

UNITED STATES PATENT OFFICE.

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PROCESS OF MANUFACTURING COMPOUNDS OF METALS OF THE RARE EARTHS.

1,371,741.

Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, OTTO DIETSCHKE, a German citizen, and resident of Berlin-Lichtenberg, Germany, have invented certain new and useful Improvements in Processes of Manufacturing Compounds of Metals of the Rare Earths, of which the following is a specification.

The present invention relates to the production of compounds of the rare earth metals and more especially to a method for producing such compounds from solutions containing a rare earth metal.

The invention is based upon the fact hitherto unknown that those mineral containing salts of the metals of the alkali metal group (and also the alkaline earth metals and aluminum) which are little or not at all soluble in water, will, upon being added to a hot solution of a rare earth metal, precipitate the rare earth metal from such solution.

Besides those minerals which contain the ordinary insoluble or little soluble salts of calcium, strontium, barium, or aluminum also those which contain the insoluble complex salts of the alkali metals proper, such as titanopotassium fluorid, boropotassium fluorid, silicopotassium fluorid, may be used. The use of natural fluorids in general, but also of natural phosphates and tungstates is advantageous, and special advantages are obtained if finely comminuted natural minerals such as fluor-spar or apatite are employed as precipitating agents. According to whether a fluorid, a phosphate or a tungstate be present in the mineral used for precipitating, the respective rare earth metal is obtained under the form of a fluorid, phosphate, or tungstate, the respective salt settling down very quickly as a homogeneous precipitate which can be easily treated further.

The solution of the rare earth metals may contain the chlorid or any other soluble salt of the metal, and it is possible according to the present invention, to precipitate the salts from waste liquors resulting for instance in the manufacture of thorium or from decomposed monazite sand or from cerite solutions.

An addition of some suitable mineral acid, such as hydrochloric acid, will prove advantageous in many cases, especially so when fluor-spar is used as a precipitant, inasmuch as the reaction is expedited thereby.

Instead of the fluorids the double fluorids of the rare earth metal and of the precipitating agent may be produced, such double fluorid being formed in some cases, especially so, when little acid only is present and the reaction is interrupted before completion. These double fluorids, and especially the double fluorid of a rare earth metal and calcium form a very valuable product. There cannot be any doubt as to such double fluorids being really formed. In a mere mechanical mixture of the ordinary fluorids washing with water would cause the two salts to be separated owing to the difference in the respective specific weights. Moreover the compound obtained is absolutely insoluble in acid. By causing a solution of rare earth metals to act upon such double fluorid it may be decomposed, the single fluorids of the rare earth metals being then formed.

It has been ascertained further that the tendency to form double fluorids is especially great in the presence of an acid of the oxalic acid series such as for instance oxalic acid, the acid having either been added by design or being present as an impurity. In this case the rare earth metal solution may either be mixed with the oxalic acid and fluor-spar and the mixture then heated, or else the metal solution and the acid may be allowed to react with each other, oxalates of the metals being formed, and fluor-spar added afterward. Of oxalic acid not more than about 5 per cent. of the quantity of rare earth metals contained in the solution need be used.

The principal advantage offered by the method according to the present invention, as compared with the older methods practised up to this day lies in the very favorable qualities owned by the precipitates thus obtained.

Heretofore the rare earth metal solutions were precipitated as a rule with acids or easily soluble salts of an alkali, such as hy-

drofluoric acid or sodium fluorid. The precipitates thus obtained, however, are in a state of extremely fine division and settle down very slowly, thus offering great difficulties with regard to purification. This is probably due to the fact that the finely divided precipitate contains besides rare earth metal fluorids, also double fluorids of a rare earth metal and an alkali. However this may be, the deposit will retain most tenaciously the alkali compound serving as a precipitating agent as well as all other impurities. In contradistinction thereto the precipitate obtained with fluor-spar and with other compounds of the alkaline earth metals including magnesium and aluminum settles down very quickly and allows of being purified with the greatest ease. Moreover the danger connected with the use of hydrofluoric acid both as regards the operators and the apparatus used is totally avoided. The precipitate obtained according to the new method offers the further advantage of not sintering when being calcined, in contradistinction to the products obtained with hydrofluoric acid or alkali metal fluorids. This is of the greatest importance in the case where the product must be heated in order to increase its density, such as in the manufacture of luminous admixtures for arc light electrodes. The product obtained according to the present invention, upon being strongly heated, gets denser without however forming solid stone-like masses, and need not, therefore, be ground. A quantitative output is obtained and there are no losses caused by complicated washing operations, as in the former methods.

