

DESCRIPTION

METHOD FOR RECYCLING ABRASIVE

5 FIELD OF THE INVENTION

[0001] The present invention relates to a method for recycling an abrasive from a used cerium oxide based abrasive for glass (hereinafter, frequently referred to as "abrasive waste").

10 BACKGROUND ART

[0002] A cerium oxide based abrasive for glass has been industrially widely used in various glass polishing processes due to its chemical polishing effect derived from its chemical composition. Conventionally, because of the price and supply condition of a cerium oxide based abrasive, the used slurry containing polished glass debris after the
15 abrasive is used in polishing glass has generally been subjected to a process, such as solid-liquid separation, and then disposed of. However, a change of the social environment in recent years causes the supply of the abrasive to be unstable and a rise in the price, and, in such a situation, there are important tasks to be achieved including a reduction of the amount used in the glass polishing process, a recycling of an abrasive
20 from the used abrasive, and the development of a new source.

[0003] As a method for recycling abrasive material from the abrasive waste, a method has been known in which the abrasive is treated to separation from the deposits of the abrasive waste slurry according to the diameters of the particles (patent document 1). However, this method has a problem in that a prolonged period of time is required to
25 cause the abrasive to settle, and that the investment for the recycle plant is increased.

[0004] Thus, a method using a flocculant for promoting the flocculation of the abrasive has been proposed (patent document 2). However, this method has a problem in that both cerium oxide to be recovered and the other components to be removed together suffer flocculation.

30 [0005] A technique has been proposed in which, for causing the abrasive waste slurry to have good condition for dispersion, the abrasive waste slurry is adjusted to alkaline condition and changed in the zeta potential, and the abrasive is recovered by centrifugal separation (patent document 3). However, the method using an alkali has a problem in that the removal rate for the silicon component and aluminum component, which lower
35 the polishing effect, is low.

[0006] Further, a method has been proposed in which the abrasive waste slurry is

treated with hydrochloric acid and hydrofluoric acid (patent document 4). However, in the method using a treatment with an acid, a recycled product having an polishing effect equivalent to that of an unused new abrasive cannot be obtained unless the recycled product is calcined (Example 1 of patent document 4).

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PRIOR ART REFERENCES

Patent Documents

[0007] Patent document 1: Japanese Laid-open Patent [Kokai] Publication No. 2005-14187

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Patent document 2: Japanese Laid-open Patent [Kokai] Publication No. Hei 9-327603

Patent document 3: Japanese Laid-open Patent [Kokai] Publication No. 2002-28662

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Patent document 4: Japanese Laid-open Patent [Kokai] Publication No. 2007-276055

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0008] An object of the present invention is to provide a method for recycling an abrasive wherein an abrasive having polishing performance equivalent to that of an unused new abrasive can be recycled easily and at high removal rate for the silicon component and aluminum component.

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Means to Solve the Problems

[0009] The present inventors have the follow finding. Specifically, shavings caused in a glass polishing process, including molecular glass (SiO_2) formed by chemical polishing, are attached onto the surfaces of the particles of abrasive waste and they are together in an aggregate state. By controlling the pH of a slurry of the abrasive waste to be in a predetermined range, the dispersibility of such shavings can be improved to cause the abrasive component to suffer aggregation and rapidly settle on the bottom, making it possible to easily separate the concentrated phase of the abrasive particles from the concentrated phase of the polished glass debris and others. Accordingly, the abrasive concentrated phase which has settled contains almost no glass component, and thus an abrasive having a polishing effect equivalent to that of an unused new abrasive can be easily recovered. The present invention has been completed, based on the above finding.

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[0010] The present invention is as follows.

1. A method for recycling an abrasive from a used cerium oxide based abrasive for glass, wherein the method comprises the step of adjusting the pH of a slurry of a used cerium oxide based abrasive for glass to be within the range of from 0.5 to 3.0.

5 2. The method for recycling an abrasive according to item 1 above, wherein hydrochloric acid or sulfuric acid is used as an agent for adjusting the pH.

3. The method for recycling an abrasive according to item 1 or 2 above, wherein the temperature at which the pH of the slurry of the used cerium oxide based abrasive for glass is adjusted is 100°C or lower.

10 4. The method for recycling an abrasive according to any one of items 1 to 3 above, which comprises the steps of: dispersing the used cerium oxide based abrasive for glass in water to obtain a slurry, adjusting the pH of the slurry to be within the range of from 0.5 to 3.0, and recovering an abrasive from the slurry.

