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(54) Title: PROCESS FOR RECOVERING RARE EARTH OXIDE FROM WASTE LIQUID CONTAINING RARE EARTH ELEMENT, AND PROCESS FOR PRODUCING RARE EARTH OXIDE USING SAME

(57) Abstract: ABSTRACT Rare earth oxides capable of being re-used as an abrasive are recovered from an abrasive waste liquid by a process comprising the steps of (1) mixing and heating a rare earth element-containing waste liquid with an acid, to dissolve rare earth elements contained in the liquid; (2) removing insoluble matter from the rare earth element solution; (3) incorporating a soluble carbonate salt or a soluble hydrogencarbonate salt, or an oxalic acid in the rare earth element solution, to convert the rare earth elements to rare earth carbonates or rare earth oxalates; (4) separating the rare earth carbonates or rare earth oxalates from a slurry of the rare earth carbonates or rare earth oxalates; (5) baking the separated rare earth carbonate or rare earth oxalate to produce rare earth oxides; and (6) recovering the rare earth oxides.

DESCRIPTION

Process for Recovering Rare Earth Oxide from Waste Liquid Containing Rare Earth Element, and Process for Producing Rare Earth Oxide Using Same

CROSS-REFERENCE TO RELATED APPLICATION

This application is an application filed under 35 U.S.C. § 111(a) claiming benefit pursuant to 35 U.S.C. § 119(e)(1) of the filing dates of Provisional Application 60/410,285 filed September 13, 2002, and Provisional Application 60/416,577 filed October 8, 2002, pursuant to 35 U.S.C. § 111(b).

TECHNICAL FIELD

This invention relates to a process for recovering rare earth oxides from a waste liquid containing rare earth elements. More particularly, it relates to a process for recovering rare earth oxides from an abrasive waste liquid containing rare earth elements, wherein the recovered rare earth oxides have a high quality such that they can be used as an abrasive for high-precision polishing.

BACKGROUND ART

In recent years, an abrasive containing rare earth elements is being used in various fields. Particularly, a cerium-based abrasive is popularly used for polishing a glass material or a rock crystal material. More specifically, this abrasive is used for polishing a glass substrate for photodisc or magnetic disc, a glass plate for liquid crystal display (LCD) such as thin film transistor (TFT) LCD and twisted nematic (TN) LCD, a color filter for liquid crystal TV, a TV cathode-ray tube (CRT), a spectacle lens, an optical lens, a glass plate LSI photomask, a wired plate glass, and a substrate for quartz oscillator.

By the term "rare earth element-containing abrasive" as used herein is meant an abrasive containing powdery oxide of cerium (Ce), lanthanum (La), praseodymium (Pr), neodymium (Nd) or other rare earth elements.

The ore as a raw material of an abrasive containing rare earth elements is produced, for example, as bastnaesite or monazite in China, U.S.A. and other countries.

In the case of producing rare earth oxides from an ore containing rare earth elements, such as bastnaesite or monazite, the following steps (1) through (9) are usually performed:

(1) sulfuric acid is gradually added to and mixed with an ore in a rotary kiln and the ore is then dried;

(2) the ore is roasted by elevating the temperature to 500 to 600°C;

(3) the roasted ore is leached with water to elute a rare earth-containing material in the water;

(4) the obtained solution is concentrated by a thickener and impurities such as $BaSO_4$, $CaSO_4$ and SiO_2 to obtain $R_2(SO_4)_3$, wherein R represents a rare earth element;

(5) sodium sulfate is added to $R_2(SO_4)_3$ and Fe, Ca and phosphoric acid are separated by filtration to obtain a double sulfate of rare earth element;

(6) sodium hydroxide is added to the double salt of rare earth element to precipitate a hydroxide of rare earth element;

(7) hydrochloric acid is added to the hydroxide of rare earth element to produce a chloride of rare earth element;

(8) ammonium hydrogencarbonate is added to the chloride of rare earth element to produce a rare earth carbonate; and

(9) the rare earth chloride is baked to form a rare earth oxide.

The reserves of ore as a raw material for the rare earth element-containing abrasive are limited and in combination with recent increase of demand for the rare earth element-containing abrasive, the ore as a raw material is foreseen to run short. Therefore, it is eagerly desired to recover rare earth oxides from an abrasive waste liquid containing rare earth elements, for the reuse of rare earth oxides as an abrasive.

Also, in the field of an abrasive based on a rare earth oxide powder, it is required to polish a substrate with highly enhanced precision. For this requirement, there is an increasing demand for providing an abrasive characterized as containing extremely reduced amounts of coarse particles and foreign matter. However, it is difficult or even impossible to recover rare earth oxides from an abrasive waste liquid, which rare earth oxides have a high quality to an extent such that they are capable of being reused as an abrasive for polishing with high precision.

An abrasive, particularly a cerium-rich abrasive, is prepared by mixing a rare earth oxide such as cerium oxide with water, a dispersant, a surfactant and other ingredients to form a slurry, and is used for the polishing of glass, rock crystal or other materials. Accordingly, a rare earth element-containing abrasive waste liquid produced upon polishing contains at least abrasive, water, dispersant, surfactant, ground powders such as glass powder, and polishing pad powder. The rare earth element-containing abrasive waste liquid is different from a rare earth element-containing ore in many points in addition to the above-described difference, for example, these differ in the rare earth element content, the content ratio of each rare earth element, the kind of materials contained other than rare earth elements, and the content ratio of the materials. Therefore, it is difficult to treat these ore and abrasive waste liquid by the same method to obtain a rare earth oxide. Thus, it is very costly and of no practical utility to recover rare earth oxides having a high quality from an abrasive waste liquid, which rare earth oxides are capable of being reused as an abrasive for polishing with high precision.

Several proposals have been made for recovering a rare earth oxide powder for use as an abrasive from an abrasive waste liquid produced upon polishing using an abrasive containing rare earth elements.

For example, a method has been proposed wherein an abrasive waste liquid is washed with an aqueous alkali, and then, abrasive material such as a rare earth element for abrasive is sieved from foreign matter such as dust (for example, see Japanese Unexamined Patent Publication (hereinafter abbreviated to as "JP-A") H11-90825.

A process for recovering rare earth hydroxides from an abrasive waste liquid has been proposed, wherein the abrasive waste liquid is diluted with sulfuric acid, oxalic acid is added to convert rare earth elements in the liquid to rare earth oxalates, the liquid is then neutralized with an alkali to covert the rare earth oxalates to rare earth hydroxides, followed by recovery thereof (for example, see JP-A 2000-87154).

A method of recovering rare earth elements from an abrasive waste liquid containing the rare earth elements has been proposed, wherein ground glass powder or particles are dissolved with hydrofluoric acid to allow the rare earth element to be separated therefrom (for example, see JP-A H11-319755).

A method of recovering rare earth elements from an abrasive waste liquid containing the rare earth elements has also been proposed, wherein the abrasive waste liquid is subjected to a flocculation treatment and then to a solid-liquid separation (for example, see JP-A H10-280060).

It is to be noted, however, that foreign matter contained in an abrasive waste liquid cannot be removed by these heretofore proposed methods and processes to a desired extent such that a rare earth oxide recovered from the abrasive waste liquid is capable of being reused as an abrasive for polishing with high precision.

DISCLOSURE OF THE INVENTION

In view of the foregoing, a primary object of the present invention is to provide a process for recovering rare earth oxides from a liquid containing rare earth elements, especially from an abrasive waste liquid produced upon polishing using a rare earth oxide abrasive, whereby rare earth oxides capable of being reused as an abrasive for polishing with high precision can be obtained in an industrially advantageous manner.

