}{n_1\,([\text{Ce IV}]_i - [\text{Ce IV}]_f)}$$

- $[OH^-]$ represents the concentration of moles/litre of the basic solution
- $[\text{Ce IV}]_f$ represents the concentration of Ce IV in moles/litre of the final colloidal dispersion
- $[\text{Ce IV}]_i$ represents the concentration of Ce IV in moles/litre of the aqueous solution of the cerium IV salt
- n_1 and n_2 are determined by conventional determination of the aqueous solution of the cerium IV salt :
  - . n_1 by potentiometric titration with the help of a solution of a ferrous salt
  - . n_2 by acid-base titration after complexing of the cerium with the help of oxalate ions.

One can establish the correspondance between a given rate of supersaturation and an introduced quantity of base, expressed as a percentage of moles of the theoretical quantity of base necessary to completely neutralize the cerium IV present in the reaction medium, to obtain $Ce(OH)_4$

To a rate of supersaturation greater than 3 and less than 4 corresponds an introduced molar quantity of base greater than 75 % and less than 100 % of the theoretical quantity.

By way of example, we mention that, to rates of supersaturation of 3.5 and 3.8, correspond respectively introduced molar quantities of base representing 87.5 and 95 % of the theoretical quantities.

A preferred method of the invention consists in obtaining a rate of supersaturation by controlling the pH of the reaction medium.

Obtaining a rate of supersaturation less than 4 corresponds to a final pH of the colloidal dispersion of the cerium IV compound less than or equal to 3.0. The pH ranges from 0.3 to 3.0 for a rate of supersaturation greater than 3 and less than 4.

Without limiting the scope of the invention, we shall specify by way of example, that, in the case of a solution of ceric nitrate with a concentration such that the final concentration of the Ce IV in the colloidal dispersion obtained is 0.7 M, the following rates of supersaturation are respectively obtained which correspond to the pH ranges defined below :

$0.2 < pH < 0.7$ $3 < r < 3.3$
$0.7 < pH < 2.7$ $3.3 < r < 3.7$

The reaction between the aqueous solution of the cerium IV salt and the base used in the quantities defined earlier is carried out at a temperature which can lie between 0°C and 60°C but preferably at ambient temperature (most often 15 to 25°C).

Mixing of the above reagents can be carried out according to several variants. For example, one can mix, simultaneously and with agitation, the aqueous solution of the cerium IV salt and the basic solution or else one can add, continuously or all at once, the base in the aqueous solution of cerium IV salt and vice versa.

It is preferred to add a concentrated basic solution until a rate of supersaturation of 3.3 is obtained which corresponds to a pH of 0.6 then, with the more diluted basic solution, one achieves the desired final pH.

Mixing time is not critical and is dependent on the capacities of the equipment. It can range from 0.1 second to 30 hours.

Whatever the order in which the reagents are introduced, one obtains a colloidal dispersion of a cerium IV compound in aqueous medium which will be referred to from now on as "sol".

In accordance with the present invention, the cerium IV compound is in the form of a colloidal dispersion in water, which means that said compound is composed of particles of colloidal dimensions but this does not exclude the presence of cerium IV in ionic form. It should be noted that the percentage of cerium IV in colloidal form can be more or less correlated with the rate of supersaturation. Almost all the cerium IV is in colloidal form when r lies between 3.4 and 3.8.

The chemical composition of the colloids is determined from the residue obtained after ultracentrifugation of the dispersion by titration of the cerium IV according to the abovementioned method and by titration of the nitrate ions by acid-base solution analysis of the NH_4^+ obtained after reduction of the nitrate ions.

The chemical composition corresponds to the following chemical formula (I) :

$$Ce\ (OH)_x\ (NO_3)_{4-x}$$

in which x ranges between 0.3 and 0.7.
It is however possible to observe the presence of adsorbed ammonium ions adsorbed on the colloidal particles.

X-ray diffraction analysis of the solid residue shows that it is a badly crystallized product which exhibits a fluorite-type CeO_2 phase, that is face-centered cubic having a lattice parameter of about 5.42 Å and a rate of crystallization ranging from 15 to 40 %.

The aqueous sol obtained according to the invention can exhibit a strong concentration of cerium IV compound since it can contain up to about 30 % by weight of CeO_2.