15 5. The method for recycling an abrasive according to any one of items 1 to 4 above, wherein, in the step of recovering an abrasive from the slurry, for separating and recovering the phase comprised mainly of the abrasive particles which have settled, the supernatant phase is removed while letting the abrasive particles remain in a settling state.

20 Effect of the Invention

[0011] The present invention provides a method for recycling an abrasive wherein an abrasive having polishing performance equivalent to that of an unused new abrasive can be recycled easily and at high removal rate for the silicon component and aluminum component.

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BRIEF DESCRIPTION OF THE DRAWING

[0012] Fig. 1 shows particle diameter distribution data obtained in the recycling treatment for abrasive waste by the method of the present invention.

30 MODE FOR CARRYING OUT THE INVENTION

[0013] The present invention is directed to a method for recycling an abrasive from a used cerium oxide based abrasive for glass (abrasive waste). As a cerium oxide based abrasive for glass is used, the polishing performance becomes poor. Therefore, the abrasive is disposed of at a certain point in time. The present invention is directed to a
35 method for recycling an abrasive from abrasive waste which has conventionally been disposed of.

[0014] The abrasive waste is not particularly limited as long as it is generated when a cerium oxide based abrasive for glass is used in polishing glass. For Example, the forms of the abrasive waste include dry powder, a water-containing cake, and a slurry. The used cerium oxide based abrasive for glass is generated in the form of a slurry in water, however, for facilitating the storage or transportation thereof, the used abrasive is frequently in the form of a cake by dehydrating.

[0015] The recycling method of the present invention comprises adjusting the pH of a slurry of a used cerium oxide based abrasive for glass to be within the range of from 0.5 to 3.0. The pH value of the slurry is preferably 1.0 to 2.5, more preferably 1.0 to 2.0.

[0016] The pH adjustment of the slurry of the abrasive waste is performed by adding an inorganic or organic acid to the slurry, preferably by adding an inorganic acid. The inorganic acid includes hydrochloric acid, nitric acid, hydrochloric acid, phosphoric acid and the like. Hydrochloric acid is preferred. The organic acid includes formic acid, acetic acid, and oxalic acid and the like. Although Acids may be used in combination of two or more acids, the use of a single acid is satisfactory when the pH of the slurry can be adjusted to a predetermined range by using only the single acid.

The pH adjustment of the slurry of the abrasive waste is performed at a temperature of 100°C or lower, more preferably 90°C or lower. From the viewpoint of removing the unnecessary components, the pH adjustment of the slurry is performed while heating, for example, at a temperature of 50 to 100°C, preferably 60 to 100°C, especially 80 to 90°C.

[0017] In the slurry of the abrasive waste, it is preferred that the zeta potential is adjusted simultaneously with the pH adjustment. The adjustment of the zeta potential of the slurry can be performed by adding an acid or an alkali to the slurry. The acid for adjusting the zeta potential, the same acid as that used for adjusting the pH can be used. The alkali used for adjusting the zeta potential includes alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide.

[0018] The state of the abrasive waste is not particularly limited, and can be appropriately selected according to the object. The state of the abrasive waste includes, for example, dry powder, a dehydrated cake, a water-containing cake, and a slurry. In the process or company using the cerium oxide based abrasive, when it is desired that the abrasive waste is in a state of dry powder, dehydration and drying are performed in the recovery method so that the recovered material is obtained in a state of dry powder, and the recovered material can be provided as a dry powder. When it is desired that the abrasive waste is in a state of being dispersed in water as used in a polishing process, the recovered material is obtained in a state of a slurry having an appropriate pulp

concentration, and thus the dehydration and drying steps can be omitted and the recovered material can be obtained at a low cost.

[0019] When the abrasive waste is recovered in the form of a dehydrated cake or a water-containing cake, the abrasive waste is preferably subjected to milling treatment before subjected to recycling.

[0020] The milling treatment is not particularly limited as long as it is a step in which the abrasive waste in a cake form containing a cerium oxide based abrasive and polished glass debris is mixed with, for example, water and milled by means of a milling machine, and the milling treatment can be appropriately selected according to the object. The abrasive waste is preferably mixed with any one of an aqueous acid solution and an aqueous alkali solution. The term "milling" means pulverization of the cerium oxide based abrasive in a flocculate state in the abrasive waste.

[0021] The cerium oxide based abrasive in the abrasive waste is in an flocculate state due to, for example, a flocculant. In the milling treatment, the abrasive waste is milled so that the cerium oxide based abrasive is separated from the other components including the abrasive for glass, making it easy to recover the cerium oxide based abrasive.