As a result of extensive investigations to achieve the above-described object, the present inventors have found that rare earth oxides reusable as an abrasive for polishing with high precision can be obtained in an industrially advantageous manner from an abrasive waste liquid containing rare earth elements, by adopting a process comprising a specific combination of steps, for example, comprising the following steps (1) through (6): (1) mixing and heating a liquid containing a rare earth element with an acid, to dissolve the rare earth element contained in the liquid; (2) removing insoluble matter from a rare earth element solution obtained in step (1); (3) incorporating a soluble carbonate salt or a soluble hydrogencarbonate salt, or an oxalic acid in the rare earth element solution obtained in step (2), to convert the rare earth element in the solution to a rare earth carbonate or a rare earth oxalate; (4) separating the rare earth carbonate or rare earth oxalate from a slurry of the rare earth carbonate or rare earth oxalate, obtained in step (3); (5) baking the separated rare earth carbonate or rare earth oxalate to produce a rare earth oxide; and (6) recovering the rare earth oxide. The present invention has been completed based on this finding.

Thus, in accordance with the present invention, there are provided the following processes for recovering a rare earth element, process for producing or reusing an abrasive, and polishing process.

1. A process for recovering a rare earth oxide from a liquid containing a rare earth element, which comprises the following steps (1) through (6):

(1) mixing and heating a liquid containing a rare earth element with an acid, to dissolve the rare earth element contained in the liquid;

(2) removing insoluble matter from a rare earth element solution obtained in step (1);

(3) incorporating a soluble carbonate salt or a soluble hydrogencarbonate salt, or an oxalic acid in the rare earth element solution obtained in step (2), to convert the rare earth element in the solution to a rare earth carbonate or a rare earth oxalate;

(4) separating the rare earth carbonate or rare earth oxalate from a slurry of the rare earth carbonate or rare earth oxalate, obtained in step (3);

(5) baking the separated rare earth carbonate or rare earth oxalate to produce a rare earth oxide; and

(6) recovering the rare earth oxide.

2. The process according to preceding item 1, wherein, in step (1), the liquid containing a rare earth element and the acid are mixed and heated together with hydrogen peroxide, to dissolve the rare earth element contained in the liquid.

3. The process according to preceding item 1 or 2, wherein the acid in step (1) is hydrochloric acid.

4. The process according to preceding item 1 or 2, wherein the acid in step (1) is nitric acid.

5. The process according to any one of the preceding items 1 to 4, wherein, in step (1), a mixed liquid of the liquid containing a rare earth element with the acid is heated under reflux, and further concentrated whereby insoluble solid matter contained in the mixed liquid is allowed to float on the liquid surface.

6. The process according to preceding item 5, wherein

the mixed liquid is concentrated while bubbles are formed.

7. The process according to preceding item 6, wherein the mixed liquid is heated in the presence of a boiling stone to form bubbles.

8. The process according to preceding item 1, wherein, in step (2), the insoluble matter is removed by filtration.

9. The process according to preceding item 1, wherein, in step (3), pH value of the rare earth element solution is adjusted to a value in the range of 1 to 7, and then, the soluble carbonate salt or the soluble hydrogencarbonate salt, or oxalic acid is incorporated in the rare earth element solution to convert the rare earth element in the solution to a rare earth carbonate or a rare earth oxalate.

10. The process according to preceding item 9, wherein pH value of the rare earth element solution is adjusted to a value in the range of 1 to 7 by adding ammonia.

11. The process according to preceding item 1 or 9, wherein the soluble carbonate salt or the soluble hydrogencarbonate salt in step (3) is an alkali metal salt, an alkaline earth metal salt or an ammonium salt.

12. The process according to claim 1, wherein, in step (4), the rare earth carbonate or the rare earth oxalate is separated by filtration.

13. A process for recovering a rare earth hydroxide from a liquid containing a rare earth element, which comprises the following steps (i) through (vi):

(i) mixing and heating a liquid containing a rare earth element with sulfuric acid to convert the rare earth element contained in the liquid to a rare earth sulfate;

(ii) incorporating water with the rare earth sulfate to dissolve the rare earth sulfate;

(iii) removing insoluble matter from the thus-obtained rare earth sulfate solution;

(iv) incorporating sodium sulfate in the rare earth sulfate solution obtained in step (iii), to produce a double salt of the rare earth element; and then, separating the double salt from the solution;

(v) suspending the separated double salt in water, and then adjusting pH value of the thus-obtained aqueous double salt suspension to a value in the range of 8 to 13 to convert the double salt of rare earth element to a rare earth hydroxide; and then

(vi) separating the rare earth hydroxide for recovery.

14. The process according to preceding item 13, wherein, in step (iii), the insoluble matter is removed by filtration.

15. The process according to preceding item 13, wherein, in step (v), the adjustment of pH value of the aqueous double salt suspension to a value of 8 to 13 is carried out by adding an alkali, aqueous ammonia or ammonia gas.

16. The process according to preceding item 13, wherein, prior to mixing the liquid containing a rare earth element with sulfuric acid in step (i), aluminum sulfate, poly-aluminum chloride or a polymeric flocculant is added to the liquid containing a rare earth element to allow a solid content containing the rare earth element to precipitate; and then the thus-produced precipitate is separated, followed by mixing the thus-separated precipitate with sulfuric acid.

17. The process according to preceding item 13 or 16, wherein, after the mixing of the liquid containing a rare earth element with sulfuric acid in step (i), aqueous hydrogen peroxide is added to the thus-prepared mixed liquid.

18. A process for recovering a rare earth oxide, which comprises recovering a rare earth hydroxide from a liquid containing a rare earth element by the process as described in any one of preceding items 13 to 17; and then, baking the recovered rare earth hydroxide to convert to a rare earth oxide, followed by recovering the thus-obtained rare earth oxide.

19. A process for recovering a rare earth oxide, which

comprises recovering a rare earth hydroxide from a liquid containing a rare earth element by the process as described in any one of preceding items 13 to 17; suspending the recovered rare earth hydroxide in water; and then, recovering a rare earth oxide from the thus-obtained aqueous suspension of rare earth hydroxide by the process as described in any one of preceding items 1 to 12.

20. The process according to any one of the preceding items 1 to 19, wherein the liquid containing a rare earth element is a waste liquid produced when an abrasive is used for polishing.

21. A process for producing an abrasive containing a rare earth oxide, which comprises recovering a rare earth oxide by the process as described in any one of the preceding items 1 to 20; and fabricating the recovered rare earth oxide into an abrasive.

22. A process for reusing an abrasive containing a rare earth oxide for polishing which comprises recovering a rare earth oxide from a waste liquid produced upon polishing using an abrasive, by the process as described in any one of preceding items 1 to 20; and fabricating the recovered rare earth oxide into an abrasive.

23. A method for polishing a substrate by an abrasive containing a rare earth oxide wherein said abrasive is made from a rare earth oxide, which is recovered from a waste liquid produced upon polishing using an abrasive, by the process as described in any one of preceding items 1 to 20.

BEST MODE FOR CARRYING OUT THE INVENTION

The invention will now be described with particular reference to the following process for recovering rare earth oxides with high quality from an abrasive waste liquid as a typical example of a rare earth element-containing liquid.

According to the recovering process of the present invention, plural kinds of rare earth oxides are usually obtained from an abrasive waste liquid containing plural kinds of rare earth elements. However, rare earth oxides containing an extremely large proportion of a specific rare earth element (for example, cerium) can be obtained from an abrasive waste liquid containing an extremely large proportion of the specific rare earth element. The relative amounts of rare earth elements in the starting waste liquid and the recovered rare earth oxides are not particularly limited.

