

PROCESS FOR THE MANUFACTURE OF AMMONIUM RARE-EARTH
DOUBLE OXALATES AND THEIR USES FOR THE MANUFACTURE OF
RARE-EARTH OXIDES

The present invention relates to a process
5 for the manufacture of ammonium rare-earth double
oxalates, and to their use for obtaining rare-earth
oxides.

It relates more especially to a process
enabling double oxalates possessing specified
10 morphology and particle size to be obtained.

Rare-earth oxides find numerous applications
in the field, in particular, of ceramics and
electronics but, at the present time, an increasing
demand is observed in the market for products having
15 controlled particle size.

One of the conventional methods for obtaining
rare-earth oxides, and which is amply described in the
literature, in particular in the NOUVEAU TRAITE DE
CHIMIE MINERALE (New Treatise on Inorganic Chemistry),
20 Volume VII, (1959), p. 1007 by Paul PASCAL, consists in
calcining at between 500 and 900°C rare-earth oxalates
obtained by precipitation, using oxalic acid, of rare-
earth salts in the form of an aqueous solution.
However, such a process of manufacture leads only to
25 rare-earth oxides possessing coarse particle size.

It is also known, according to JP 53-095911-A
(Chemical Abstracts 90, 40940 w), to prepare fine rare-
earth oxides, and more especially fine yttrium oxide,

by calcination of an ammonium yttrium oxalate, which consists in starting with an aqueous solution of an yttrium salt, in precipitating the yttrium in the form of its hydroxide, prepared by reaction of the aqueous solution of an yttrium salt and a basic aqueous solution such as ammonia solution, then in treating the resulting hydroxide slurry with oxalic acid, and finally in separating the precipitate obtained, washing it and calcining it at a temperature of 750°C. The said process leads, according to the description given in JP 53-095911-A, to the production of fine yttrium oxide. The particle diameter is between 0.9 and 4.5 μm , the crystals having the shape of small plates with rounded edges.

However, control of the particle size as well of the particle size distribution is relatively difficult, since these are greatly influenced by the conditions of implementation of the process.

One of the objects of the present invention is, in particular, to remedy these drawbacks by proposing a process for the manufacture of ammonium rare-earth double oxalates possessing a narrow particle size distribution, with average crystal sizes which can be controlled.

Ammonium rare-earth double oxalate should be understood to mean a compound comprising one or more rare earths combined with ammonium and oxalate ions enabling simple or mixed oxides to be produced after

calcination.

The expression rare earths should be understood to mean the elements bearing atomic numbers between 57 and 71 (inclusive) belonging to the lanthanide family, as well as yttrium bearing atomic number 39.

To this end, the invention proposes a process for the manufacture of an ammonium rare-earth double oxalate, characterised in that it consists in:

- 10 - mixing, in an aqueous medium, at least one compound capable of liberating oxalate ions in solution with at least one water-soluble rare-earth compound and one ammonium salt,
- separating the precipitate obtained,
- 15 - and, where appropriate, drying it.

According to a feature of the invention, the ammonium salt is selected from ammonium nitrate, ammonium chloride and ammonium acetate.

Thus, the use of an ammonium salt such as, for example, ammonium nitrate, which is the preferred compound of the invention, permits better control of the precipitation of the double oxalate, since it precipitates directly without prior precipitation of the rare-earth hydroxide as in the previous process mentioned above. This direct precipitation enables the particle size and the spread of crystallite sizes of the precipitated double oxalate to be controlled.

According to a first, preferred embodiment of

the invention, the ammonium salt and the rare-earth compound are mixed in an aqueous medium to form a first solution.

5 In this embodiment, the compound capable of liberating in solution oxalate ions in solution is added to the first solution.

The state or concentration of this compound enables the size of the crystallites of precipitated double oxalate, as well as their particle size
10 distribution, to be modified.

Advantageously, the compound capable of liberating oxalate ions is selected from oxalic acid, crystallised or in solution, alkali metal oxalates, crystallised or in solution, or the like.

15 Thus, addition of the compound capable of liberating oxalate ions in solid form enables a precipitate with small-sized crystallites, for example of the order of 1 to 4 μm , to be obtained, while addition of this compound in the form of an aqueous
20 solution, thereby forming a second solution, enables larger crystallite sizes to be obtained.

In a second embodiment of the invention, the first solution containing an ammonium salt and a rare-earth compound is added to the second solution
25 containing the compound capable of liberating oxalate ions.

However, in this embodiment, the rare-earth compound and the ammonium salt may be added in the form

of a solution or in crystallised form. These compounds may be added either in the form of a solid mixture or of a common solution, or in separate form, but they should then preferably be added simultaneously to the second solution.

As rare-earth compounds which are suitable for the invention, there may be mentioned nitrates, chlorides and sulphates, for example, or a mixture of rare-earth salts, nitrates being the preferred compounds of the invention.

Among these compounds, yttrium nitrate, europium nitrate, lanthanum nitrate, neodymium nitrate, dysprosium nitrate, cerium nitrate, gadolinium nitrate, terbium nitrate or a mixture of these are preferred.