[0022] When the abrasive waste to be placed in a milling machine is in the form of a water-containing cake, only less energy is required for changing the abrasive waste into a slurry form and the process can be shortened, and further the amount of water used in the milling treatment can be reduced, improving the treatment efficiency in the milling treatment.

[0023] (1) Abrasive waste

Abrasive waste contains at least a cerium oxide based abrasive and polished glass debris, and optionally further contains another component, such as a flocculant. The abrasive waste is representatively in a cake form.

[0024] The abrasive waste in a cake form is obtained by, for example, adding a flocculant to a mixture slurry containing both the used cerium oxide based abrasive and polished glass debris to cause flocculation of the cerium oxide based abrasive, and then reducing or removing water from the resultant flocculation by, for example, solid-liquid separation means to obtain a wet cake form (dehydrated cake form), or then drying the cake. The water content of the abrasive waste is generally about 30 % by mass to 60 % by mass.

[0025] Here, the term "cake" means a solid material containing water in a compressed state by, for example, pressing by means of a filtration apparatus, and the term "slurry" means a solid material in a liquid state or a mud state in which the solid material is

dispersed in a liquid, such as water. The slurry of the abrasive waste may be a slurry in which a solid component such as abrasive particle is dispersed in water. However, generally, a preferred solids content of the slurry is 1 to 60% by weight, preferably 3 to 40% by weight. When the abrasive waste is in the form of a cake, water is added to the cake of the abrasive waste to form a slurry. In this case, it is preferred that the abrasive particles and the like are milled using, for example, a ball mill.

[0026] The state (size) of the abrasive waste is not particularly limited, and may be a size possible to be fed into a milling machine (generally, about several cm or less).

[0027] (2) Cerium oxide based abrasive for glass

The material, form, size, and structure of the cerium oxide based abrasive are not particularly limited, and can individually be appropriately selected according to the object.

[0028] The material for the cerium oxide based abrasive for glass is not particularly limited, and can be appropriately selected according to the object. For example, it is included a cerium oxide based abrasive containing at least cerium oxide and optionally further containing lanthanum oxide, praseodymium oxide and the like. The formulation of cerium oxide, lanthanum oxide, praseodymium oxide, and other components in the cerium oxide based abrasive for glass depends on the constituents of ore used as a raw material for the abrasive.

[0029] The average particle size of the cerium oxide based abrasive for glass is not particularly limited, and can be appropriately selected according to the object, and is, for example, 0.5 to 10 μm . Here, the average particle size can be measured by, for example, a laser diffraction type particle size distribution measuring system (as an example, a particle diameter distribution measuring system Partica LA-950V2, manufactured by Horiba, Ltd.).

[0030] Rare earth elements contained in the cerium oxide based abrasive for glass, such as cerium, lanthanum, and praseodymium, are valuable resources and elements desired to be reused by recovering them.

[0031] (3) Polished glass debris

The polished glass debris is polished debris generated when polishing a glass material, such as a glass disc, a crystal wafer, or a liquid crystal panel, using a cerium oxide based abrasive for glass.

[0032] It is considered that polishing the above-mentioned glass material using a cerium oxide based abrasive for glass is different from physically or mechanically polishing a material using a general abrasive (for example, aluminum oxide), and the silicon component of the glass material causes a chemical reaction when the cerium

oxide based abrasive is in contact with the glass material, and the silicon component is removed in a size at an atomic level and attached to the cerium oxide to achieve polishing. For this reason, the resultant polished glass debris has an even smaller size than that of the cerium oxide based abrasive. Further, in the abrasive waste, the polished glass debris is attached mainly to the cerium oxide based abrasive.

[0033] (4) Flocculant

As mentioned above, a flocculant is generally used when obtaining the abrasive waste in a cake form. The flocculant can be appropriately selected according to the object, and includes iron chloride, aluminum chloride, aluminum sulfate, and polymer flocculants, such as polyaluminum chloride.

In the present invention, the abrasive waste containing a flocculant can be used, however preferred is a use of the abrasive waste containing no flocculant.

[0034] (5) Milling machine

The milling machine is not particularly limited, and can be appropriately selected according to the object. The milling machine includes a media mill, a roll mill, a strong agitation type agitator, a line mixer, a colloid mill and the like.

[0035] The media mill is not particularly limited as long as it is an apparatus in which balls or beads (hereinafter, frequently referred to as "media") are placed in a container and stirred together with a solid or a liquid, and can be appropriately selected according to the object.