The recovering process of the present invention comprises the following steps (1) through (6).

Step (1) (step for dissolving rare earth element in waste liquid to prepare solution of rare earth element)

A reaction vessel is charged with an abrasive waste liquid containing rare earth elements, and an acid or a combination of an acid with hydrogen peroxide is added to the abrasive waste liquid, and the mixture is heated.

The acid as used herein is not particularly limited provided that it is capable of dissolving the rare earth elements contained in the abrasive waste liquid. As preferable examples of the acid, there can be mentioned hydrochloric acid, nitric acid and sulfuric acid. Of these, hydrochloric acid and nitric acid are more preferable. Hydrochloric acid is especially preferable.

The heating is carried out to an extent such that at least rare earth elements (which are usually in the form of rare earth oxide) contained in the waste liquid are thoroughly dissolved. For example, in the case when hydrochloric acid is used as the acid, the heating is preferably carried out at a temperature in the range of 90°C to 120°C. More preferably, the heating is carried out at a temperature in the range of 90°C to 120°C for a period of 5 hours to 72 hours while being stirred under reflux, and then, the mixture is concentrated.

The concentration of hydrochloric acid used is not particularly limited, but is usually in the range of 15% to 45% by mass, preferably 20% to 35% by mass. For example, hydrochloric acid with a concentration of 35% by mass can preferably be used. The amount of hydrochloric acid is preferably in the range of 200 parts to 500 parts by mass, as hydrochloric acid with a concentration of 35% by mass, based on 100 parts by mass of the solid content in the abrasive waste liquid.

The concentration of nitric acid used also is not particularly limited, but is preferably in the range of 62% to 98% by mass. The amount of nitric acid is preferably in the range of 112 parts to 177 parts by mass based on 100 parts by mass of the solid content in the abrasive waste liquid.

In the case when an acid having a low reducing power such as nitric acid or sulfuric acid is used, a reducing substance such as hydrogen peroxide is preferably used in combination with the acid for suppressing oxidation of rare earth element and lowering the valency of rare earth nitrate or rare earth sulfate to a desired extent for enhancing the solubility of these rare earth salts. The addition of hydrogen peroxide is advantageous also in that organic substances contained in the abrasive waste liquid are decomposed and easily removed. For example, in the case when nitric acid is used, the amount of hydrogen peroxide is preferably in the range of 9 parts to 27 parts by mass based on 100 parts by mass of nitric acid. Even when hydrochloric acid is used, hydrogen peroxide may be used so that organic substances contained in the abrasive waste liquid are decomposed and easily removed.

By mixing and heating the abrasive waste liquid with an acid and optional hydrogen peroxide, a rare earth oxide contained in the liquid is dissolved to form an aqueous acidic solution containing a rare earth element which is in the form of, for example, a rare earth chloride or a rare earth nitrate. The glass powder or particles remaining in the abrasive waste liquid is converted to silica sol, which is gradually gelled into silica gel.

The silica gel, powdery or finely divided debris of polishing pad, and other undissolved matter can be separated by filtration of the heated mixture of the abrasive waste liquid with an acid. But, the undissolved matter contains part of the aqueous acidic solution entrapped therein which is not easily separated by filtration. Therefore, the heating is followed by concentration as described below.

When the aqueous acidic solution containing rare earth elements is heated and further concentrated, the concentration (thus, specific gravity) of the solution is enhanced, and hence, relative weight of silica gel is reduced with the results that the silica gel is floated together with the undissolved matter on the surface of liquid. Therefore, the aqueous acidic solution can easily be separated in the succeeding separation step (2).

When the aqueous acid solution is further heated and concentrated, the liquid surface is lowered and thus the floated silica gel and undissolved matter are deposited on the inner wall of the reaction vessel. When the amount of the silica gel and undissolved matter is large relatively to the area of the inner surface of reaction vessel, the effective inner surface area may be increased, for example, by providing partition plates within the reaction vessel.

When the temperature is further elevated, the deposited silica gel and undissolved matter are shrunk in volume whereby the aqueous acidic solution containing rare earth element, entrapped within the silica gel and undissolved matter, is released therefrom. Therefore the temperarture of the inner wall of reaction vessel and the partition plates is preferably maintained at a temperature higher than the liquid temperature so that the shrinking of the silica gel and undissolved matter easily occurs.

Preferably, the aqueous acidic solution is concentrated until its volume is reduced to about 25% to 75%, more preferably about 40% to 60%, of the initial volume before heating. By the heating and concentration, the rare earth-containing aqueous acidic solution can be separated from the silica gel and undissolved matter with an enhanced recovery ratio in the succeeding separation step (2).

When the aqueous acidic solution containing rare earth elements is concentrated under heating, bubbles are preferably formed. More preferably fine and uniform bubbles are formed. For example, when boiling stones are placed in the reaction vessel, fine and uniform bubbles rise vigorously from the boiling stones to the liquid surface in accompanied by the silica gel and undissolved matter. The formation of such bubbles enhances the separation of the aqueous acidic solution containing rare earth elements, from the silica gel and undissolved matter in step (2).

The boiling stone can be selected from those composed of material insoluble in the heated aqueous acidic solution, which includes, for example, ceramics such as glass, and a plastic material. Preferably the boiling stone has a configuration such that small projections are formed on the surface thereof for promoting formation of a multiplicity of fine bubbles.

Step (2) (step for separating rare earth element-containing aqueous acidic solution)

The rare earth element-containing aqueous acidic solution is taken from the reaction vessel and subjected to separation for removing the silica gel and undissolved matter such as polishing pad debris. No limitation is imposed to a separating procedure, but, filtration or centrifugal separation can be adopted. Filtration is preferable because of ease in operation. Thus, a rare earth element-containing aqueous acidic solution from which silica gel and undissolved matter have been removed is obtained in step (2).

Step (3) (step for forming rare earth carbonate or rare earth oxalate from rare earth element-containing aqueous acidic solution)

To the aqueous acidic solution containing rare earth elements, a soluble carbonate salt or a soluble hydrogencarbonate salt, or oxalic acid is added to convert the rare earth elements in the solution to rare earth carbonates or rare earth oxalates.

The soluble carbonate salt and the soluble hydrogencarbonate salt include those which are soluble in the aqueous acidic solution, and are preferably selected from alkali metal salts, alkaline earth metal salts and ammonium salts. As examples of the alkali metal, sodium, potassium and lithium are mentioned. Of these, sodium and potassium are preferable. As examples of the alkaline earth metal, calcium, strontium and barium are mentioned. Among the carbonate salts and hydrogencarbonate salts of alkali metals, alkaline earth metals and ammonium, sodium hydrogencarbonate and potassium hydrogencarbonate are preferable, and ammonium hydrogencarbonate is especially preferable.

If desired, prior to incorporation of the carbonate salt, hydrogencarbonate salt, or oxalic acid, the aqueous acidic solution containing rare earth elements can be diluted with water to control size of the resulting particles. The larger the extent to which the solution is diluted, the larger the particle diameter.

Preferably the pH value of the aqueous acidic solution containing rare earth elements is adjusted to 1 to 7, more preferably 1 to 3, and then, ammonium hydrogencarbonate or oxalic acid is added. The pH value can be adjusted by adding an alkali such as aqueous ammonia, sodium hydroxide, potassium hydroxide or calcium hydroxide. Of these, aqueous ammonia is preferable because it can be easily removed. The amount of alkali is not particularly limited provided that the desired pH value is obtained. For example, in the case when aqueous ammonia is used, its amount is usually in the range of 5% to 28% by mass.