In particular, it is possible to employ an aqueous solution containing rare-earth salts which originates directly or indirectly from the processing of rare-earth ores.

Although the process of the invention applies perfectly well to the cerium rare earths, it is more especially suited to the yttrium rare earths.

"Cerium rare earths" is understood to mean the lighter rare-earth elements beginning with lanthanum and extending up to neodymium in accordance with the atomic number, and "yttrium rare earths" denotes the heavier rare-earth elements in accordance with the atomic number, beginning with samarium and finishing with lutecium and including yttrium.

The concentration of rare-earth compound is not critical.

According to another preferred feature of the process, the $C_2O_4^{2-}/RE$ and NH_4^+/RE mole ratios at completion of the precipitation are not less than 2, and preferably not less than 2.5.

However, the concentration of $(C_2O_4)^{2-}$ and NH_4^+ ions in the solutions is not critical and can vary within wide limits.

According to a preferred embodiment, the oxalate concentrations as well as the rare-earth and ammonium ion concentration in the different solutions and the volumes of the first and second solutions, as well as the masses of crystallised products added, will be determined so as to obtain in the final reaction medium a mole ratio of oxalate ion to rare earths ($(C_2O_4)^{2-}/RE$) of not less than 2, and advantageously not less than 2.5, and a ratio of ammonium to rare earths (NH_4^+/RE) of not less than 2, and preferably not less than 2.5.

The conditions of implementation of the process are fairly uncritical for obtaining a double oxalate. Nevertheless, control of the rate of mixing of the different solutions or the rate of introduction of the crystallised products into the solutions, of temperature and of the stirring of the mixture enables the morphology of the precipitated double oxalate to be modified and controlled.

Moreover, the temperature has an influence on the precipitation yield, since the solubility coefficient of the double oxalate increases with a rise in temperature.

5 According to a preferential feature of the invention, the precipitation is carried out at a temperature of between 30°C and 90°C, and preferably between 35°C and 70°C.

10 According to another preferential feature of the invention, the separation of the precipitate is carried out between 5 min and 2 h approximately after completion of precipitation. During this period, the reaction medium may be kept stirring or otherwise.

15 This step permits a rearrangement of the crystals and is generally referred to as a step of ageing of the precipitate.

20 The precipitate obtained is separated from the supernatant liquid by any solid/liquid separation process such as, for example, filtration, centrifugation, decantation or the like. It may also be subjected to one or more washes in order, for example, to remove soluble salts.

25 The ammonium rare-earth double oxalate can undergo a drying in order to evaporate unbound water, for example by a thermal treatment at between 50°C and 100°C or a drying under reduced pressure.

 The process of the invention enables an ammonium rare-earth double oxalate possessing a

homogeneous particle size to be obtained, as well as a very narrow particle size distribution of the crystals.

The crystals obtained are, for example, between 1 and 4 μm approximately in size, and have the shape of a small plate.

One of the uses of these ammonium rare-earth double oxalates is the production of rare-earth oxides obtained by thermal decomposition of these oxalates.

The morphology and particle size of the rare-earth oxides obtained by decomposition of a double oxalate is generally similar to that of the said double oxalate used as a precursor. However, depending on the conditions of thermal treatment of the double oxalate, the particle size of the oxide may be slightly different from that of the oxalate.

The thermal treatment or calcination is generally carried out at a temperature of between 600°C and 1200°C, and advantageously between 800°C and 1000°C.

The calcination time is determined in a conventional manner by checking for constant weight. As a guide, the calcination time can vary between 30 minutes and 6 hours approximately.

The invention will be illustrated by some examples given below, exclusively as a guide.

Example 1

A solution containing yttrium nitrate at a concentration of 1.36 mol/l is mixed with a 2 M ammonium nitrate solution to obtain an NH_4^+/Y ratio = 5.

5 This solution is heated to 45°C.

85 g of crystallised oxalic acid are added, this resulting in a $(\text{C}_2\text{O}_4)^{-}/\text{Y}$ ratio = 2.5.

The mixture is kept stirring for one hour at this temperature.

10 The precipitate is then recovered by filtration and washed with water.

The washed precipitate is dried at 100°C and then subjected to X-ray analysis to confirm its ammonium yttrium double oxalate structure.

15 This salt is converted to oxide by calcination at 900°C for 1 hour.

Particle size analysis carried out by means of a CILAS® granulometer shows that the oxide possesses a mean particle diameter of 2.55 μm , with a particle size dispersion factor $\frac{\sigma}{m}$ of 0.53.

The factor $\frac{\sigma}{m}$ is calculated by the formula

$$25 \quad \frac{\sigma}{m} = \frac{\phi_{84} - \phi_{16}}{2 \phi_{50}}$$

in which:

ϕ_{84} : represents the diameter for which 84% of the particles have a diameter not exceeding ϕ_{84} .

30 ϕ_{16} : represents the diameter for which

16% of the particles have a diameter not exceeding ϕ_{16} .

ϕ_{50} : represents the mean particle diameter.

Example 2

5 In a manner similar to Example 1, a solution is prepared containing yttrium nitrate and ammonium nitrate with an NH_4^+/Y ratio = 3.90.