[0036] The media mill includes a paint shaker in which a closed container is mechanically shaken to strongly stir media, a ball mill in which a closed container is mechanically rotated to stir media, an attritor and a sand mill, in which a stirrer (of which form varies depending on the apparatus manufacturer, for example, a stirrer having a number of rods fitted to a rotating shaft, or a stirrer having multi-stage discs fitted to a rotating shaft) is placed in a container having a cover and rotated to strongly stir media, a bead mill in which a closed container has therein a rotating shaft having a number of discs (called agitator discs) fitted thereto and the rotating shaft is rotated to strongly stir media and the like.

[0037] The name of the media mill apparatus frequently varies depending on the production manufacturer, but any apparatus has a feature that a solid or a liquid can be strongly milled by the force of collision of the media stirred together with the solid or liquid. There can be used the above apparatuses which have been widely used in, for example, grinding, dispersing, or mixing an inorganic material, or kneading or dispersing a paint pigment.

[0038] The material for the media is not particularly limited, and can be appropriately

selected according to the object. Examples of the materials for the media include soda glass, alumina, zirconia, and Teflon (registered trademark).

[0039] The size of the media is not particularly limited, and can be appropriately selected according to the object. A diameter of the media is preferably 5 to 30 mm, more preferably 10 to 20 mm.

[0040] The roll mills include, for example, a two-roll mill and a three-roll mill. Of these, preferred is a three-roll mill in view of the milling power. The operating condition for the three-roll mill is not particularly limited, and can be appropriately selected according to the object. Preferred are conditions such that the rotational speed of the front roll is 50 rpm to 200 rpm and the front roll:middle roll:back roll rotational ratio is 1.0:1.5:5.0 to 1.0:3.0:8.0.

[0041] The operating time for the milling machine, i.e., milling time, is not particularly limited, and can be appropriately selected according to the object. For example, when the strength of the cake is high due to, for example, a high flocculant content of the abrasive waste or a low water content of the cake, the increase of the milling time can improve the effect of milling. Appropriate conditions for the milling vary depending on the composition of the abrasive waste or the state of the cake. However, when the milling time is too short, the milling may be unsatisfactory so that the acid treatments cannot affect the inside of the solid material kept in a flocculate state, making it difficult to obtain a desired composition and particle size of the recycled abrasive (recovered material). When the milling time is too long, the primary particles formed after the milling may be ground to an excess extent, causing the particle size of the recycled abrasive (recovered material) to be unsuitable for the object of the use of recycling, for example, an abrasive. When the milling time is in a preferred range, there is obtained an advantage at the same time not only in that the abrasive can be uniformly milled into primary particles to effectively separate the solid material to be recovered and the component to be removed from each other, but also in that the particles having a particle size suitable for an abrasive and other uses without grinding the abrasive particles to an excess extent.

[0042] The average particle size of the milled material obtained by the milling treatment is not particularly limited, and can be appropriately selected according to the object, and includes, for example, 0.5 μm to 10 μm . Here, the average particle size can be measured by, for example, a laser diffraction type particle size distribution measuring system (as an example, SALD2000A, manufactured by Shimadzu Corporation).

[0043] The pH adjustment of the present invention is performed with respect to the

slurry of the abrasive waste. The pH adjustment can be performed simultaneously with preparation of the slurry from the abrasive waste. Specifically, an aspect in which when a slurry is prepared from the abrasive waste, the pH of the slurry being prepared is adjusted to be within the range of from 0.5 to 3.0 is involved in the present invention. The pH adjustment can be performed using the above-mentioned acid, however preferred is at least one of hydrochloric acid, sulfuric acid, nitric acid, and oxalic acid.

The recycling method of the present invention can further comprise the steps of recovering an abrasive from the slurry, and washing, drying, and grinding the recovered abrasive.

[0044] The step of recovering an abrasive from the slurry is a step in which an abrasive in a flocculate state is separated from the slurry having the pH adjusted. As a method for separation, for example, a settling separation method, a centrifugal separation method, or a filtration method can be employed. The step of recovering an abrasive from the slurry can be a step in which, for separating and recovering the phase comprised mainly of the abrasive particles which have settled, the supernatant phase is removed using, for example, a pump while letting the abrasive particles remain in a settling state. The step of recovering an abrasive can be performed using a centrifugal separator, particularly, a screw decanter.

A series of the step of dispersing a used cerium oxide based abrasive for glass in water to obtain a slurry, the step of adjusting the pH of the obtained slurry to be within the range of from 0.5 to 3.0, and the step of recovering an abrasive from the slurry is taken as one cycle, and this cycle can be repeated twice, or three or more times.