The aqueous sol can exhibit an important ionic force owing to the presence of a strong concentration of the salt of the base which lies between 0.3 and 8.0 moles/litre.

The density of the colloids is measured on the colloidal dispersion by determination of the molecular mass by means of the conventional method of light-scattering and by correlation with the hydrodynamic diameter defined according to the quasi-elastic light-scattering method.

The density of the colloids is always less than that of CeO_2 (d = 7.2). It ranges from 3.5 to 6.0 and increases with the rate of supersaturation.

The size of the colloids is defined by measuring the hydrodynamic diameter of colloids determined by quasi-elastic light-scattering according to the method described by Michael L. McConnell in "Analytical Chemistry, vol. 53, n° 8, 1007 A (1981)".

It depends on the concentration of cerium IV and on the rate of supersaturation.
For a concentration of cerium IV lying between 0.1 M and 2 M and a supersaturation rate ranging from 3 to 3.8, the hydrodynamic diameter of the colloids lies between 50 and 400 Å.

It will be noticed that the sols obtained according to the process of the invention are perfectly stable in the usual storage conditions, a fact clearly brought out in the examples.

The present invention is also concerned with mixed aqueous colloidal dispersions of a cerium IV compound and of another metallic cation M^{n+} : n^+ symbolizes the degree of oxidation of the metal which is generally equal to + 3 or + 4.

As a metallic cation, referred to generically as cation of metal M, one can use a cation of a metal which can be chosen from group lb, 2b, 3b, 4b, 5b, 6b, 7b, group 8 and group 3a and 4a of the periodic table as defined in "Handbook of Chemistry and Physics B-4 (57th edition)".

One prefers to choose a metallic cation of an acid nature.

By metallic cation of an acid nature is meant a cation whose metallic hydroxide precipitates at low values of pH, preferably at a pH less than 4. As an example of acid cations used in preference, one can mention those of the following metals : iron, titanium, zirconium and tin.

0.1 to 50 % of the moles of cerium IV can be replaced by the metallic cation as defined earlier.

The process used to obtain these mixed aqueous colloidal dispersions of a cerium IV compound and of a cation M^{n+} is similar to that which allows one to obtain a colloidal dispersion of a cerium IV compound alone.

According to the invention, an aqueous solution of a cerium IV salt and of a salt of metal M is made to react so as to obtain a supersaturation rate expressed as greater than 3 and less than 5.5 in proportion to the cerium IV.

The quantity of base added to obtain $Ce(OH)_4$ and $M(OH)_n$, can range from 60 to 95 %; it is expressed in percentage of moles of the theoretical quantity of base necessary to completely neutralize the cerium IV and the cation M^{n+} which are present in the reaction medium.

In practice, obtaining said supersaturation rate corresponds to a final pH of the mixed colloidal dispersion which is less than or equal to 3.0.

The characteristics of the reagents and the conditions in which they are used correspond to what has been described previously.

Metal M is used preferably in the same form as that of the cerium salt. The nitrate form is preferred.

The salt of metal M can be used in anhydrous or hydrated form.

It can be used in solid form or in the form of an aqueous solution whose concentration can range from 0.01 mole/litre up to the maximum solubility of the salt of metal M used.

A practical method of preparation of the invention consists in introducing the salt of metal M in solid form into the solution of the cerium IV salt, then, in adding the base.

One can also put the salt of metal M in the form of an aqueous solution, then mix said solution with the aqueous solution of the cerium IV salt and, finally, add the base.

One obtains a colloidal dispersion of a cerium IV compound and of a cation of metal M^{n+} in aqueous medium, which can exhibit a strong concentration of cerium IV compounds and of metal M since it can contain up to 30 % by weight of CeO_2 and of M_2O_n.

The hydrodynamic diameter of its colloids, determined according to the method mentioned above, can range from 50 to 2000 Å.

In order to better illustrate the uses of the invention, different examples are given below which, of course, do not limit its applications.

The first example illustrates the preparation of a colloidal dispersion by supersaturation with OH^- ions of a solution of ceric nitrate.

EXAMPLE 1 -

Into a 6 litre three-necked flask, fitted with a thermometer, an agitating device and a system for introducing the reagent (metering pump), one introduces, at ambient temperature, $2000cm^3$ of a solution of ceric nitrate containing 1.2 moles/litre of cerium IV, 0.04 mole/litre of cerium III and having a free acidity of 0.5 N prepared by electrolysis in accordance with FR-A 2 570 087.

