

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

5 The present invention relates to a process  
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 by  
conversion of a rare-earth neutral oxalate.

Rare-earth oxides find numerous applications  
in the field, in particular, of ceramics and  
electronics but, at the present time, an increasing  
15 demand is observed in the market for products having  
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  
20 CHIMIE MINERALE (New Treatise on Inorganic Chemistry),  
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.

25 However, such a process of manufacture leads only to  
rare-earth oxides possessing a particle size of between  
3 and 6  $\mu\text{m}$ .

It is also known, according to JP 53-095911-A

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(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  $\mu\text{m}$ , the crystals having the shape of small plates with rounded edges.

However, in some applications, rare-earth oxides such as yttrium oxide possessing larger particle sizes are required. Such sizes cannot be obtained with rare-earth neutral oxalates used as a precursor.

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 large particle sizes, for example between 5 and 10  $\mu\text{m}$ .

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:

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

Rare-earth neutral oxalate is understood to mean a salt in which all the acid functions of oxalic acid have been neutralised by a rare-earth cation or cations.

According to a feature of the invention, the quantity of oxalate ions added is sufficient to have a mole ratio of oxalate ions to rare-earth ions which is advantageously not less than 2 at completion of precipitation. In effect, the yield of conversion of the neutral oxalate to a double oxalate will be higher and equal to 100 % if the  $C_2O_4^{2-}/RE$  ratio is high, and in particular greater than 2.

Compounds capable of liberating ammonium ions in solution which are suitable for the invention are all water-soluble or -insoluble compounds which liberate ammonium ions when brought into contact with water.

As a non-limiting example, ammonium nitrate, ammonium chloride, ammonium acetate, ammonium hydroxide or the like may be mentioned.

Likewise, compounds capable of liberating oxalate ions which are suitable for the invention are all water-soluble or -insoluble compounds which liberate oxalate ions when brought into contact with water.

As a non-limiting example, oxalic acid, crystallised or in solution, or alkali metal oxalates or the like may be mentioned.

In one of the embodiments of the invention, ammonium oxalate is used as a compound for the simultaneous provision of ammonium and oxalate ions. However, it is possible to use this ammonium oxalate mixed with a compound providing ammonium ions, such as ammonia, for example, or a compound providing oxalate ions, such as, for example, oxalic acid.

According to another feature of the invention, the quantities of compounds capable of liberating oxalate ions and/or ammonium ions added to the medium containing the rare-earth neutral oxalate are determined so as to have  $C_2O_4^{2-}/RE$  and  $NH_4^+/RE$  mole

ratios of not less than 2, and preferably not less than 2.5, at completion of precipitation.

Rare-earth neutral oxalates which are advantageously suitable for the invention are yttrium, europium, lanthanum, neodymium, dysprosium, cerium, gadolinium or terbium oxalate, or a mixture of these.

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.

The rare-earth neutral oxalates are obtained by all known and conventional processes such as, for example, by precipitation of the rare-earth oxalate by adding oxalic acid to a solution of a soluble rare-earth salt such as a rare-earth nitrate.

The compounds capable of liberating oxalate or ammonium ions may be added to the medium containing the rare-earth neutral oxalate in crystallised form or in the form of aqueous solutions.

These compounds may be added simultaneously

or successively, rapidly or slowly without influencing the yield of conversion of the neutral oxalate to a double oxalate. However, the rate of introduction can have an influence on the particle size of the double oxalate, for example on the particle size distribution.

Moreover, the concentrations of  $(C_2O_4)^{-}$  and  $NH_4^{+}$  ions in the solutions are not critical and can vary within wide limits.

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 medium containing the neutral oxalate, of temperature and of the stirring of the mixture enables the morphology of the precipitated double oxalate to be modified and controlled.

Furthermore, the temperature has an influence on the conversion yield, since the solubility coefficient of the double oxalate and of the neutral oxalate increases with a rise in temperature.

According to a preferential feature of the invention, the process is performed at a temperature of between  $50^{\circ}C$  and  $90^{\circ}C$ , and preferably between  $60^{\circ}C$  and  $90^{\circ}C$ .

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.

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

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  
10 subjected to one or more washes in order, for example, to remove soluble salts.

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  
15 100°C or a drying under reduced pressure.

The process of the invention enables an ammonium rare-earth double oxalate possessing a mean particle size of between 5 and 10  $\mu\text{m}$  approximately, and advantageously between 7 and 10  $\mu\text{m}$ , to be produced.  
20 These particles are cubic in shape.

Moreover, the size of the particles of rare-earth double oxalate obtained is dependent on the size of the particles of neutral oxalate used, the size of the double oxalate being greater than that of the  
25 starting neutral oxalate.

One of the uses of these ammonium rare-earth double oxalates is the production of rare-earth oxide 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.