The carbonate salt or hydrogencarbonate salt of an alkali metal, an alkaline earth metal or ammonium can be added in the form of either solid or an aqueous solution, but an aqueous solution is preferable.

The concentration of these carbonate salt and hydrogencarbonate salt, and oxalic acid is not particularly limited and can be appropriately determined usually in the range of 5% to 97% by mass.

The amounts of the carbonate salt and hydrogencarbonate salt of an alkali metal, alkaline earth metal and ammonium, and oxalic acid are preferably in the range of 193 parts to 540 parts by mass based on 100 parts by weight of rare earth element.

By the incorporation of the carbonate salt or hydrogencarbonate salt, or oxalic acid, an aqueous slurry of rare earth carbonate or an aqueous slurry of rare earth oxalate is formed from the aqueous acidic solution containing rare earth elements.

Step (4) (step for forming separating rare earth carbonate or rare earth oxalate)

An aqueous slurry of rare earth carbonate or an aqueous slurry of rare earth oxalate, formed in step (3), is subjected to separation, for example, by filtration, whereby the rare earth carbonate or rare earth oxalate is separated. If desired, the separated rare earth carbonate or rare earth oxalate is washed with water and again filtered.

Step (5) (step for baking separated rare earth carbonate or rare earth oxalate)

The separated rare earth carbonate or rare earth oxalate is baked into rare earth oxide.

The baking is carried out by maintaining the rare earth carbonate or rare earth oxalate in the air atmosphere at a temperature of 600 to 1,200°C, preferably 800 to 1,100°C for 0.5 to 3 hours, preferably 0.5 to 2 hours. The baking apparatus used may be conventional baking furnaces such as a cube type furnace, a rotary furnace and a tunnel furnace.

Step (6) (step for recovering rare earth oxides)

The rare earth oxide obtained by baking is recovered, pulverized and classified depending upon the particle diameter and particle size distribution. Thus, the rare earth oxide is reused as an abrasive for precision polishing. The particle diameter may be either the same as or different from that of the abrasive as originally used. The average particle diameter can be in the range of 0.1 to 2 μm.

By the above-described recovering process, rare earth oxides with high quality capable of being reused as an abrasive for polishing with high precision can be obtained. But, a pretreatment process can be carried out prior to the above-described recovering process. More specifically, a pretreatment process comprising the following steps (i) through (vi) can be carried out to obtain an aqueous slurry containing rare earth hydroxide, and subsequently, the above-described recovering process comprising the steps (1) through (6) can be carried out wherein, in step (1), the aqueous slurry containing rare earth hydroxide is used as the starting liquid containing a rare earth element.

The pretreatment process comprises the following steps (i) through (vi):

(i) mixing and heating a liquid containing rare earth elements with sulfuric acid to convert the rare earth elements contained in the liquid to rare earth sulfates;

(ii) incorporating water with the rare earth sulfates to dissolve the rare earth sulfates;

(iii) removing insoluble matter from the thus-obtained rare earth sulfate solution;

(iv) incorporating sodium sulfate in the rare earth sulfate solution obtained in step (iii), to produce a double salt of the rare earth element; and then, separating the double salt from the solution;

(v) suspending the separated double salt in water, and then adjusting pH value of the thus-obtained aqueous double salt suspension to a value in the range of 8 to 13 to convert the double salt of rare earth element to rare earth hydroxide; and then

(vi) separating the rare earth hydroxide for recovery.

Step (i) (step for converting rare earth element in waste liquid to rare earth sulfate)

Sulfuric acid is added to an abrasive waste liquid containing rare earth elements, and the mixture is heated.

The concentration of sulfuric acid is not particularly limited. For example, concentrated sulfuric acid having a concentration of 95% to 99% by mass is used. The amount of sulfuric acid is preferably in the range of 80 parts to 450 parts by mass based on 100 parts by mass of the solid content in the abrasive waste liquid.

The heating is carried out usually at a temperature of 90 to 120°C for 10 minutes to 1 hour.

Hydrogen peroxide can be added to the mixture of the abrasive waste liquid and sulfuric acid to decompose organic matter such as polishing pad debris so that free carbon resulting from the decomposition can be removed as carbon dioxide gas. Then, the hydrogen peroxide-added mixed liquid is re-heated at a temperature of 200 to 600°C for 1 minute to 1 hour thereby converting rare earth element in the liquid to a rare earth sulfate.

Preferably the rare earth sulfate is separated from the rare earth sulfate-containing liquid, for example, by filtration or decantation.

Step (ii) (step for adding water to rare earth sulfate to dissolve rare earth sulfate)

Water is added to the separated rare earth sulfate or the rare earth sulfate-containing liquid to thereby dissolve or dilute the rare earth sulfate. By dissolving or diluting the rare earth sulfate, glass powder or particles and polishing pad debris and other insoluble matter can be removed at enhanced efficiency in the succeeding step (iii).

The amount of water added is usually in the range of 525 parts to 1,900 parts by mass based on 100 parts by mass of the solid content of rare earth sulfate.

Step (iii) (step for removing insoluble matter from rare earth sulfate-containing solution)

The rare earth sulfate-containing solution is subjected to separation, for example, by filtration to remove glass particles and polishing pad debris and other insoluble matter from the solution.

Step (iv) (step for adding sodium sulfate to rare earth sulfate-containing solution to form double salt of rare earth element)

After the rare earth sulfate-containing solution is subjected to separation for removing insoluble matter therefrom in step (iii), sodium sulfate is added to the solution (e.g., filtrate) to form a double salt of rare earth element.

Sodium sulfate can be added either as solid or an aqueous solution. That is, solid sodium sulfate or its aqueous solution with a concentration of 5% to 100% by mass is added in an amount of 1.25 parts to 95 parts by mass, preferably 12.5 parts to 80 parts by mass, based on 100 parts by mass of the rare earth sulfate-containing solution. Thus, a slurry of a double salt of rare earth element, for example, $R_2(SO_4)_3\cdot Na_2SO_4\cdot 2H_2O$ (R is an rare earth element), is obtained.

The slurry is subjected to separation, for example, by filtration, to thereby obtain the double salt of rare earth element.

Step (v) (step for adding alkali to double salt of rare earth element to convert double salt to rare earth hydroxide)

Water is added to the double salt obtained in step (iv), and then the pH value of the double salt solution is adjusted to a value in the range of 8 to 13, preferably 12 to 13, whereby the double salt is converted to a rare earth hydroxide. The pH adjustment is effected by adding an alkali, aqueous ammonia or ammonia gas. A rare earth hydroxide formed by the pH adjustment is highly soluble and thus it can be recovered at a high yield in the succeeding step (vi).

The alkali includes, for example, sodium hydroxide and potassium hydroxide. The alkali may be used either as solid or as an aqueous solution. Preferably an aqueous alkali solution having a concentration of 10% to 95% by mass is added in an amount of 33 parts to 322 parts by mass based on 100 parts by mass of the double salt. The amount of aqueous ammonia or ammonia gas is usually in the range of 3 parts to 30 parts by mass, as ammonia (NH_3), based on 100 parts by mass of the double salt.

Step (vi) (step of recovering rare earth hydroxide)

The rare earth hydroxide-containing solution obtained in step (v) is subjected to separation, for example, by filtration, whereby rare earth hydroxide is recovered. The recovered rare earth hydroxide is suspended in water to prepare a slurry.

The thus-obtained rare earth hydroxide-containing slurry can be subjected to the above-mentioned process comprising steps (1) through (6) wherein, in step (1), the rare earth hydroxide-containing slurry is used as the starting liquid containing a rare earth element.