Under constant agitation, a first solution of 6.6 N concentrated ammonium hydroxide is added to said solution, at ambient temperature, progressively and over 13.7 hours, at the rate of $100cm^3$/hour.

One obtains an aqueous colloidal dispersion of a cerium IV compound with a concentration expressed as CeO_2 equal to 107 g/l and a pH equal to 2.67.

The percentage of cerium in colloidal form is determined by measuring the total cerium in the supernatent solution obtained after ultracentrifugation (45 000 r.p.m. - 1 hour) by potentiometric titration by means of a titrated solution of ferrous iron. Analysis of the supernatent solution reveals a very weak concentration of total cerium of the order of 0.02 mole, which allows one to determine a percentage of cerium in colloidal form in the supersaturated dispersion close to 100 %.

The size of the colloids is determined by quasi-elastic light-scattering, according to the method described by Michael L. McConnell in "Analytical Chemistry", vol. 53 n° 8 1007 A (1981). The hydrodynamic diameter of the colloids is of the order of 147 Å.

It is noted that the sol obtained demonstrates good stability in storage and there is no settling after at least one year in storage.

In the following example, a mixed colloidal dispersion is prepared by supersaturation of an aqueous solution of ceric nitrate and ferric nitrate.

EXAMPLE 2 -

Into the same type of equipment as that described in example 1, are introduced, at ambient temperature, 1744 cm³ of a solution of ceric nitrate containing 1.2 moles/litre of cerium IV, 0.04 mole/litre of cerium III and having a free acidity of 0.5 N and 86.15 g of ferric nitrate $Fe(NO_3)_3$, $9H_2O$ which is 98 % pure.

Under constant agitation, one adds to said mixture, at ambient temperature, 1256 cm³ of a concentrated 6.19 N solution of ammonium hydroxide at the rate of 100 cm³/hour, then 100 cm³ of a 2.48 N solution of ammonium hydroxide.

An aqueous colloidal dispersion is obtained which exhibits a concentration of CeO_2 of the order of 116.13 g/l and a pH of 1.5.

The examination of an aliquot part (290 cm³) by quasi-elastic light-scattering reveals the presence of two populations of colloids ranging respectively from 76 Å to 199 Å in hydrodynamic diameter.

By continuing with the addition of the 2.48 N solution of ammonium hydroxide for 66 minutes, one obtains a colloidal aqueous dispersion exhibiting a concentration of CeO_2 of 111.7 g/l and a pH equal to 2.

From a sampling of 240 cm³, two populations of colloids are evidenced by their respective hydrodynamic diameters of 167 Å and 977 Å.

By continuing the addition of the solution of ammonium hydroxide for 18 minutes, at the rate of 100 cm³/hour, one obtains a dispersion (pH = 2.56) presenting two populations of colloids with hydrodynamic diameters of 229 Å and 1270 Å.

The quantity of base thus added in the reaction medium represents 84 % in moles of the theoretical quantity necessary for the complete neutralization of the cerium and iron present in the reaction medium ($OH^-/Fe^{3+} = 3$ and $OH^-/Ce^{4+} = 4$).

Next one determines the chemical composition of the species present in colloidal form in the aqueous sol. This composition is determined by fluorescent X-ray analysis of the solid residue obtained by ultracentrifugation (45 000 r.p.m, 1 hour) after drying and calcination at 1 000°C for 2 hours.

The Fe/Ce molar ratio, worked out by comparison with standards of specific Fe/Ce composition, has a value of the order of 0.1.

The following examples illustrate the achievement of a mixed colloidal dispersion by supersaturation with OH^- ions of a mixed solution of ceric nitrate and of zirconyl nitrate.

EXAMPLE 3 -

55.85 g of zirconyl nitrate $ZrO(NO_3)_2\ 2H_2)$ are added in 1744 cm³ of a solution of ceric nitrate containing 1.2 moles/litre of cerium IV, 0.04 mole/litre of cerium III and having a free acidity of 0.5 N.

Under constant agitation and at ambient temperature, one adds to the mixture 1256 cm³ of a 6.19 N solution of ammonium hydroxide at the rate of 100 cm³/hour, then 165 cm³ of a 2.48 N solution of ammonium hydroxide, at the same rate.