Thus, the oxides obtained by calcination of the double oxalates of the present invention have mean particle sizes of between 5 and 10  $\mu\text{m}$  approximately, and preferably between 7 and 10  $\mu\text{m}$ , with a  $\frac{\sigma}{\bar{m}}$  of between 0.35 and 0.6.

The factor  $\frac{\sigma}{\bar{m}}$  represents the particle or grain size dispersion and is calculated by the following formula:

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

in which:

$\phi_{84}$  : represents the particle diameter for which 84% of the particles have a diameter of less than  $\phi_{84}$ .

$\phi_{16}$  : represents the particle diameter for which 16% of the particles have a diameter of less than  $\phi_{16}$ .

$\phi_{50}$  : represents the mean particle diameter.

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.

5 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.

10 Example 1.

A suspension containing an yttrium neutral oxalate dried beforehand at 30°C is brought to 85°C.

A 0.255M solution of ammonium oxalate is added in order to have the following ratios of species:

15 
$$\text{C}_2\text{O}_4^{2-}/\text{Y} = 2$$

$$\text{NH}_4^+/\text{Y} = 2$$

The reaction medium is kept stirring for one hour.

20 The precipitate is recovered by filtration and washing with water, and is then dried at 100°C.

Its ammonium yttrium double oxalate structure is confirmed by X-ray analysis.

This salt is then calcined at 900°C for one hour.

25 The particle size characteristics of the oxide obtained are determined by analysis with a CILAS® granulometer.

The yttrium oxide possesses a mean diameter

$\phi_{50}$  equal to 5.9  $\mu\text{m}$  and a  $\frac{\sigma}{m}$  equal to 0.44.

### Example 2

Example 1 is reproduced, but with the  
5 following ratios of species:

$$\text{C}_2\text{O}_4^{2-}/\text{Y} = 2.63$$

$$\text{NH}_4^+/\text{Y} = 4$$

The oxide obtained possesses a  $\phi_{50}$  equal to  
8  $\mu\text{m}$  and a  $\frac{\sigma}{m}$  equal to 0.6.

10

The yttrium oxide obtained by calcination of  
this double oxalate is illustrated in Figure 1  
(magnification 1200 times).

For comparison, Figure 2 illustrates the  
15 oxide obtained by calcination of the starting neutral  
oxalate (magnification 1200 times).

### Example 3

Oxalic acid is added to a suspension of  
yttrium neutral oxalate in order to have a  $\text{C}_2\text{O}_4^{2-}/\text{Y}$  ratio  
20 equal to 2.35.

This suspension is heated to 85°C.

A 3.1N solution of ammonia is added so as to  
obtain an  $\text{NH}_4^+/\text{Y}$  ratio equal to 1.13.

The mixture is kept stirring for 30 minutes  
25 and the precipitate is then filtered off and washed  
with water.

After drying and calcination according to the  
process described in Examples 1 and 2, the oxide

obtained is analysed with a CILAS<sup>®</sup> granulometer. It possesses a  $\phi_{50}$  equal to 7  $\mu\text{m}$  and a  $\frac{\sigma}{\bar{m}}$  equal to 0.43.



## 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 rare-earth neutral oxalate with a compound capable of liberating ammonium ions and a compound capable of liberating oxalate ions in solution,
- separating the precipitate obtained,
- 10           - and, where appropriate, drying it.

2. Process according to claim 1, characterised in that the mole ratio of oxalate ions to rare-earth ions is not less than 2.

3. Process according to claim 1 or 2, characterised in that the compound capable of liberating ammonium ions is selected from ammonium nitrate, ammonium chloride, ammonium acetate and ammonium hydroxide.

15

4. Process according to one of the preceding claims, characterised in that the compound capable of liberating oxalate ions is selected from oxalic acid, crystallised or in solution, and alkali metal oxalates.

20

5. Process according to one of claims 1 and 2, characterised in that ammonium oxalate is used as a compound capable of simultaneously liberating ammonium and oxalate ions.

25

6. 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.

5        7.    Process according to one of the preceding claims, characterised in that the rare-earth neutral oxalate is an yttrium, europium, lanthanum, neodymium, dysprosium, cerium, gadolinium or terbium oxalate, or a mixture of these.

10       8.    Process according to one of the preceding claims, characterised in that the precipitation is carried out at a temperature of between  $50^\circ C$  and  $90^\circ C$ , and preferably between  $60^\circ C$  and  $90^\circ C$ .

15       9.    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.

20       10.   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.

25       11.   Process according to claim 10, characterised in that the calcination temperature is between  $600$  and  $1200^\circ C$ , and preferably between  $800^\circ C$  and  $1000^\circ C$ .

12.   Rare-earth oxide obtained according to one of claims 10 and 11, characterised in that it



possesses a particle size of between 5 and 10  $\mu\text{m}$ , and preferably between 7 and 10  $\mu\text{m}$ , with a dispersion index  $\frac{g}{m}$  of between 0.35 and 0.6.