

UNITED STATES PATENT OFFICE.

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PROCESS OF OBTAINING THORIUM OXIDS.

SPECIFICATION forming part of Letters Patent No. 617,636, dated January 10, 1899.

Application filed July 12, 1897. Serial No. 644,311. (No specimens.)

To all whom it may concern:

Be it known that I, WILHELM BUDDEUS, a citizen of the Empire of Germany, residing at Munich, in the Kingdom of Bavaria and Empire of Germany, have invented certain new and useful Improvements in the Art of Obtaining Thorium Oxids; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the art of obtaining thorium oxid or thoria, (ThO_2), and more particularly to the method of treating monazite sands for such purpose, its object being to concentrate such monazite sands, with a view of enriching them in thorium oxid. The monazite sands occurring, *e. g.*, in North Carolina, which contain an amount of monazite varying from a few per cent. to about ninety per cent., contain a corresponding amount of thorium oxid—that is to say, from about one-fourth to four per cent. It is due to this fact that only the high-grade sands, which contain from three to four per cent. of the oxid, have been put upon the market.

The purpose of this invention is to render the low-grade monazite sands, which contain an average of one per cent. of thorium oxid, marketable; and the said invention, with this object in view, consists in a method whereby these low-grade sands are enriched in the thorium oxid—*i. e.*, converted into a product containing from about ten per cent. to about twenty per cent. thorium oxid, according to the average percentage of monazite in the raw material.

The costs of carrying out the process embodying my invention are entirely covered by the utilization of the waste products formed in the course of the process, so that the preparation of the high-grade product from the hitherto worthless low-grade sand results in an additional advantage whereby the high-grade product under my invention may be obtained more economically than similar products hitherto employed.

My invention also involves such additional features, steps, and methods as will be hereinafter set forth, and pointed out in the claims.

The following is a detailed description of what I consider the best way of carrying out my invention:

Monazite sand generally consists of a mixture of monazite proper, ferrous titanate, (titaniferous iron,) and zircon. Since the monazite contains the thorium oxid, it follows that the proportional amount of the latter increases with that of the former. A poor or low-grade sand containing, *e. g.*, fifteen per cent. of monazite contains about 0.5 per cent. thorium oxid. Now under my invention the zircon and titaniferous sand, amounting to about eighty-five per cent. in this grade of monazite sand, are almost completely separated out in an unchanged condition. Moreover, the phosphoric acid combined with the oxids of cerium, lanthanum, didymium, and thorium, amounting in this case to about four per cent., is concurrently thrown out. From one thousand kilograms of the raw material containing fifteen per cent. monazite a resulting product of theoretically one hundred and ten and practically one hundred and thirty kilograms containing about four per cent. thorium oxid is obtained.

The chemical composition of the natural sand or raw material is as follows: Monazite = $(\text{CeLaDi})_2\text{O}_3\text{P}_2\text{O}_5 + \text{ThO}_2\text{P}_2\text{O}_5$. Ferrous titanate = FeTiO_3 or FeO.TiO_2 . Zircon = $\text{ZrO}_2.\text{SiO}_2.\text{H}_2\text{O}$.

The process is conducted as follows: The sand is crushed between crushing-rollers or otherwise to the fineness of the Brazilian sand—*i. e.*, so that the grains are from one-fourth to one-half millimeters in diameter. It should not be ground fine, since the decomposition of its ingredients depends in a measure upon the size of the grains. The sand so comminuted is then introduced into melted caustic soda or caustic potash having a temperature of about 400° to 500° centigrade. This results in completely depriving the monazite of its phosphoric acid and the generation of steam. The caustic alkali readily attacks the grains of monazite sand having the size above specified, leaving the ferrous titanate and zircon almost entirely unchanged, however. The resulting mass on solidifying consists in a mixture of, first, unchanged fer-

