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(71) Applicants
United Kingdom Atomic
Energy Authority
(Great Britain),
11 Charles II Street,
London SW1Y 4QP
(72) Inventor
James Louis Woodhead
(74) Agents
United Kingdom Atomic
Energy Authority
(Clive Stephen Bennett),
Patents Branch,
11 Charles II Street,
London SW1Y 4QP

(54) **Improvements in or relating to**
compounds

(57) The invention provides a process for the preparation of a dispersible product containing a cerium compound which comprises heating a cerium (IV) oxide hydrate in the presence of a salt to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dispersible product containing a cerium compound.

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SPECIFICATION

Improvements in or relating to compounds

5 The present invention relates to compounds and more particularly to cerium compounds and cerium compounds in association with other elements.

According to one aspect of the present invention there is provided a process for the preparation of a dispersible product containing a cerium compound which comprises heating a cerium (IV) oxide hydrate in the presence of a salt to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dispersible product containing a cerium compound.

In accordance with one embodiment of the present invention there is provided a process for the preparation of a dispersible product containing a cerium compound which comprises heating a substantially dry cerium (IV) oxide hydrate in the presence of a salt to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dry dispersible product containing a cerium compound.

It is to be understood that the concentration of salt used and the temperature and time of heating is such that the desired degree of deaggregation is effected. The concentration, temperature and time can be determined by experimentation for a particular cerium (IV) oxide hydrate starting material.

By "dispersible product" as used in this Specification it is meant that the dispersible product is dispersible in aqueous media (e.g. water or aqueous acid solutions) to give a colloidal dispersion (i.e. a sol). The dry dispersible product may, of course, still contain "structural" water.

The salt may be, for example, a metal salt such as a metal nitrate, metal chloride or metal perchlorate. Other salts, for example ammonium nitrate, may also be used in accordance with the present invention.

The salt may be chosen such that a selected chemical element is present in the dispersible product.

Thus, according to another aspect of the invention further provides a process for the preparation of a dispersible product containing a cerium compound in association with a selected element which comprises heating a cerium (IV) oxide hydrate in the presence of a salt of the element to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dispersible product containing a cerium compound in association with the element.

The dispersible product prepared in accordance with the immediately foregoing aspect of the present invention may comprise, for example, a mixture of a cerium compound and a compound of the element, or a mixture of a cerium compound with which ions of the element are associated (e.g. by being sorbed and thereby taken up by the cerium compound).

By way of example dispersible products containing yttrium or a rare earth element may be prepared by heating cerium (IV) oxide hydrate in the presence of an yttrium salt or rare earth element salt (e.g.

$M(\text{NO}_3)_3$ where M is yttrium or a rare earth element).

Mixed colloidal dispersions of ceria- M_2O_3 have been prepared in accordance with the present invention at concentrations of up to 14^m mM_2O_3 where M is as defined above.

70 The present invention enables mixed colloidal dispersions to be prepared which are difficult or impossible to prepare by other routes such as adding $M(\text{NO}_3)_3$ salts to ceria sols, or by mixing $M(\text{NO}_3)_3$ with $\text{Ce}(\text{NO}_3)_3$ and then processing by aqueous routes to cerium (IV) sols containing added M_2O_3 .

The mechanism by which a salt effects deaggregation is not fully understood. However, it is believed that the salt gives rise to ionic species which interact with the crystallites (possibly in conjunction with water in the oxide hydrate) to effect the deaggregation.

More than one selected chemical element may be arranged to be present in the dispersible product if desired. Thus, optionally, a cerium (IV) oxide hydrate may be heated in the presence of a plurality of salts of selected elements to produce a dispersible product containing a cerium compound in association with the elements.

90 The present invention may also be used to prepare a dispersible product containing a selected element (e.g. silicon) which does not form a salt convenient for use in accordance with the present invention.

Thus, in accordance with a further aspect the present invention provides a process for the preparation of a dispersible product containing a cerium compound in association with a selected element which comprises heating a cerium (IV) oxide hydrate in the presence of the selected element and a salt of a further element to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate.