[0045] The step of washing, drying, and grinding the recovered abrasive is a step in which the silicate component and aluminum component attached onto the recovered abrasive are removed by washing, and the washed abrasive is dried using a general dryer, and then ground by a general grinding method.

[0046] The recycled abrasive obtained by the method of the present invention has a high removal rate for the silicon component and aluminum component and has polishing performance equivalent to that of an unused new abrasive.

EXAMPLES

[0047] The present invention will be described with reference to the following Examples.

[0048] 1. Recycling of abrasive waste comprised mainly of cerium oxide
(Examples 1 to 3 and Comparative Examples 1 and 2)

An abrasive waste slurry discharged from a glass polishing process and comprised mainly of cerium oxide was used as a raw material. The solid content (pulp concentration) of this slurry was 47.3 g/L.

[0049] A chemical composition of solids of the slurry was as shown in Table 2 at the column indicated by "Test raw material".

[0050] (Experiment 1)

200 mL of the above-mentioned abrasive waste slurry, which had been well stirred so as to be in a uniform state, was placed in a glass beaker having a capacity of 500 ml and further well stirred using a stirrer (rotational speed for stirring: 200 rpm).

A concentrated HCl having a concentration of 35% was added to the resultant slurry in an addition amount at the individual levels shown in Table 1 to prepare samples. Each of the prepared samples was placed in a measuring cylinder having a capacity of 500 ml and evaluation with respect to the settling property with the passage of time was performed. As a result, the pH of the slurry at the HCl addition amount levels individually was as shown in Table 1.

[0051] With respect to the test raw material and systems having HCl added to the raw material, when the slurry was allowed to stand for a predetermined period of time, a difference in the settling speed of the solid material between them was confirmed.

Among the conditions shown in Table 1, under the condition "HCl addition amount: 3 vol%" (pH = 1.33) in Example 1, the solid material settled the most quickly, specifically, after one minute from the stop of stirring, the boundary between the sediment phase of the solid material and the supernatant phase became clear and these phases were completely separated, and the height of the boundary was a height corresponding to about 50% of the capacity of the measuring cylinder. In Example 2 (pH = 1.06) and Example 3 (pH = 0.72), after one minute from the stop of stirring, the sediment and supernatant phases were substantially separated, and, after 10 minutes from the stop of stirring, the phases were completely separated. In contrast, under the conditions in Comparative Example 1 (pH = 3.34) and Comparative Example 2 (pH = 0.40), even after allowed to stand for one hour, a clear boundary was not made. From this result, it has been found that both the satisfactory removal of impurities and high yield required for separating the sediment and supernatant phases cannot be achieved under the conditions in Comparative Examples 1 and 2 and thus those are inappropriate conditions.

[0052] [Table 1]

	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 4
	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5

HCl addition amount [vol%]	1	3	5	10	15
pH	3.34	1.33	1.06	0.72	0.40

[0053] (Experiment 2)

500 mL of the above-mentioned abrasive waste slurry, which had been well stirred so as to be in a uniform state, was placed in a glass beaker having a capacity of 2 L and further well stirred using a stirrer (rotational speed for stirring: 300 rpm). A concentrated HCl having a concentration of 35% was added to the resultant slurry until the pH became 1.33 to obtain a slurry having the same condition as in Example 1.

[0054] After adjusting the pH, the resultant slurry was further stirred for 10 minutes, and then allowed to stand for 20 minutes. As a result, a clear separation between the sediment phase having the abrasive and the supernatant phase having high transparency was made, and then the supernatant phase was removed using a tubular pump.

Subsequently, pure water was added to the remaining sediment phase so that the total volume became 500 mL, and the resultant mixture was subjected to sedimentation treatment for 20 minutes two times, and finally, the supernatant phase was similarly removed to recover the sediment phase. The recovered sediment was dried under conditions in an atmosphere of air at a temperature of 105°C for 12 hours. A compositional analysis for the obtained dried recovered material was conducted using a fluorescent X-ray analyzer: XRF (SuperMini, manufactured by Rigaku Corporation). The results of the analysis of the recovered material as well as those of the test raw material are shown in Table 2.

[0055] In Table 2, the compositional data of the abrasive (unused abrasive) as an object for the test are also shown.