As a modified embodiment, the rare earth hydroxide recovered in step (vi) can be baked at a temperature of 600 to 1,400°C in the air atmosphere to obtain rare earth oxide. This rare earth oxide can be re-used as an abrasive, but its quality is somewhat inferior to the rare earth oxide obtained by further treating the rare earth hydroxide by the process comprising steps (1) through (6).

In the above-mentioned step (i), if desired, prior to mixing the liquid containing a rare earth element with sulfuric acid, aluminum sulfate, poly-aluminum chloride or a polymeric flocculant can be added to the liquid containing a rare earth element to allow the solid content containing the rare earth element to precipitate; and then the thus-produced precipitate is separated, followed by mixing the thus-separated precipitate with sulfuric acid.

The aluminum sulfate and poly-aluminum chloride can be used either as solid or an aqueous solution. The polymeric flocculant used is commercially available and includes, for example, Kurifloc™ (Kurita Water Industries Ltd.) and Orfloc™ (Organo Corporation).

The rare earth oxides recovered by the process comprising the steps (1) through (6) are pulverized and classified into particles having desired particle size and particle size distribution, and re-used as an abrasive used for polishing with high precision.

Examples

The invention will now be described specifically by the following examples that by no means limit the scope of the invention.

Example 1 (Recovery of rare earth oxides from abrasive waste liquid)

Rare earth oxides were recovered by the following procedures from an abrasive waste liquid having a solid composition shown in Table 1, which liquid was produced when a glass disc was polished.

To 1 liter of the abrasive waste liquid, 38 g of an aqueous aluminum sulfate solution having a concentration of 20% by mass and 0.2 g of a polymeric flocculant (Kurifloc™; available from Kurita Water Industries Ltd.) were added and mixed to aggregate and precipitate solid contents. The precipitate was separated and recovered.

Then, 100 g of the recovered solid was placed in a beaker containing 262 g of concentrated sulfuric acid having a concentration of 95% by mass, and the mixture was stirred for 5 minutes. The beaker was heated to 100°C and the organic materials were decomposed by the dehydrating action of hot sulfuric acid to give a black liquid. Thereto, 20 g of aqueous hydrogen peroxide was added dropwise whereby free carbons were removed as carbon dioxide gas. By such a treatment, the organic materials contained in the abrasive waste liquid containing rare earth elements were removed.

The beaker was again heated at 300°C to produce rare earth sulfate as a yellow solid. This rare earth sulfate was dissolved in cold water at 5°C to obtain a brown transparent acidic aqueous sulfate solution. This acidic aqueous sulfate solution containing rare earth sulfate was filtered to remove undissolved matter such as glass debris. By this treatment, carbide and the like were also removed as undissolved matter.

Subsequently, 413 g of an aqueous Na_2SO_4 solution having a concentration of 10% by mass was added to the filtrate and stirred to produce a double salt. This double salt was recovered by filtration and formed into a slurry by adding 1,500 g of pure water. Thereafter, 851 g of an aqueous sodium hydroxide solution having a concentration of 20% by mass was added, and the mixture was stirred to obtain a basic rare earth hydroxide slurry. This rare earth hydroxide slurry was filtered, and about 110 g of rare earth hydroxide was recovered as a solid. At this treatment, the pH value was 11.7.

The recovered solid and 1,500 g of pure water were mixed together to form a slurry, the slurry was heated to 95°C. 182 g of aqueous hydrochloric acid having a concentration of 35% by mass was added to the slurry to dissolve the solid, thereby obtaining an aqueous rare earth chloride solution. The aqueous rare earth chloride solution was obtained as a yellow or green transparent solution. This aqueous rare earth chloride solution was filtered to remove undissolved matter. To the resulting aqueous rare earth chloride solution, 1,653 g of an aqueous ammonium hydrogencarbonate solution having a concentration of 10% by mass was added and stirred to obtain a rare earth carbonate as a white precipitate. This precipitate was filtered and washed. The obtained solid was placed in a porcelain container and baked at 1,000°C for 1 hour in the air atmosphere to obtain 93 g of rare earth oxides.

The composition of the recovered material obtained as rare earth oxide is shown in Table 1.

Example 2 (Recovery of rare earth oxides from abrasive waste liquid)

Powdery rare earth oxides were recovered by the following procedures from an abrasive waste liquid having a solid composition shown in Table 1, which liquid was produced when a glass filter was polished.

In an SUS beaker containing 245 g of aqueous sulfuric acid having a concentration of 98% by mass, 100 g of the recovered powder was charged, and the mixture was stirred with an SUS spatula. Thereafter, the beaker was covered with a watch glass, placed on a heater, heated at 600 W for 30 minutes, and then allowed to cool.

The obtained yellow solid (rare earth sulfate) was placed in a mortar and cracked with a pestle. Separately, 1 liter of cold water was charged in a beaker surrounded by ice water, and stirred. To this ice water, the cracked material obtained above was gradually added and mixed to obtain an aqueous acidic sulfate solution (brown transparent solution) containing rare earth sulfate. This aqueous acidic sulfate solution containing rare earth sulfate was filtered using a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.) and the filtrate was recovered.

To the filtrate, 276 g of an aqueous sodium sulfate solution having a concentration of 15% by mass was added and stirred. Furthermore, about 769 g of an aqueous sodium hydroxide solution having a concentration of 20% by mass was added and stirred to adjust the pH to 6 thereby producing a double salt. This double salt was filtered through a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.) and about 217 g of a solid content was recovered in a beaker. To the recovered solid content, water was added and stirred to obtain about 1.5 liter of a slurry. To this slurry, 20% by mass of an aqueous sodium hydroxide solution was added and stirred to adjust the pH to 12 to give a rare earth hydroxide slurry. The rare earth hydroxide slurry was filtered through a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.) and about 120 g of a solid content was recovered.

Thereafter, water was added to the recovered solid to give 1 liter of a slurry, and, while being stirred, the slurry was heated to have a liquid temperature of 95°C. To this solution, 182 g of aqueous hydrochloric acid having a concentration of 35% by mass was added and then 21 g of aqueous hydrogen peroxide having a concentration of 30% by mass was added to dissolve the solid content, thereby obtaining a yellow or green transparent aqueous rare earth chloride solution.

This solution was filtered through a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.) and the filtrate was recovered in a beaker. While the recovered filtrate was stirred, aqueous ammonia having a concentration of 5% by mass was added dropwise to adjust the pH to 1 to 2. To this solution, 833 g of an aqueous ammonium hydrogencarbonate solution having a concentration of 20% by mass was added and stirred to give a rare earth carbonate slurry.

The obtained rare earth carbonate slurry was filtered through a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.) and about 197 g of a solid content was recovered. To the recovered solid content, 1.5 liter of pure water was added, and stirred. Then, the resulting solution was filtered through a filter paper (No. 5C, available from Toyo Roshi Kaisha, Ltd.), and the solid content was recovered. This operation was repeated until a neutral slurry having a pH value of 6 to 8 was obtained.

The recovered solid content was baked at 1,000°C for 1 hour in the air atmosphere to obtain about 95 g of rare earth oxides. The composition of the recovered material obtained as rare earth oxide is shown in Table 1.

Example 3 (Recovery of rare earth oxides from abrasive waste liquid)

Rare earth oxides were recovered by the following procedures from an abrasive waste liquid having a solid composition shown in Table 1, which liquid was produced when a glass substrate for hard disc was polished.