The salt of the further element may be, for example, a nitrate or a chloride (e.g. ammonium chloride).

The selected element may be provided in any suitable form such as a heat stable oxide powder (e.g. silica produced by a vapour phase condensation method such as flame hydrolysis).

Thus, by way of example, cerium (IV) oxide hydrate can be heated in the presence of silica produced by a vapour phase condensation method and a salt of a further element to give a dispersible product.

A mixed colloidal dispersion may also be formed by dispersing a dispersible product prepared in accordance with the present invention in a sol (e.g. a SiO_2 sol) or dispersing the dispersible product in water to form a sol and mixing this with another sol.

Cerium (IV) oxide hydrate for treatment in accordance with the present invention can be obtained commercially or, alternatively, can be prepared by any suitable route. For example, it can be prepared from readily available cerium salts, (e.g. of "reagent grade"). The preparation may be by precipitation from a cerium salt.

125 Thus, for example, as disclosed in British Patent Application No. 22835/78 (now BP 1603794) (UKAEA) (to which West German Offenlegungsschrift No. 2857146 corresponds), high purity cerous carbonate can be dissolved in aqueous nitric or hydrochloric acid to give a neutral solution and then oxidised with

$\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ to give cerium (IV) oxide hydrate.

By way of further example cerium (IV) oxide hydrate for treatment in accordance with the present invention may be prepared by the conventional routes disclosed at page 1 lines 40 to 61 of B.P. No. 1342893 (UKAEA).

The degree of hydration of the cerium (IV) oxide hydrate starting material may vary over a wide range.

By way of example, dry dispersible products have been prepared in accordance with the present invention from cerium (IV) oxide hydrate starting materials having respectively 8% water and 60% water.

Also by way of example, dispersible products have been prepared from oxide hydrate starting materials having other water contents.

Where, in accordance with the present invention substantially dry cerium (IV) oxide hydrate is heated in the presence of a salt, it is preferred that the temperature of heating of the cerium (IV) oxide hydrate is in the range 200-450°C and it has been found that heating in the range of 300-350°C is particularly useful in producing a dry dispersible product which can be dispersed to give highly concentrated sols (e.g. > 600 g l^{-1} (3.5M in Ce (IV))).

A time of ~1 to 2 hours has been found to be suitable for heating substantially dry cerium (IV) oxide hydrate in the range of 200°C to 450°C to effect deaggregation in accordance with the present invention.

Preferably the nitrate/CeO₂ ratio in the dry dispersible product is in the range 0.05 to 0.25 and a particularly preferred range is 0.8-0.15.

The cerium (IV) oxide hydrate starting material typically can consist of insoluble particles of up to ~2000 Å diameter (i.e. greater than colloidal dimensions), the particles comprising aggregates of crystallites.

Colloidal dispersion prepared from dispersible products prepared in accordance with the present invention show, for example, a 10 to 20-fold reduction in this size in that such dispersions include colloidal size particles comprising individual crystallites (~50 Å) and small aggregates of crystallites of say ~100 Å.

Thus, the heating in the presence of a salt in accordance with the present invention achieves deaggregation of the crystallites to enable particles of colloidal dimensions to be obtained.

Deaggregation in accordance with the present invention can involve breaking of bonds between crystallites in an aggregate of crystallites or a weakening of bonds or attractive forces between crystallites in an aggregate of crystallites to a degree that the crystallites can separate when the dispersible product is introduced into an aqueous medium.

A dispersible product prepared in accordance with the present invention may be used in the preparation of a colloidal dispersion (i.e. a sol).

Thus the present invention also provides a process for the preparation of a colloidal dispersion containing a cerium compound which comprises dispersing in an aqueous medium a dispersible product containing a cerium compound prepared in accordance with the present invention.

The invention further provides a process for the preparation of a mixed sol containing a cerium compound in association with a selected element comprising dispersing in an aqueous medium a dispersible product containing a cerium compound in association with a selected element prepared in accordance with the invention.