[0056] [Table 2]

Example 1				
		Test raw material	Recycled product	Virgin product
Chemical composition [wt%]	CeO ₂	68.70	93.20	99.60
	La ₂ O ₃	N.D.	N.D.	N.D.
	Pr ₆ O ₁₁	N.D.	N.D.	N.D.
	Nd ₂ O ₃	N.D.	N.D.	N.D.
	TREO	68.70	93.20	99.60
	F	N.D.	N.D.	N.D.
	SiO ₂	17.70	2.14	0.11
	Al ₂ O ₃	5.49	0.27	0.07
	ZrO ₂	0.36	0.78	0.04
	SO ₃	0.13	0.05	0.06
	Fe ₂ O ₃	N.D.	N.D.	N.D.
	CaO	0.86	0.06	0.05

ZnO	N.D.	N.D.	N.D.
K ₂ O	0.13	0.05	N.D.
P ₂ O ₅	2.10	3.12	N.D.
Cl	0.10	0.36	0.08
SrO	0.15	N.D.	N.D.
SnO ₂	N.D.	N.D.	N.D.
MgO	N.D.	N.D.	N.D.

[0057] By the present treatment, the amount of CeO₂ content (wherein CeO₂ is the main component of the abrasive) was increased from 68.7% of the test raw material (used slurry) to 93.2% of the recycled product. Further, from the CeO₂ content of the recovered solid material and the amount of the recovered solid material, a CeO₂ recovery rate was calculated. The calculated CeO₂ recovery rate was 94.5%. Thus, it was found that most of the CeO₂ component contained in the raw material (used slurry) was recovered.

[0058] Further, the above-mentioned supernatant portion removed using a tubular pump was neutralized, and, from the resultant supernatant portion, the solid material was recovered by sedimentation. As a result, it was found that the main components of the solid material were as follows: SiO₂: 48.1 wt% and Al₂O₃: 14.0 wt%. This result has confirmed that the components generated in the glass polishing process are efficiently removed.

[0059] 2. Recycling of abrasive waste comprised mainly of cerium oxide and lanthanum oxide

An abrasive waste slurry discharged from a glass polishing process and comprised mainly of cerium oxide and lanthanum oxide was used as a raw material. A solid content (pulp concentration) of this slurry was 434.5 g/L.

[0060] (Examples 4 to 9 and Comparative Examples 3 to 6)

500 mL of the above-mentioned abrasive waste slurry, which had been well stirred so as to be in a uniform state, was placed in a glass beaker having a capacity of 2 L and further well stirred using a stirrer (rotational speed for stirring: 300 rpm). A concentrated HCl having a concentration of 35% was added to the resultant slurry so that the pH became values under the individual conditions shown in Table 3. After adding HCl, the resultant slurry was further stirred for 10 minutes, and then the stirring was stopped, followed by natural sedimentation for 20 minutes. The supernatant phase was removed using a tubular pump and the sediment phase was washed with pure water in the same manner as in Example 1, and the resultant solid material concentrated slurry was subjected to filtration, followed by drying under conditions in an atmosphere of air at 105°C.

[0061] (Examples 10 to 15 and Comparative Examples 7 to 10)

Slurries having pH adjusted to various levels were individually prepared by the method and under the conditions shown in Experiment 1, and each of the slurries was placed in a container (centrifuge tube) for a centrifugal separator and subjected to centrifugal sedimentation treatment by means of a centrifugal separator (J2-21,
5 manufactured by BECKMAN Coulter, Inc.) at a rotational speed set value of 4,000 rpm for one minute. The supernatant phase resulting from the centrifugal sedimentation treatment was removed, followed by drying under conditions in an atmosphere of air at a temperature of 105°C for 12 hours.

[0062] The XRF compositional analysis data obtained for the above-mentioned test
10 conditions for Experiments as well as a sample obtained by directly drying the test raw material slurry are shown in Table 3.

[0063] [Table 3]