0.5 liter of a abrasive waste liquid having a solid content of 100 g and 250 g of aqueous hydrochloric acid having a concentration of 35% by mass were placed in a flask provided with a water-cooling tube. The content was heated and maintained at a temperature of 103°C. The vapor emitted by heating was cooled by the water-cooling tube, and returned to the flask so that the liquid surface is not lowered. When the content was heated for 48 hours, the abrasive waste liquid became a mixed liquid composed of a green aqueous acidic solution containing rare earth chloride, a white silica gel, and undissolved matter such as polishing pad debris.

The water-cooling tube was removed from the flask, and the mixed liquid was heated and concentrated to about a half in volume. By the heating, the silica gel and undissolved matter were floated on the liquid surface. Thereafter, the concentrated mixed liquid was taken from the flask, and filtered through a filter paper (No. 5C, available from Advantec Toyo Kaisha, Ltd.), whereby undissolved matter was separated and removed from the rare earth chloride-containing aqueous acidic solution.

By the heating and concentration, most of the silica gel was removed from the rare earth chloride-containing aqueous acidic solution, and hence, as compared with the case where the heating and concentration were not carried out, the time required for filtration using a filter paper was drastically reduced from about 1 hour to about 10 minutes. Further, a rare earth element-containing aqueous acidic solution entrapped in the silica gel was removed by the heating and concentration, and hence, the yield of the rare earth chloride-containing aqueous acidic solution was increased from 82% to 98%, as expressed by the amount of final rare earth oxides, as compared with the case where the heating and concentration were not carried out.

The vapor emitted upon during the heating and concentration was introduced into the flask provided with the water-cooling tube where the vapor was liquefied and recovered as hydrochloric acid. This hydrochloric acid can be re-used as a raw material.

The above-mentioned rare earth chloride-containing aqueous acidic solution recovered by filtration was diluted with water into a volume of 1 liter. To this solution, 1,653 g of an aqueous ammonium hydrogencarbonate solution having a concentration of 10% by mass was added, and the mixture was stirred to give a white precipitate of rare earth carbonate.

The aqueous solution containing the rare earth carbonate precipitate was filtered through a filter paper (No. 5C, available from Advantec Toyo Kaisha, Ltd.), and the thus-separated precipitate was washed with water.

The obtained precipitate was placed in a porcelain container and baked at 1,000°C for 1 hour in the air atmosphere to obtain 98 g of rare earth oxides.

The composition of the recovered material obtained as rare earth oxides is shown in Table 1.

Example 4 (Recovery of rare earth oxides from abrasive waste liquid)

Rare earth oxides were recovered by the following procedures from an abrasive waste liquid having a solid composition shown in Table 1, which liquid was produced when a glass substrate for liquid crystal display (LCD) was polished.

0.5 liter of a abrasive waste liquid having a solid content of 100 g and 250 g of aqueous hydrochloric acid having a concentration of 35% by mass were placed in a flask provided with a water-cooling tube. The content was heated and maintained at a temperature of 103°C. When the content was heated for 48 hours, the abrasive waste liquid became a mixed liquid composed of a green aqueous acidic solution containing rare earth chloride, a white silica gel, and undissolved matter such as polishing pad debris.

The water-cooling tube was removed from the flask. A boiling stone was placed in the mixed liquid, and the mixed liquid was heated and concentrated to about a half in volume. By the heating, fine and uniform bubbles were formed from the boiling stone and floated on the liquid surface, in accompanied by the silica gel and undissolved matter. The silica gel and undissolved matter were transferred to the inner wall of flask, and deposited on the inner wall by the lowering of the liquid surface due to evaporation. The silica gel deposited on the inner wall was further heated by the hot inner wall, and hence, was shrunk in volume whereby the rare earth chloride-containing aqueous acidic solution entrapped in the silica gel was released therefrom.

It is to be noted that, when the heating and concentration were not conducted, the yield of the rare earth chloride-containing aqueous acidic solution was 73%, as expressed by the amount of final rare earth oxides. In contrast, the yield of the rare earth chloride-containing aqueous acidic solution was increased to 95% by the heating.

Thereafter, the concentrated mixed liquid was filtered through a filter paper (No. 5C, available from Advantec Toyo Kaisha, Ltd.), whereby undissolved matter was separated and removed from the rare earth chloride-containing aqueous acidic solution.

By the heating and concentration, most of the silica gel was removed from the rare earth chloride-containing aqueous acidic solution, and hence, the time required for filtration using a filter paper was drastically reduced from about 3 hour to about 10 minutes, as compared with the case where the heating and concentration were not carried out.

The above-mentioned rare earth chloride-containing aqueous acidic solution was diluted with water into a volume of 2 liters. To this solution, 450 g of an aqueous oxalic acid solution having a concentration of 10% by mass was added, and the mixture was stirred to give a white precipitate of rare earth carbonate.

The aqueous solution containing the rare earth carbonate precipitate was filtered through a filter paper (No. 5C, available from Advantec Toyo Kaisha, Ltd.), and the thus-separated precipitate was washed with water.

The thus-obtained precipitate was placed in a porcelain container and baked at 1,000°C for 1 hour in the air atmosphere to obtain 95 g of rare earth oxides.

The composition of the recovered material obtained as rare earth oxides is shown in Table 1.

Example 5 (Recovery of rare earth oxides from abrasive waste liquid)

The procedures for recovering rare earth oxides described in Example 3 were repeated wherein the rare earth chloride-containing aqueous acidic solution was treated with an aqueous sodium hydrogencarbonate solution instead of an aqueous ammonium hydrogencarbonate solution as follows.

The rare earth chloride-containing aqueous acidic solution, prepared in the same manner as in Example 3, was diluted with water into a volume of 1 liter. To this solution, 1,098 g of an aqueous sodium hydrogencarbonate solution having a concentration of 10% by mass was added, and the mixture was stirred to give a white precipitate of rare earth carbonate.

The aqueous solution containing the rare earth carbonate precipitate was filtered through a filter paper (No. 5C, available from Advantec Toyo Kaisha, Ltd.), and the thus-separated precipitate was washed with water.

The obtained precipitate was placed in a porcelain container and baked at 1,000°C for 1 hour in the air atmosphere to obtain 92 g of rare earth oxides.

The composition of the recovered material obtained as rare earth oxides is shown in Table 1.

Example 6 (Re-use of recovered rare earth oxide abrasive)

Using the material obtained as rare earth oxides in Example 5, an abrasive was made and its polishing performance was evaluated as follows.

(i) Water was added to 5 kg of the rare earth oxides obtained in Example 5, to prepare a slurry having a concentration of 50% by mass. Further, 150 g of a dispersant [poly(sodium acrylate)] was added to the slurry and mixed by a high-dispersion apparatus (ULTRA-TURRAX^{TM}, T50basic, available from IKA Werke GmbH & Co. KG) to prepare a uniform slurry.

(ii) The uniform slurry was subjected to wet grinding using a beads-mill, and classified by a wet shaker tube to obtain a slurry for use as an abrasive.

A fraction of slurry containing coarse particles and a fraction of slurry containing fine particles were obtained each in a small amount by the classification. The former slurry fraction was again subjected to wet grinding, and the latter slurry fraction was mixed with an abrasive waste liquid for re-use as an abrasive.

(iii) Using the slurry for use as an abrasive, prepared in (ii) above, a glass disc was polished, and an abrasive waste liquid was collected. The solid content of the abrasive waste liquid was 10% by mass due to washing water used during polishing.

(iv) The abrasive waste liquid was placed in a polyethylene vessel, and, while the liquid was stirred, aqueous hydrochloride having a concentration of 35% by mass was thereto to adjust the pH vale to 5. After the stirring was stopped, the thus-obtained slurry was allowed to settle. The supernatant of liquid was removed to obtain a slurry having a concentration of 28% by mass.