The invention further provides a process for the preparation of a gel which comprises drying a sol which has been prepared by dispersing in an aqueous medium a dispersible product containing a cerium compound prepared in accordance with the present invention.

The invention further provides a process for the preparation of a gel comprising drying a sol which has been prepared by dispersing in an aqueous medium a dispersible product containing a cerium compound in association with a selected element prepared in accordance with the invention.

The aqueous medium in which the dispersible product is dispersed can be water or aqueous acid solutions (e.g. dilute solutions of nitric acid). Gels may be produced by evaporating the sols at room temperature (~23°C) or at elevated temperatures (~50°C). The gels are glassy and may be redispersed in water.

The invention further provides a process which comprises mixing a dispersible product prepared in accordance with the present invention with water at such a concentration that coagulation occurs to form a slurry and separating the solids of the slurry from liquor of the slurry.

The separated solids may be dispersed in water to form a colloidal dispersion.

It is understood that ionic species can be removed with the liquor such that the ionic concentration in the solids is less than in the dispersible product as initially formed. In this way, if desired, the concentration of ionic species which may interfere with the formation of a colloidal dispersion is reduced and a more concentrated colloidal dispersion may be formed on admixing the separated solids with water.

It will be appreciated that where a dispersible product prepared by heating in accordance with the present invention does not have concentration of ionic species which prevents a desired concentration of sol being formed, there is no necessity for carrying out the further steps of coagulation to form a slurry, separation and dispersion to reduce the concentration of ionic species.

According to another aspect the present invention provides a sol prepared by a process in accordance with the present invention.

According to a further aspect the present invention provides a gel prepared by a process in accordance with the present invention.

According to yet a further aspect the present invention provides a dispersible product prepared by a process in accordance with the invention.

British Patent Application No. 22835/78 (UKAEA) (to which West German Offenlegungsschrift 2857146 corresponds) discloses *inter alia*:

"A process for the preparation of an aqueous dispersion of ceria which comprises forming a slurry of cerium (IV) hydroxide with water and an acid, the

acid being capable of causing deaggregation of aggregated crystallites in the cerium (IV) hydroxide, heating the slurry for such a time that the pH reaches a steady value, the quantity of acid in the slurry being such that the said steady value of pH is below 5.4, thereby to produce a conditioned slurry and admixing water with the conditioned slurry to produce an aqueous dispersion of cerium".

British Patent Application No. 22835/78 also discloses (page 6 lines 1 to 3) that certain cerium (IV) hydroxides are not easily susceptible to deaggregation in accordance with the invention disclosed therein and additionally the following passage appears at page 6 line 18 to page 7 line 2:

"Furthermore, to facilitate deaggregation as hereinbefore disclosed we believe that it is preferable that the starting cerium (IV) hydroxide should not have been heated to cause any substantial irreversible loss of water (e.g. heating to >100°C) prior to treatment in accordance with the present invention. For example we have found that a starting cerium (IV) hydroxide having 25% by weight water can be deaggregated in accordance with the present invention whereas some samples with 10% weight water content were not easily amenable to deaggregation.

Also we believe that the time and temperature and humidity of any prior heat treatment of the starting cerium (IV) hydroxide may affect the susceptibility of the cerium (IV) hydroxide to deaggregation in accordance with the present invention".

Thus, British Patent Application No. 22835/78 indicates that it is undesirable to heat cerium (IV) hydroxide to an extent which causes any substantial irreversible loss of water if it is desired to effect deaggregation to give a dispersible product.

It is surprising therefore that, in accordance with one embodiment of the present invention, a dispersible product containing a cerium compound which is readily dispersible in aqueous media to give concentrated sols may be prepared by a process which includes heating substantially dry cerium (IV) oxide hydrate to give a dry dispersible product.

British Patent Application No. 8112046 discloses *inter alia*:

"A process for the preparation of a dispersible cerium compound which comprises heating a substantially dry cerium (IV) oxide hydrate in the presence of a deaggregating agent to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dry dispersible cerium compound".