Treatment conditions			Abrasive main components						Unnecessary components					
			TREO (Ce+La+ Pr+Nd)	CeO2	La2O3	Pr6O11	Nd2O3	F	SiO2	Al2O3	CaO	(Si+Al+Ca)	(TERO+F)/(Si+Al+Ca) (Change ratio)	
Natural sedimentation after acid treatment	No pH adjustment	Comparative Example 3	90.00	56.80	29.50	3.70	N.D	3.71	2.45	0.39	0.53	3.37	27.8	-
	pH0.5	Example 4	90.58	58.50	28.70	3.38	N.D	4.36	2.37	0.11	0.19	2.68	35.5	1.28
	pH1	Example 5	90.48	58.00	28.40	4.08	N.D	5.18	2.03	0.11	0.19	2.33	41.0	1.47
	pH1.5	Example 6	90.14	58.20	28.40	3.54	N.D	5.49	2.11	0.11	0.19	2.40	39.8	1.43
	pH2	Example 7	90.47	58.40	28.30	3.77	N.D	5.08	2.15	0.15	0.23	2.53	37.8	1.36
	pH2.5	Example 8	90.82	58.90	28.70	3.22	N.D	4.77	2.12	0.17	0.20	2.49	38.4	1.38
	pH3	Example 9	89.70	57.20	28.90	3.60	N.D	5.69	2.14	0.21	0.22	2.57	37.1	1.33
	pH7.5	Comparative Example 4	89.86	56.40	29.60	3.86	N.D	4.43	2.31	0.39	0.48	3.19	29.6	1.06
	pH9.4	Comparative Example 5	90.34	56.70	30.20	3.44	N.D	3.62	2.35	0.39	0.55	3.29	28.6	1.03
	pH12	Comparative Example 6	89.18	56.90	28.70	3.58	N.D	4.96	2.22	0.37	0.50	3.08	30.5	1.10
Centrifugal sedimentation after acid treatment	No pH adjustment	Comparative Example 7	90.00	56.80	29.50	3.70	N.D	3.71	2.45	0.39	0.53	3.37	27.8	-
	pH0.5 Centrifuging	Example 10	90.15	57.00	29.00	4.15	N.D	4.54	2.23	0.11	0.20	2.54	37.3	1.34
	pH1 Centrifuging	Example 11	90.13	57.80	28.60	3.73	N.D	5.43	1.92	0.12	0.21	2.25	42.5	1.53
	pH1.5 Centrifuging	Example 12	90.07	57.00	29.50	3.57	N.D	5.74	1.87	0.11	0.20	2.17	44.1	1.59
	pH2 Centrifuging	Example 13	91.14	57.50	29.70	3.47	0.47	4.72	1.87	0.16	0.19	2.23	43.1	1.55
	pH2.5 Centrifuging	Example 14	90.33	57.50	29.30	3.53	N.D	5.39	2.05	0.17	0.20	2.42	39.6	1.42
	pH3 Centrifuging	Example 15	89.52	56.40	29.30	3.82	N.D	6.12	2.10	0.26	0.24	2.60	36.9	1.33
	pH7.5 Centrifuging	Comparative Example 8	90.14	56.10	30.40	3.64	N.D	4.40	2.03	0.34	0.48	2.85	33.2	1.20
	pH9.4 Centrifuging	Comparative Example 9	90.50	56.40	30.50	3.60	N.D	4.12	2.06	0.35	0.50	2.92	32.4	1.17
	pH12 Centrifuging	Comparative Example 10	88.53	56.30	28.70	3.53	N.D	5.51	2.12	0.36	0.52	2.99	31.4	1.13

[0064] The XRF analysis results in Table 3 show, as representative components, the main components of a general abrasive (CeO_2 , La_2O_3 , Pr_6O_{11} , Nd_2O_3 , F) and components (SiO_2 , Al_2O_3 , CaO) presumed to be attached to the abrasive due to polishing and removal from glass by a CMP (chemical mechanical polishing) action in the glass polishing, namely, the components to be removed. As an index of the recycling treatment effect for the used abrasive slurry, a ratio of the main components of abrasive to the components to be removed was calculated and shown in Table 3. For example, in the present sample, the pH range can be controlled so as to achieve advantageous conditions for the recycling treatment such that the value of the above ratio is 35 or more, wherein the value of the ratio before the recycling treatment is 27.8. Further, taking into consideration dispersion caused due to the abrasive waste as a raw material, a change ratio to the value of the untreated slurry is calculated. It has been found that an increase of the change ratio to 1.25 or more is advantageous to the recycling conditions. Specifically, by adjusting the pH to be within the range of 0.5 or more and 3.0 or less by adding HCl, high recycling treatment effect can be obtained. When a centrifugal sedimentation treatment is further conducted, an equivalent value or more can be efficiently obtained, as compared to the case in which merely a natural sedimentation treatment is conducted. When the pH range falls outside the range for appropriate conditions, the removal efficiency for unnecessary components attached to the abrasive particles in the glass polishing is low. When the resultant recycled product is used, the satisfactory polishing performance for glass cannot be achieved.

[0065] (Example 16)

With respect to the recycled abrasive prepared in Example 7, measurement of the particle diameter distribution and evaluation of the polishing performance for glass were conducted.

[0066] The particle diameter distribution is measured as follows. Using a measuring system (particle diameter distribution measurement apparatus, Partica LA-950V2, manufactured by Horiba, Ltd.), the slurry diluted to a slurry concentration suitable for the measurement was analyzed while subjecting it to ultrasonic dispersion (power: 30 W). With respect to the results of the measurement, the representative diameters respectively at cumulative frequencies of 10%, 50%, and 90% are shown in Table 4, and a graph of the particle diameter distribution as well as the result of the evaluation using an unused abrasive (virgin product) are shown in Fig. 1.