rous titanate and zircon; second, an extremely fine powder of the oxids of cerium, lanthanum, didymium, (which, for the sake of brevity, I will term the "cerium bases,") and of thorium, together with slight amounts of ferrous titanate and zirconium oxid, and, third, phosphate of sodium or potassium with excess of unchanged caustic soda or caustic potassium. Hot water is now added to this mass, whereby the alkali phosphate and hydrate are brought into solution. The tribasic alkali phosphate readily crystallizes out of this solution in a condition ready for the market, or the phosphoric-acid radical may be recovered out of the remaining solution by precipitating it with lime-water, barium, strontium, or other suitable hydrate, whereby the corresponding phosphate—*i. e.*, the phosphate of calcium, barium, strontium, &c.—is formed and precipitated, and the entire amount of caustic alkali or alkali hydrate is recovered by separating the remaining solution from the precipitate by filtering, decanting, or other suitable methods. The remaining solution, after separation from the crystals of alkali phosphate or from the precipitate—the phosphate of calcium, barium, or other alkaline earth or equivalent—is evaporated, and the residue, after melting, is again employed for the decomposing process. The product from which the phosphoric acid and alkali have thus been separated after being thoroughly washed is now stirred with water made somewhat alkaline, whereby the lighter oxids free from phosphoric acid are suspended and are thus readily washed or separated from the heavier undecomposed grains of ferrous titanate and zircon by elutriation or decanting the water containing the lighter oxids in suspension. This is effected with extreme ease and thoroughly. The oxids thus decanted or washed off are allowed to settle and the resulting sediment is then dried. It is readily decomposed, and by reason of its fineness it does not require to be ground. This sediment or magma, which contains all of the thorium oxid of the raw material, is now treated with aqueous sulfurous acid or other aqueous inorganic or organic acids for the purpose of further concentrating the percentage of the thorium oxid contained therein. As a consequence of this treatment the greater portion of the cerium bases are brought into solution, leaving a residue which contains all of the thorium oxid. This is due to the previous treatment with caustic alkali, whereby the thorium oxid has been brought into a condition wherein it is not soluble in dilute acids, while the cerium bases are completely and readily dissolved. The most suitable acid for this purpose is sulfurous acid by virtue of its cheapness and its ready manufacture at the places where the monazite sand is found. This operation may be carried out by putting the above-described sediment or magma of oxids mixed with wa-

ter into a wooden vat or receptacle, which may be lined with lead on its interior, and then introducing the sulfurous acid into the mass. Since the gases generated in the calcining-furnaces, in which the sulfurous acid is prepared by calcining or roasting pyrites or other minerals yielding sulfurous acid, leave the same in a hot condition, the heat required for solution in the vats is furnished by the gases from the furnaces themselves. It should be observed, however, that such solution takes place also in the cold or with moderate heat, though by no means so rapidly. After the contents of the vats have been saturated with sulfurous acid the mass is allowed to stand for some time, during which the precipitate containing all of the thorium oxid readily settles to the bottom. This precipitate is readily obtained as a sediment or magma by drawing off the acid liquor which contains the cerium bases (*i. e.*, the cerium, lanthanum, and didymium compounds) and washing with water. This sediment or magma, either dried or moist, is now ready for the market as a commercial product, or it may be further treated with a view to obtaining pure thorium preparations or compounds, which can be separated from their solutions in any appropriate manner. This product is very readily worked into pure thorium compounds. Its percentage of thorium oxid varies between ten and twenty per cent., according to the original composition of the monazite sand.

To illustrate my process, I will describe the treatment of a high-grade and of a low-grade monazite sand.

I. Monazite sand of Brazilian origin and having the following composition: thorium oxid, 3.5 per cent.; cerium bases, (oxids of cerium, lanthanum, and didymium,) fifty-five per cent.; phosphoric acid, twenty-one per cent.; ferrous titanate and zircon, twenty per cent.; loss in roasting or calcining, 0.5 per cent.; total, one hundred per cent. First, by treating with molten caustic soda and washing with water there are separated twenty per cent.; second, by washing or decanting from the ferrous titanate and zircon eighteen per cent.; third, by extraction with sulfurous acid forty per cent.; total, seventy-eight per cent. In other words, by the first step in this process twenty per cent., by weight, of ballast or compounds worthless in the treatment of the monazite sand are eliminated from the raw material. By the second step eighteen per cent. more are removed, and by the last step forty per cent. more, making in all seventy-eight per cent. of ballast removed. From a ton or one thousand kilograms of such sand there are hence obtained two hundred kilograms of a product containing about sixteen per cent. thorium oxid.

II. Monazite sand from North Carolina having the following composition: thorium

oxid, one per cent.; cerium bases, fifteen per cent.; phosphoric acid, five per cent.; ferrous titanate and zircon, seventy-nine per cent.; total, one hundred per cent. First, by treating with caustic soda and washing with water there are removed five per cent.; second, by washing or decanting from ferrous titanate and zircon seventy-five per cent.; third, by extraction with sulfurous acid twelve per cent.; total, ninety-two per cent.—that is to say, the first step of this process results in the elimination of five per cent. of ballast, the second step removes further seventy-five per cent., and the last step twelve per cent. more, making an aggregate of ninety-two per cent., by weight, of ballast removed. From a ton or one thousand kilograms of such hitherto worthless sand I hence obtain eighty kilograms of the final product, containing 12.5 per cent. thorium oxid.