In accordance with Application No. 8112046 preferably the deaggregating agent comprises acid species.

As hereinbefore disclosed, cerium (IV) oxide hydrate for treatment in accordance with the present invention can be obtained commercially or, alternatively, can be prepared by any suitable route.

Thus, a salt may, for example, be added to previously prepared cerium (IV) oxide hydrate prior to heating in accordance with the present invention.

By way of further example, cerium (IV) oxide hydrate optionally, may be co-precipitated with a salt, or a precursor therefor, prior to being heated to

effect deaggregation. Thus the salt, optionally, may be formed in situ during formation of the cerium (IV) oxide hydrate rather than being added to previously prepared cerium (IV) oxide hydrate.

For example, cerium (IV) oxide hydrate may be precipitated from a cerous salt solution in the presence of a salt of an element to form a mixture of cerium (IV) oxide hydrate and the salt of the element. Where a mixture contains cerium (IV) oxide hydrate and a precursor for the salt the mixture may be treated after formation to form the salt.

Thus, for example, the mixture may contain cerium (IV) oxide hydrate and the hydroxide of another element which may be converted to a salt prior to heating to effect deaggregation (e.g. nitric acid may be used to give a nitrate of the element).

Gels prepared by a process in accordance with the present invention may be heated to form ceramic materials.

The invention will now be further described, by way of example only, as follows:

Example 1

700g of a 99.5% pure cerium IV hydrate (71.4% oxide) was stirred with 0.1341 of a yttrium nitrate solution containing 55.6g of Y_2O_3 to give a mixture with the nominal composition of 10 w/o Y_2O_3 -90 w/o CeO_2 . The mixture was dried at 105°C for 3 hours to yield a dry product containing total oxide: 77.6 w/o and NO_3 , 18.2 w/o with a $NO_3/Y_2O_3 + CeO_2$ mole ratio = 0.67. A portion of the dry product (140g) was heated in air at 320°C for 4.5 hours using a bed-depth of 2.0 cm and yielded 114g of dispersible product containing oxide, 94.0 w/o and NO_3 , 5.6 w/o with a $NO_3/Y_2O_3 + CeO_2$ mole ratio = 0.17.

Example 2

A sol was prepared from the dispersible product prepared in accordance with Example 1. Thus the dispersible product prepared in Example 1 readily dispersed in water to form a 10 w/o Y_2O_3 - CeO_2 sol containing 200g/l of $Y_2O_3 + CeO_2$ with a pH of 4.7 and conductivity of 5.9 mmhos (22°).

Example 3

107g of a 99.5% pure cerium IV hydrate (93.2 w/o oxide) was mixed with 0.0481 of a yttrium chloride solution containing the equivalent of 11.1g Y_2O_3 to give a nominal composition of 10 w/o Y_2O_3 - 90 w/o CeO_2 . The mixture was dried at 105°C for 18 hours to give 13g of a dry product containing: $Y_2O_3 + CeO_2$, 83.6 w/o and Cl^- , 7.1% with a $Cl^-/Y_2O_3 + CeO_2$ mole ratio of 0.42. The dry product was heated in air at 300-320°C for between 0.5 and 1.0 hours to give a dispersible product containing: 94.7 w/o oxide and 6.2% Cl^- . The dispersible product was dispersed in water to give a dilute sol.

Example 4

Dispersible product prepared in accordance with Example 3 was dispersed in water at high concentration (100g l⁻¹) to cause coagulation to form a slurry. The slurry was heated to 90°C and centrifuged to give a clear superantant liquor containing 0.38M chloride. The solids of the slurry were readily dispersed in water to give a sol >200g l⁻¹ in oxide with a pH of 3.9 and a conductivity of 8.6 mmhos. The Cl^- /oxide mole ratio in the sol was 0.13.