An aqueous colloidal dispersion is obtained, with a CeO_2 concentration of the order of 113.7 g/l and a pH of about 1.57.

Examination of an aliquot part (250 cm³) by quasi-elastic light-scattering allows to ascertain a hydrodynamic diameter of the order of 121 Å.

40 cm³ of the 2.48 N solution of ammonium hydroxide are further added.

The quantity of base thus added in the reaction medium represents 80 % in moles of the theoretical quantity necessary for the complete neutralization of the cerium and zirconium present in the reaction medium ($OH^-/Zr^{4+} = 4$ and $OH^-/Ce^{4+} = 4$).

One obtains an aqueous colloidal dispersion with a CeO_2 concentration of the order of 112 g/l and a pH of 2.58.

The hydrodynamic diameter of the colloids measured by light-scattering is of 490 Å.

The chemical composition of the species present in colloidal form in the aqueous sol is determined as above.

The molar Zr/Ce ratio is found to be of the order of 0.1.

EXAMPLE 4 -

320.7 g of zirconyl nitrate $ZrO(NO_3)_2$, $2H_2O$ are added in 1000 cm³ of a solution of ceric nitrate containing 1.2 moles/litre of cerium IV, 0.04 mole/litre of cerium III and having a free acidity of 0.5 N : the molar ratio Zr^{4+}/Ce^{5+} is 1.

Under constant agitation and at ambient temperature, one adds 650 cm³ of a 6.9 solution of ammonium hydroxide at the rate of 100 cm³/hour, then 1016 cm³ of a 2.425 N solution of ammonium hydroxide, at the same rate.

The quantity of base thus added in the reaction medium represents 67 % in moles of the theoretical quantity necessary for the complete neutralization of the cerium and the zirconium present in the reaction medium ($OH^-/Zr^{4+} = 4$ and $OH^-/Ce^{4+} = 4$).

One obtains an aqueous colloidal dispersion with a CeO_2 concentration of the order of 77.4 g/l and a pH of about 2.

Examination of an aliquot part (250 cm³) by quasi-elastic light-scattering shows a hydrodynamic diameter of the colloids of the order of 350 Å.

The molar Zr/Ce ratio is found to be of the order of 0.65.

EXAMPLE 5 -

139.6 g of zirconyl nitrate $ZrO(NO_3)_2$, $2H_2O$ are added in 1744 cm³ of a solution of ceric nitrate containing 1.2 moles/litre of cerium IV, 0.05 mole/litre of cerium III and having a free acidity of 0.5 N : the molar Zr^{4+}/Ce^{4+} ratio is 0.25.

Into the mixture, under constant agitation and at ambient temperature, one adds 1256 cm³ of a 6.19 N solution of ammonium hydroxide at the rate of 100 cm³/hour, then 696 cm³ of a 2.4 N solution of ammonium hydroxide, at the same rate.

The quantity of base thus added in the reaction medium represents 82 % of the theoretical quantity necessary for the complete neutralization of the cerium and zirconium present in the reaction medium ($OH/Zr^{4+} = 4$ and $OH^-/Ce^{4+} = 4$).

One obtains an aqueous colloidal dispersion exhibiting a CeO_2 concentration of the order of 97 g/l and a pH of about 2.6.

Analysis of the supernatent solution shows a very weak concentration of total cerium, of the order of 3.5 g/l, which allows one to determine a percentage of cerium in colloidal form in the supersaturated dispersion in the neighbourhood of 96 %.

The chemical composition of the species present in colloidal form in the aqueous sol is determined as earlier.

The molar Zr/Ce ratio is found to be of the order of 0.13.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. An aqueous colloidal dispersion of a cerium IV compound supersaturated with OH^- ions.

2. A colloidal dispersion according to claim 1, wherein the proportion of cerium in colloidal form is less than or equal to 96%.

3. A colloidal dispersion according to claim 1 or 2, wherein the colloid has the chemical formula (I)

$$Ce(OH)_x(NO_3)_{4-x}$$

in which x is from 0.3 to 0.7.

4. A colloidal dispersion according to anyone of the preceding claims having a strong concentration of CeO_2 of up to 30% by weight.

5. A colloidal dispersion according to anyone of the preceding claims having ionic characteristics due to the concentration of the salt in the base of from 0.3 to 8 moles/litre .