(v) A 20 liter glass separable flask was charged with 3.5 kg of the slurry obtained in (iv) above, and then, 8.4 kg of aqueous hydrochloride having a concentration of 20%

by mass was added thereto.

(vi) The separable flask was fitted with a three-necked separable flask cover provided with a water-cooling tube, a rod thermometer and a two-way cock, and then, placed in a mantle heater to be thereby heated. The vapor emitted was condensed in the water-cooling tube and returned to the separable flask.

(vii) The content in the flask was maintained at 120°C for three hours, the two-way cock was connected through a tube to a 10 liter flask provided with a water-cooling tube. After the water-cooling tube of the 20 liter separable flask was closed, the two-way cock was opened to introduce vapor into the 10 liter flask provided with the water-cooling tube where the vapor was cooled and excessive hydrochloric acid was collected. The collected hydrochloric acid was re-used for another process for recovering rare earth oxides.

(viii) By the procedures described in (vii) above, a rare earth chloride-containing aqueous acidic solution in the 20 liter separable flask was concentrated, and silica gel and undissolved matter were floated on the liquid surface and deposited on the inner wall of flask.

(ix) After the heating of mantle heater was stopped, the rod thermometer was removed, and a glass tube was inserted to the bottom of separable flask. The rare earth chloride-containing aqueous acidic solution was suctioned for recovery.

(x) The procedures described above in (v) through (ix) were repeated, and the obtained rare earth chloride-containing aqueous acidic solution was filtered. Ammonium hydrogencarbonate was added to the thus-obtained filtrate to obtain a rare earth carbonate slurry. The rare earth carbonate slurry was subjected to solid-liquid separation by a centrifugal dehydrator to obtain a solid of rare earth carbonate. The rare earth carbonate was baked to obtain rare earth oxides. The composition of recovered material obtained as rare earth oxides is shown in Table 1.

Table 1

Ingredients	Na_2O	SO_3	SiO_2	Al_2O_3	Cl	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Glass debris
Ex.1 Raw material	1.2	0.30	4.9	0.40	0.20	30.4	59.4	3.5	0.2	—
Rcd material	<0.1	0.01	0.5	0.30	0.01	30.1	58.2	3.5	0.2	0
Ex.2 Raw material	0	0.08	0	0.04	0.08	31.1	60.6	4.7	0	—
Rcd material	0	0.01	0	0.01	0.01	30.7	60.6	4.5	0	0
Ex.3 Raw material	0	0.10	0.74	0.30	0.05	30.8	59.2	4.1	0	—
Rcd material	0	0.07	0.03	0.28	0.11	27.7	62.1	5.2	0	0
Ex.4 Raw material	0	0.09	3.59	0.23	0.05	29.1	56.0	4.2	1.7	Several debris
Rcd material	0	0.07	0.03	0.14	0.01	31.4	59.7	4.0	0	—
Ex.5 Raw material	0	0.05	0.74	0.32	0.05	30.8	59.2	4.1	0	—
Rcd material	0	0.04	0.03	0.10	0.15	26.8	63.0	5.2	0	0
Ex.6 Raw material	0.03	0.10	0.54	0.18	0.10	30.8	59.5	4.6	0.06	—
Rcd material	0	0.18	0.07	0.25	0.18	26.0	64.0	5.4	0.09	0
Comp.Ex.1	0.03	0.08	0.01	0.03	0.07	31.6	58.8	4.8	0	—

Note, Ex.: Example, Comp.Ex.: Comparative Example

Raw material: Solid content in abrasive waste liquid used

Rcd material: Recovered material

Each element was measured by fluorescent X-ray analysis and its amount was expressed as amount of oxide except for Cl

Note, an abrasive in Comparative Example 1 in Table 1 was used for polishing a glass substrate for hard disc to produce an abrasive waste liquid, from which rare earth oxide was recovered in Example 3.

Example 7 (Polishing test)

Using each of the abrasives prepared in Example 5 and Example 6, and the abrasive used for polishing a glass substrate for hard disc in Example 3, an abrasive slurry was prepared by the same procedures as described in Example 6, paragraphs (i) and (ii).

Polishing of a glass substrate was conducted by using the abrasive slurry. A four-way type double side polishing machine (5B Type available from Fujikoshi Machinery Corp.), and a suede-type polishing pad (Politex DG, available from Rodel, Inc.) were used. The feed rate of slurry was 60 ml/min, the revolution speed of under surface plate was 90 rpm, the polishing pressure was 75 g/cm^2, and the polishing time was 10 minutes.

The glass substrate to be polished was an aluminosilicate-based glass substrate for magnetic disc having a diameter of 2.5 inches. The glass substrate was pre-polished by a commercially available cerium oxide-based abrasive ("SHOROX H-1" available from Tohoku Kinzoku Kagaku K.K.). The surface roughness Ra of the pre-polished substrate was 9 angstrom.

After the completion of polishing, the polished glass substrate was taken from the polishing apparatus, and subjected to ultrasonic washing with pure water. The washed glass substrate was dried and then the following characteristics were evaluated. The evaluation results are shown in Table 2.

(1) Rate of Removal

The rate of removal of a glass substrate (μm/min) was determined by the change in mass as measured before and after the polishing.

(2) Surface Roughness (Ra)

The surface roughness (Ra) of a glass substrate was measured on a surface of the substrate by an atomic force microscope (AFM).

(3) Surface Defect and Scratches

A polished surface of the glass substrate was observed by a differential difference microscope. The state of adhesion, and occurrence of scratches and pits were examined. The examination results of scratches were expressed by the number of scratches as observed on the surface. The surface defect was expressed according to the following three ratings.

Rating A: occurrence of pits was not observed to any appreciable extent, and the surface appearance was good.

Rating B: pits occurred to a small extent and the substrate has poor practicability.

Rating C: pits were observed to a great extent and the surface appearance was bad.

Table 2

	Rate of removal (μm/min)	Surface roughness (Angstrom)	Number of scratches	Surface defects
Ex.5, abrasive slurry of recovered material	0. 75	2. 9	20	A
Ex.6, abrasive slurry of recovered material	0. 75	2. 8	18	A
Comp.Ex.1, conventional abrasive slurry	0. 75	3. 0	35	A

Note, conventional abrasive slurry in Comparative Example 1 was used for polishing a glass substrate for hard disc to produce an abrasive waste liquid, from which rare earth oxide was recovered in Example 3.

As seen from Table 2, when polishing is conducted by using abrasive slurry in Example 5 or 6, a polished surface having a reduced number of scratches and good appearance can be obtained with the same rate of removal and approximately the same surface roughness as those of the conventional abrasive slurry in Comparative Example 1.

INDUSTRIAL APPLICABILITY

According to the process of the present invention for recovering rare earth oxides from a liquid containing rare earth elements, rare earth oxides of high purity which is capable of being re-used as an abrasive for precision polishing can be easily recovered with enhanced efficiency.

The application of an abrasive made of the recovered rare earth oxides is similar to that made initially from an ore containing rare earth elements, for example, cerium (Ce), lanthanum (La), praseodymium (Pr) and neodymium (Nd). The abrasive is used for polishing, for example, a glass substrate for photodisc or magnetic disc, a glass plate for liquid crystal such as thin film transistor (TFT) LCD and twisted nematic (TN) LCD, a color filter for liquid crystal TV, a TV cathode-ray tube (CRT), a spectacle lens, an optical lens, a glass plate LSI photomask, a wired plate glass, a substrate for quartz oscillator, and the like.