Example 5

107g of a 99.9% pure cerium IV hydrate (93.2% oxide) was mixed with an aqueous solution of ammonium chloride (75ml) containing 7.7g of NH_4Cl to give a Cl^-/CeO_2 mole ratio of 0.25. The resulting mixture was dried at 105°C for 18 hours and then heated in air at 300°C for 0-5 hours (bed depth 2.0 cm) to give a dispersible product containing: oxide 94.0 w/o; and Cl^- , 4.5 w/o with a Cl^-/CeO_2 mole ratio of 0.23. This dispersible product was dispersed in water to give a sol containing 100 g l^{-1} .

Example 6

Dispersible product prepared in accordance with Example 5 was dispersed in water at high concentration ($>100\text{ g l}^{-1}$) and heated at 90°C to cause coagulation to give a slurry. The slurry was centrifuged to give a clear supernatant liquor was discarded. The solids of the slurry were readily dispersed in water to a sol having an oxide concentration $>200\text{ g l}^{-1}$ with a pH of 1.7 and a conductivity of 14.0 mmhos (22°C).

Example 7

107g of a 99.9% pure cerium IV hydrate (93.2 w/o oxide) was mixed with 75ml of an ammonium nitrate solution containing 11.5g of NH_4NO_3 ($\text{NO}_3^-/\text{CeO}_2$ mole ratio = 0.23). The resulting mixture was dried at 105°C and then heat treated at 300°C for 0.5 hour to give a dispersible product containing: oxide, 93.8 w/o and nitrate, 4.8 w/o with a $\text{NO}_3^-/\text{CeO}_2$ mole ratio = 0.14.

This dispersible product was dispersed in water to give a dilute sol ($>100\text{ g l}^{-1}$).

Example 8

Dispersible product prepared in accordance with Example 7 (i.e. $>100\text{ g l}^{-1}$) to cause coagulation to form a slurry. The slurry was centrifuged, the supernatant liquor discarded and the solid dispersed in water to give a sol of high concentration ($>200\text{ g l}^{-1}$).

Example 9

50g of 99.5% pure cerium (IV) oxide hydrate were mixed with 21ml of 2M yttrium perchlorate solution (4.79 g Y_2O_3 equivalent – giving ~ 10 wt % yttrium oxide/total oxide) and the resulting mixture heated in air at 320°C for 30 minutes to give a dispersible product.

Example 10

0.039 l of yttrium nitrate solution containing the equivalent of 251 g l^{-1} Y_2O_3 was added to 0.248 l of a cerous nitrate solution containing the equivalent of 361 g l^{-1} cerium oxide. To the mixture so formed (which contained the equivalent of 9.8g of Y_2O_3 and the equivalent of 89g CeO_2) 0.25 l of a europium nitrate solution containing the equivalent of 39g Eu_2O_3 was added and the whole diluted to 1 litre with water to give a mixed metal nitrate solution.

Whilst stirring a mixture containing 0.037 l of 100 volume H_2O_2 and 0.115 l of 18M NH_4OH made to 0.1 l with water was added to the mixed metal nitrate solution. A precipitate formed and this was stirred for 15 minutes after which it was centrifuged. The residue was washed with two successive 1 l volumes of water to remove entrained salts.

The resulting washed residue was stirred with 0.04 l of 2.5M HNO_3 , dried at 105°C for 3 hours, and subsequently heated at 320°C for 4 hours.

The resulting dispersible product was completely dispersible in water, contained 91.2 wt % oxide and

had a nitrate : oxide mole ratio of 0.23.

CLAIMS

1. A process for the preparation of a dispersible product containing a cerium compound which comprises heating a cerium (IV) oxide hydrate in the presence of a salt to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dispersible product containing a cerium compound.

2. A process as claimed in claim 1 which comprises heating a substantially dry cerium (IV) oxide hydrate in the presence of a salt to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dry dispersible product containing a cerium compound.

3. A process as claimed in claim 1 or claim 2 for the preparation of a dispersible product containing a cerium compound in association with a selected element which comprises heating a cerium (IV) oxide hydrate in the presence of a salt of the element to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate and produce a dispersible product containing a cerium compound in association with the element.