6. A colloidal dispersion according to anyone of the preceding claims wherein the colloid has a density of from 3.5 to 6.0.

7. A colloidal dispersion according to anyone of the preceding claims wherein the hydrodynamic diameter of the colloids is from 50 to 400 Å.

8. A colloidal dispersion according to anyone of the preceding claims which is stable at ambient temperature and when it is subjected to a temperature increase.

9. A method of preparation of an aqueous colloidal dispersion of a cerium IV compound supersaturated with OH^- ions and described in anyone of the claims 1 to 8, comprising the step of reacting an aqueous solution of a cerium IV salt with a base so as to obtain a supersaturation ratio of from 3 to 4.

10. A process according to claim 9 wherein the solution of cerium IV salt is an aqueous solution of ceric nitrate or an aqueous solution of ammoniacalcerium nitrate.

11. A process according to claim 9 or 10 wherein the concentration of cerium IV salt expressed as cerium IV is from 0.1 to 3 moles/litre.

12. A process according to claim 11, wherein the concentration of cerium IV salt expressed as cerium IV is from 0.1 to 1.5 moles/litre.

13. A process according to anyone of the claims 9 to 12, wherein the base is an aqueous solution of ammonium hydroxide of soda or potash, or ammonia.

14. A process according to claim 13, wherein the normality of the basic solution is from 5 to 11 N.

15. A process according to claim 13, wherein the normality of the basic solution is from 0.1 to 5 N.

16. A process according to anyone of the claims 9 to 15 wherein the supersaturation ratio is from 3 to 3.8.

17. A process according to claim 9 wherein the final pH of the colloidal dispersion of the cerium IV compound is less than or equal to 3.0.

18. A process according to claim 9 wherein the final pH of the colloidal dispersion of the cerium IV compound is from 0.3 to 3.0.

19. A process according to claim 9 wherein the reaction temperature is from 0°C to 60°C.

20. A process according to claim 19 wherein the reaction temperature is ambient temperature.

21. A process according to any one of the claims 9 to 20, wherein the aqueous solution of the cerium IV salt and the basic solution are mixed simultaneously.

22. A process according to anyone of the claims 9 to 20, wherein the base is added to the solution of cerium IV.

23. A process according to claim 22 wherein initially, a concentrated basic solution is added to the solution of cerium (IV) followed by the addition of diluted basic solution.

24. A mixed aqueous colloidal dispersion of a cerium IV compound and a cation of a metal M, said colloidal dispersion being supersaturated with OH- ions; said cation M being chosen from the group consisting of 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8, 3a and 4a.

25. A mixed aqueous colloidal dispersion according to claim 24, wherein the cation of metal M is a metallic

cation of acidic nature.

26. A mixed aqueous colloidal dispersion according to claim 24 or 25 wherein metal M is iron or Zirconium.

27. A mixed aqueous colloidal dispersion according to anyone of the claims 24 to 26 wherein the cation of metal M replaces from 0.1 to 50% of the moles of cerium IV.

28. A mixed aqueous colloidal dispersion according to anyone of the claims 24 to 27 wherein the hydrodynamic diameter of the colloids is from 50 to 2000 Å.

29. A process for preparing the mixed aqueous colloidal dispersion of a cerium IV compound and a cation M^{n+} described in anyone of the claims 24 to 28 comprising the steps of preparing an aqueous solution of a cerium IV salt and a salt of metal M and reacting the mixed aqueous solution with a base so as to obtain a supersaturation ratio of between 3 and 5.5.

30. A process according to claim 29, wherein the quantity of base introduced represents from 60 to 95% in moles of the theoretical quantity of base necessary for the complete neutralization of the cerium IV and of the cation M^{n+} present in the reaction medium.

31. A process according to claim 29, wherein the salt of metal M is introduced in solid form into the solution of the cerium IV salt and that the base is then added.

32. A process according to claim 29, wherein the salt of metal M is put in the form of an aqueous solution having a concentration of from 0.01 mole/litre to its maximum solubility and the solution is mixed with the aqueous solution of the cerium IV salt base subsequently added.

33. A process of preparing an aqueous colloidal dispersion of a cerium IV compound supersaturated with OH^- ions substantially as herein described with reference to any one of the examples 1 to 5.

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