The double fluorids obtained in accordance with the method described above are coarsely grained and can be washed out easily. However, if it is desired to obtain the ordinary fluorids, the solution of rare earths containing the double fluorids need only be heated, thus yielding the simple fluorids in the form of a grained substance, unlike the amorphous powder obtained after the old methods.

In practising my invention I may for instance proceed as follows:—

Example I.

15.7 kgs. of rare earth metal chlorids, consisting half of cerium chlorid and half of lanthanum and didymium chlorids is dissolved in 84.3 kgs. water and heated to boiling point. To this solution 7.5 kgs. fluor-spar and 1 to 2 kgs. hydrochloric acid are added under permanent stirring. The solution is kept boiling until all the rare earth metal salts have been precipitated, this being the case after 1 or 2 hours. It is advisable to add some sodium chlorid or the like in order to hasten the reaction. The

precipitate formed is washed with water, filtered and dried. 12.1 kgs. of dry fluorid are obtained, this being 96 per cent. of the theoretical quantity.

Example II.

To 100 kgs. of a neutral solution of rare earth metals, said solution containing 10.5 per cent. of metallic oxids, 10 kgs. of calcium phosphate are added, the solution being heated and stirred all the while. After a few minutes the reaction will be completed; the rare earth metal phosphates are deposited as heavy flakes and can easily be washed. The quantitative output of 15 kgs. is obtained.

Example III.

11 kgs. of raw oxids of the rare earth metals, such as obtained as waste products in the manufacture of thorium, are dissolved in hydrochloric or nitric acid slightly in excess and water is added to get 100 kgs. The solution thus obtained is heated to boiling point and after adding 13 kgs. of fluor-spar boiling is continued for about half an hour, until the precipitation is complete. The precipitate is a grained product easily washed out. 18.2 kgs. of the dry product are obtained, 18.4 kgs. being the theoretical quantity.

Example IV.

13.5 kgs. of rare earth metal oxids of the greatest possible purity are dissolved in the least possible quantity of hydrochloric acid or nitric acid, water being added to make it 100 kgs. To this slightly acid solution 1 kg. of a saturated oxalic acid solution is added. A light precipitate will form, but be dissolved again upon the solution being heated. As soon as the boiling point is reached, 9.6 kgs. fluor-spar are added and boiling is proceeded with for about two hours. 15.6 kgs. of dry fluorid, equal to 96 per cent. of the theoretical quantity are obtained.

In the same manner freshly precipitated pure oxalates of the rare earth metals can be made to react with the required quantity of fluor-spar in the presence of some acid. It is true that in this case the reaction will take some more time but the fluorids of the rare earth metals are of better quality and more coarse-grained.

The term "alkali group" used in the claims shall include, besides the alkali metals proper, the alkaline earth metals, and aluminum.

The term "not easily soluble" as used in the claims is meant to comprise little soluble as well as practically insoluble salts.

I claim:—

1. The process which consists in causing a dissolved rare earth metal compound to react

with a mineral containing a not easily soluble fluorid of a metal of the alkali group.

2. The process which consists in causing a dissolved rare earth metal compound to react
5 with fluor-spar.

3. The process which consists in causing the solution of a rare earth metal compound to react with a mineral containing a not easily soluble salt of a metal of the alkali
10 group in the presence of an acid of the oxalic acid series.

4. The process which consists in causing a dissolved rare earth metal compound to react with a mineral containing a fluorid of a
15 metal of the alkali group and interrupting the reaction at the point where a double salt

of the rare earths and the precipitating medium has formed.

5. The process which consists in causing a dissolved rare earth metal compound to react
20 with a mineral containing a not easily soluble fluorid of a metal of the alkali group and interrupting the reaction at the point where a double fluorid of the rare earths and the precipitating medium has formed.
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In witness whereof I have hereunto set my signature in the presence of two subscribing witnesses.

OTTO DIETSCHKE.

Witnesses:

HENRY HASPER,
WOLDEMAR HAUPT.