4. A process as claimed in any one of the preceding claims wherein the salt is a metal salt or an ammonium salt.

5. A process as claimed in claim 4 wherein the metal salt is a metal nitrate, a metal chloride, or a metal perchlorate.

6. A process as claimed in claim 4 wherein the ammonium salt is ammonium nitrate.

7. A process as claimed in claim 4 or 5 wherein the metal salt is an yttrium salt or a rare earth element salt.

8. A process as claimed in claim 7 wherein the yttrium salt is yttrium nitrate or the rare earth element salt is a rare earth nitrate.

9. A process as claimed in any one of the preceding claims wherein a cerium (IV) oxide hydrate is heated in the presence of a plurality of salts.

10. A process as claimed in any one of the preceding claims for the preparation of a dispersible product containing a cerium compound in association with a selected element which comprises heating a cerium (IV) oxide hydrate in the presence of the selected element and a salt of a further element to cause deaggregation of aggregated crystallites in the cerium (IV) oxide hydrate.

11. A process as claimed in claim 10 wherein the salt of the further element is a nitrate or a chloride.

12. A process as claimed in claim 10 or 11 wherein the selected element is provided in the form of a heat stable oxide powder.

13. A process as claimed in claim 12 wherein the heat stable oxide powder is silica produced by a vapour phase condensation method.

14. A process as claimed in any one of claims 1 to 13 wherein substantially dry cerium (IV) oxide hydrate is heated in the presence of a salt at a temperature in the range 200°C to 450°C .

15. A process as claimed in claim 14 wherein the temperature is in the range 300°C to 350°C .

16. A dispersible product prepared by a process as claimed in any one of claims 3 to 15 comprising a

mixture of a cerium compound and a compound of an element.

17. A dispersible product prepared by a process as claimed in any one of claims 3 to 15 comprising a mixture of a cerium compound with which ions of an element are associated.

18. A dry dispersible product prepared by a process as claimed in any one of claims 2 to 15 having a nitrate/cerium ratio in the range 0.05 to 0.25.

19. A dry dispersible product as claimed in claim 18 wherein the nitrate/cerium ratio is in the range 0.08 to 0.15.

20. A process for the preparation of a colloidal dispersion containing a cerium compound which comprises dispersing in an aqueous medium a dispersible product containing a cerium compound prepared by a process as claimed in any one of claims 1 to 15.

21. A process for the preparation of a mixed sol containing a cerium compound in association with a selected element comprising dispersing in an aqueous medium a dispersible product containing a cerium compound in association with a selected element prepared by a process as claimed in any one of claims 3 to 15.

22. A process for the preparation of a gel which comprises drying a sol which has been prepared by dispersing in an aqueous medium a dispersible product containing a cerium compound prepared by a process as claimed in any one of claims 1 to 15.

23. A process for the preparation of a gel comprising drying a sol which has been prepared by dispersing in an aqueous medium a dispersible product containing a cerium compound in association with a selected element prepared by a process as claimed in any one of claims 3 to 15.

24. A process for the preparation of a mixed colloidal dispersion comprising dispersing in a sol a dispersible product prepared by a process as claimed in claim 1 or 2.

25. A process for the preparation of a mixed colloidal dispersion comprising dispersing a dispersible product prepared by a process as claimed in claim 1 or 2 in water to form a sol and mixing this sol with another sol.

26. A process for the preparation of a colloidal dispersion which comprises mixing a dispersible product prepared by a process as claimed in any one of claims 1 to 15 with water at such a concentration that coagulation occurs to form a slurry, separating the solids of the slurry from liquor of the slurry and dispersing the separated solids in water to form a colloidal dispersion.

27. A sol or colloidal dispersion prepared by a process as claimed in any one of claims 20, 21, 24, 25 or 26.

28. A gel prepared by a process as claimed in claim 22 or 23.

29. A dispersible product prepared by a process as claimed in any one of claims 1 to 15.

30. A process substantially as hereinbefore described with reference to any one of the Examples.

31. A dispersible product substantially as hereinbefore described with reference to any one of Examples 1, 3, 5, 7, 9 and 10.

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