CLAIMS

1. A process for recovering a rare earth oxide from a liquid containing a rare earth element, which comprises the following steps (1) through (6):

(1) mixing and heating a liquid containing a rare earth element with an acid, to dissolve the rare earth element contained in the liquid;

(2) removing insoluble matter from a rare earth element solution obtained in step (1);

(3) incorporating a soluble carbonate salt or a soluble hydrogencarbonate salt, or an oxalic acid in the rare earth element solution obtained in step (2), to convert the rare earth element in the solution to a rare earth carbonate or a rare earth oxalate;

(4) separating the rare earth carbonate or rare earth oxalate from a slurry of the rare earth carbonate or rare earth oxalate, obtained in step (3);

(5) baking the separated rare earth carbonate or rare earth oxalate to produce a rare earth oxide; and

(6) recovering the rare earth oxide.

2. The process according to claim 1, wherein, in step (1), the liquid containing a rare earth element and the acid are mixed and heated together with hydrogen peroxide, to dissolve the rare earth element contained in the liquid.

3. The process according to claim 1 or 2, wherein the acid in step (1) is hydrochloric acid.

4. The process according to claim 1 or 2, wherein the acid in step (1) is nitric acid.

5. The process according to any one of claims 1 to 4, wherein, in step (1), a mixed liquid of the liquid containing a rare earth element with the acid is heated under reflux, and further concentrated whereby insoluble solid matter contained in the mixed liquid is allowed to float on the liquid surface.

6. The process according to claim 5, wherein the mixed

liquid is concentrated while bubbles are formed.

7. The process according to claim 6, wherein the mixed liquid is heated in the presence of a boiling stone to form bubbles.

8. The process according to claim 1, wherein, in step (2), the insoluble matter is removed by filtration.

9. The process according to claim 1, wherein, in step (3), pH value of the rare earth element solution is adjusted to a value in the range of 1 to 7, and then, the soluble carbonate salt or the soluble hydrogencarbonate salt, or oxalic acid is incorporated in the rare earth element solution to convert the rare earth element in the solution to a rare earth carbonate or a rare earth oxalate.

10. The process according to claim 9, wherein pH value of the rare earth element solution is adjusted to a value in the range of 1 to 7 by adding ammonia.

11. The process according to claim 1 or 9, wherein the soluble carbonate salt or the soluble hydrogencarbonate salt in step (3) is an alkali metal salt, an alkaline earth metal salt or an ammonium salt.

12. The process according to claim 1, wherein, in step (4), the rare earth carbonate or the rare earth oxalate is separated by filtration.

13. A process for recovering a rare earth hydroxide from a liquid containing a rare earth element, which comprises the following steps (i) through (vi):

(i) mixing and heating a liquid containing a rare earth element with sulfuric acid to convert the rare earth element contained in the liquid to a rare earth sulfate;

(ii) incorporating water with the rare earth sulfate to dissolve the rare earth sulfate;

(iii) removing insoluble matter from the thus-obtained rare earth sulfate solution;

(iv) incorporating sodium sulfate in the rare earth sulfate solution obtained in step (iii), to produce a double salt of the rare earth element; and then, separating the double salt from the solution;

(v) suspending the separated double salt in water, and then adjusting pH value of the thus-obtained aqueous double salt suspension to a value in the range of 8 to 13 to convert the double salt of rare earth element to a rare earth hydroxide; and then

(vi) separating the rare earth hydroxide for recovery.

14. The process according to claim 13, wherein, in step (iii), the insoluble matter is removed by filtration.

15. The process according to claim 13, wherein, in step (v), the adjustment of pH value of the aqueous double salt suspension to a value of 8 to 13 is carried out by adding an alkali, aqueous ammonia or ammonia gas.

16. The process according to claim 13, wherein, prior to mixing the liquid containing a rare earth element with sulfuric acid in step (i), aluminum sulfate, poly-aluminum chloride or a polymeric flocculant is added to the liquid containing a rare earth element to allow a solid content containing the rare earth element to precipitate; and then the thus-produced precipitate is separated, followed by mixing the thus-separated precipitate with sulfuric acid.

17. The process according to claim 13 or 16, wherein, after the mixing of the liquid containing a rare earth element with sulfuric acid in step (i), aqueous hydrogen peroxide is added to the thus-prepared mixed liquid.

18. A process for recovering a rare earth oxide, which comprises recovering a rare earth hydroxide from a liquid containing a rare earth element by the process as claimed in any one of claims 13 to 17; and then, baking the recovered rare earth hydroxide to convert to a rare earth oxide, followed by recovering the thus-obtained rare earth oxide.

19. A process for recovering a rare earth oxide, which comprises recovering a rare earth hydroxide from a liquid containing a rare earth element by the process as claimed in any one of claims 13 to 17; suspending the recovered rare earth hydroxide in water; and then, recovering a rare earth

oxide from the thus-obtained aqueous suspension of rare earth hydroxide by the process as claimed in any one of claims 1 to 12.

20. The process according to any one of claims 1 to 19, wherein the liquid containing a rare earth element is a waste liquid produced when an abrasive is used for polishing.

21. A process for producing an abrasive containing a rare earth oxide, which comprises recovering a rare earth oxide by the process as claimed in any one of claims 1 to 20; and fabricating the recovered rare earth oxide into an abrasive.

22. A process for reusing an abrasive containing a rare earth oxide for polishing which comprises recovering a rare earth oxide from a waste liquid produced upon polishing using an abrasive, by the process as claimed in any one of claims 1 to 20; and fabricating the recovered rare earth oxide into an abrasive.

23. A method for polishing a substrate by an abrasive containing a rare earth oxide wherein said abrasive is made from a rare earth oxide, which is recovered from a waste liquid produced upon polishing using an abrasive, by the process as claimed in any one of claims 1 to 20.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/07288

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C01F17/00 C22B59/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C01F17/00 C22B59/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Japanese Utility Model Gazette 1926-1996, Japanese Publication of Unexamined Utility Model Applications 1971-2003, Japanese Registered Utility Model Gazette 1994-2003, Japanese Gazette Containing the Utility Model 1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JOIS(JSTPLUS FILE),WPI/L

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 790322 A1 (SANTOKU METAL INDUSTRY CO.,LTD)1997.08.20 & JP 9-217133 A & US 5980841 A & DE 69701155 D & CN 167832 A & AT 189006 T	1-4,8-12
Y		5,20-23
A		6,7
X	JP 63-182216 A(DAIDO TOKUSYUKO K.K.)1988.07.27 whole document (Family:none)	1-4,8-10,12
Y		5,20-23
X	US 4650652 A(KASEI OPTONIX,LTD.)1987.03.17 & JP 60-161330 A & DE 3502907 A & KR 9105048 B	1-4,8-10,12
Y		5,20-23
X	JP 5-287405 A(SUMITOMO METAL MINING CO.)1993.11.02 (Family:none)	1-4,8,9,11,12
Y		5,20-23
X	JP 2000-87154 A(MITSUI MINING & SMELTING CO. LTD.)2000.03.28[0005]-[0007],[0013]-[0018] (Family:none)	1-4,8-10,12 ,20-23
Y		16,20-23

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/07288

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4198231 A(SWISS ALUMINIUM LTD.)1980.04.15 EXANPLE & JP 54-117315 A & DE 2818997 B & NL 7901108 A & GB 2014612 A & FR 2417473 A & CA 1129211 A	5
X Y	JP 61-532 A(NIPPON PLATING K.K.)1986.01.06 (Family:none)	13-15, 17-19 16,20-23