 To this solution, after being brought to 45°C, a 1 M solution of oxalic acid is added so as to
10 obtain a $\text{C}_2\text{O}_4^{2-}/\text{Y}$ ratio = 2.

 The reaction medium is then kept stirring for 30 minutes.

 After filtration and washing with water, the precipitate is dried at 100°C and then calcined at
15 900°C to convert it to yttrium oxide.

 Particle size analysis of this oxide shows that it has a mean diameter ϕ_{50} equal to 13.6 μm and a σ_m equal to 0.51.

20 The crystals of this oxide are illustrated in the single Figure (magnification 6000 times).

Example 3

 A solution containing 0.675 mol of crystallised oxalic acid is heated to 45°C.

25 To this solution, a second solution containing an ammonium nitrate and an yttrium nitrate is added to obtain the following ratios in the reaction medium:

$$\text{C}_2\text{O}_4^{2-}/\text{Y} = 2.5$$

$$\text{NH}_4^+/\text{Y} = 4.96$$

The mixture is kept stirring for 1 hour and the precipitate is then filtered off and washed with water.

5 After drying at 100°C, the double oxalate is calcined for 1 hour at 900°C.

Particle size analysis shows that it has a ϕ_{50} equal to 4.06 μm and a $\frac{\sigma}{m} = 0.48$

10 Example 4

To a solution of oxalic acid heated to 60°C, a solution of yttrium nitrate and a solution of ammonium nitrate are added simultaneously so as to obtain the following ratios in the reaction medium:

$$\begin{aligned} \text{C}_2\text{O}_4^{2-}/\text{Y} &= 2.5 \\ \text{NH}_4^+/\text{Y} &= 5.15 \end{aligned}$$

The mixture is kept stirring for one hour.

The precipitate is then filtered off and washed with water, thereafter dried and calcined as in previous examples.

The oxide thereby obtained possesses a mean particle diameter equal to 3 μm and a $\frac{\sigma}{m}$ equal to 0.6.

Example 5

25 Example 1 is reproduced, but using a solution of yttrium chloride and ammonium chloride in place of the solution of yttrium nitrate and ammonium nitrate.

The ratios of the species in the reaction medium are:

$$\text{C}_2\text{O}_4^{2-}/\text{Y} = 2.54$$

$$\text{NH}_4^+/\text{Y} = 3.26$$

5 The yttrium oxide obtained by calcination of
the precipitate, recovered according to the process
described in the previous examples, possesses a mean
particle diameter equal to $3.5 \mu\text{m}$ and a $\frac{\sigma}{m} = 0.56$.



CLAIMS

1. Process for the manufacture of an ammonium rare-earth double oxalate, characterised in that it consists in:

- 5 - mixing, in an aqueous medium, at least one compound capable of liberating oxalate ions in solution with at least one water-soluble rare-earth compound and one ammonium salt,
- separating the precipitate obtained,
- 10 - and, where appropriate, drying it.

2. Process according to claim 1, characterised in that the ammonium salt is selected from ammonium nitrate, ammonium chloride and ammonium acetate.

15 3. Process according to claim 1 or 2, characterised in that the ammonium salt and the rare-earth compound are mixed in an aqueous medium to form a first solution.

 4. Process according to claim 3, characterised in that the compound capable of liberating oxalate ions in solution is added to the first solution.

20

 5. Process according to claim 3, characterised in that the compound capable of liberating oxalate ions is selected from oxalic acid, crystallised or in solution, and alkali metal oxalates.

25

 6. Process according to one of claims 1 to 3, characterised in that the compound capable of





liberating oxalate ions is dissolved in water to form a second solution, the first solution being added to the said second solution.

7. Process according to one of the preceding claims, characterised in that the soluble rare-earth salt is selected from the group comprising nitrates, chlorides, sulphates or a mixture of rare-earth salts.

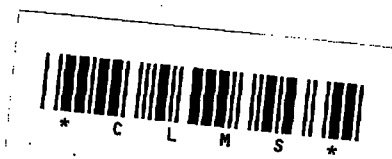
8. Process according to claim 7, characterised in that the rare-earth compounds are yttrium nitrate, europium nitrate, lanthanum nitrate, neodymium nitrate, dysprosium, cerium, gadolinium or terbium nitrate or a mixture of these.

9. Process according to one of the preceding claims, characterised in that the $C_2O_4^{2-}/RE$ and NH_4^+/RE mole ratios at completion of the precipitation are not less than 2, and preferably not less than 2.5.

10. Process according to one of the preceding claims, characterised in that the precipitation is carried out at a temperature of between 30°C and 90°C, and preferably between 35°C and 70°C.

11. Process according to one of the preceding claims, characterised in that the separation of the precipitate is carried out between 5 min and 2 h after completion of precipitation.

12. Process for the manufacture of a rare-earth oxide, characterised in that it consists in



calcining the ammonium rare-earth double oxalate
obtained according to one of the preceding claims,
after drying where appropriate.

13. Process according to claim 12,
5 characterised in that the calcination temperature is
between 600 and 1200°C, and preferably between 800°C
and 1000°C.