By this process I am hence enabled to separate the useless ferrous titanate and zircon sand, to obtain all of the phosphoric acid in a marketable condition, to continually recover all or that portion of the decomposing agent (the alkali hydrate) which has not been combined with the phosphoric acid, and, finally, as the most important result to obtain a marketable raw material rich in thorium oxid which is very readily manufactured into pure thorium oxid.

The process is manifestly suitable for the treatment of Brazilian monazite sand, whether the same be rich or poor in thorium oxid, and in general for the separation of thorium oxid from cerium bases, ferrous titanate, zircon, phosphoric acid, and other impurities.

From the above description it is manifest that the process embodying my invention may be considerably varied without departing from my invention. Thus other alkalies may be used instead of the sodium hydrate or caustic soda for the separation of the phosphoric acid, and any suitable acids may be employed for extracting the cerium bases. I do not therefore desire to be limited to the exact details hereinbefore set forth; but

What I claim, and desire to secure by Letters Patent of the United States, is—

1. In the art of concentrating raw materials containing thorium, the process which consists in crushing raw materials containing the phosphates of thorium and cerium bases, together with ferrous titanate and zircon, into coarse granular form and then introducing them into molten alkali hydrate, whereby the phosphoric acid is separated and the ferrous titanate and zircon are unaffected.

2. The process, which consists in reducing monazite sand to coarse granular form and introducing the same into molten alkali hydrate, whereby the phosphoric acid is separated and the thorium and cerium bases are converted into the oxids.

3. The process which consists in treating a raw material containing phosphate of thorium, ferrous titanate and zircon with an al-

kali hydrate, then dissolving the resulting mass in water, and then recovering the phosphoric-acid radical from the solution.

4. The process which consists in treating a raw material containing phosphate of thorium, ferrous titanate and zircon with an alkali hydrate, then dissolving the resulting mass in water, then recovering the phosphoric-acid radical from the solution, then separating the remaining solution from the solid phosphate and then evaporating the said remaining solution.

5. The process which consists in treating a raw material containing phosphate of thorium, ferrous titanate and zircon with an alkali hydrate, then dissolving the resulting mass in water, then separating the phosphoric-acid radical from the solution, then separating the remaining solution from the solid phosphate and then evaporating the said remaining solution, and then separating the thorium oxid from the residue by washing.

6. The process which consists in comminuting monazite sand and immersing the same into molten alkali hydrate, then dissolving the resulting mass in hot water, then crystallizing out the resultant alkali phosphate, then evaporating the mother-liquor after removing the crystals, then adding water to the residue and stirring and decanting or otherwise removing the liquor containing the thorium oxid from the heavy sediment of ferrous titanate and zircon.

7. The process which consists in treating raw material containing the phosphates of thorium and of cerium bases, together with zircon and ferrous titanate with alkali hydrates, then dissolving the resulting mass in hot water, then recovering the phosphoric-acid radical from the solution, then evaporating the remaining solution, then mixing the residue with water and stirring and separating the resultant oxids of thorium and of the cerium bases from the zircon and the ferrous titanate and then treating the mixture containing the oxids of thorium and of the cerium bases with sulfurous acid, whereby the oxids of the cerium bases are dissolved out from the mixture.

8. The process which consists in treating raw materials containing the phosphates of thorium and of the cerium bases, together with zircon and ferrous titanate, with alkali hydrates then dissolving the resulting mass in hot water, then separating the phosphoric-acid radical from the solution, then evaporating the mother-liquor, then mixing the residue with water and stirring and separating the resultant oxids of thorium and of the cerium bases from the zircon and the ferrous titanate and then treating the mixture containing the oxids of thorium and of the cerium bases with an acid, whereby the oxids of the cerium bases are dissolved out from the mixture.

9. The process which consists in comminuting monazite sand and then immersing the

same into molten alkali hydrate, then dissolv-
ing the resulting mass in hot water, then crys-
tallizing out the resultant alkali phosphate,
then evaporating the mother-liquor after re-
5 moving the crystals, then adding water to the
residue and stirring and decanting or other-
wise removing the liquor containing the tho-
rium oxid from the heavy sediment of ferrous
titanate and zircon, and then treating the
10 mixture containing the thorium oxid with

sulfurous acid whereby the cerium bases are
dissolved out and a product containing only
the thorium oxid is obtained.

In testimony whereof I affix my signature
in presence of two witnesses.

WILHELM BUDDEUS.

Witnesses:

W. HAUPT,
HENRY HASPER.