[0067] A method for evaluation of the polishing performance for glass is as follows. As a polishing machine, an Oscar polishing machine was used, and, as an object to be polished, a quartz glass substrate was used. 6 substrates were continuously polished

for 2 hours per substrate. Items for the evaluation include a polished amount per substrate, a polishing rate calculated therefrom, and appearance (as to whether a polishing flaw, polishing unevenness, or the like is caused) for evaluating the finishing state of the polished surface.

- 5 [0068] The obtained data as well as the result of the evaluation using an unused abrasive (virgin product) are shown in Table 4.

[0069] [Table 4]

Sample	Representative diameter [μm]		
	D ₁₀	D ₅₀	D ₉₀
Recycled product	0.85	2.55	5.02
Virgin product	0.88	2.49	4.87
Raw material (used slurry)	2.18	4.13	7.03

- [0070] The representative diameters of the recycled product are within $\pm 4\%$ of the values of the virgin product, and thus are values at substantially the same level as that of the virgin product, and further the graph of Fig. 1 has confirmed that the particle diameter distribution of the recycled product is substantially consistent with that of the virgin product. With respect to the used slurry, the distribution has shifted to the larger diameter side, as compared to those of the virgin product and recycled product. There is a marked difference in the particle diameter distribution caused due to the mixed unnecessary components between the used slurry and the virgin product, but, by conducting the treatment by the method and under the conditions shown in the present Example, the unnecessary components are removed as seen in the results of compositional analysis shown in Table 3, and the recycled product achieves values close to those of the virgin product, thus obtaining an effect such that the recycled product exhibits particle diameter distribution close to that of the virgin product.
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[0071] 3. Evaluation test

(1) Evaluation of polishing performance

- Using the recycled product obtained in Example 7 and a virgin product, evaluation of the polishing performance for glass was made. As glass to be polished, quartz glass having a spherical surface for optical use was used, and, as a polishing machine, an Oscar polishing machine specially prepared for the object to be polished was used. 6 lenses in total were polished for 2 hours per lens, and each polished glass was evaluated in respect of the polished amount and the surface state after polishing, i.e., the occurrence of, for example, a polishing flaw, polishing unevenness, or surface scorching. The results are shown in Table 5.
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[0072] [Table 5]

Item		Recycled product (Example 7, pH = 2)	Virgin product	
			(Average)	(At end of use)
Polishing rate ($\mu\text{m}/\text{min.}$)		1.47	1.50	1.33
Finishing	Polishing flaw	None	None	-
	Appearance (nothing polishing unevenness, surface scorching)	Excellent	Excellent	-

[0073] When using the virgin product, the polishing rate at the start of the test was $1.50 \mu\text{m}/\text{min.}$, and, at the end of the test, the polishing rate was reduced to 89% of the rate at the start ($1.33 \mu\text{m}/\text{min.}$). In contrast, the polishing rate of the recycled product achieved 98% of the value of the virgin product, that is, which is substantially equivalent to the value of the virgin product. Further, there was no difference in the surface state of the polished glass between the recycled product and the virgin product. Thus, there was obtained the product which can be used like the virgin product.

[0074] (Example 17) Evaluation of heating treatment

Using, as a raw material, the used slurry discharged from a glass polishing process and comprised mainly of cerium oxide and lanthanum oxide, which is a sample of the same grade as that used in Example 7 but of a different lot, the treatment test shown below was conducted.

[0075] 500 mL of the above-mentioned test raw material slurry, which had been well stirred so as to be in a uniform state, was placed in a glass beaker having a capacity of 2 L and further well stirred using a stirrer (rotational speed for stirring: 300 rpm). A concentrated HCl having a concentration of 35% was added to the resultant slurry until the pH became 1.5. After adding HCl, the resultant slurry was heated to a predetermined temperature (80 or 90°C), and then further stirred at that temperature for 10 minutes, and then the stirring was stopped, followed by natural sedimentation for 20 minutes. The supernatant phase was removed using a tubular pump and the sediment phase was washed with pure water in the same manner as in Experiment 2, and the resultant solid material concentrated slurry was subjected to filtration, followed by drying under conditions in an atmosphere of air at 105°C . The compositional analysis data for the raw material and the sample treated at 80°C and 90°C are shown in Table 6, and the particle diameter distribution data are shown in Table 7.

[0076] [Table 6]

Treatment conditions	Abrasive main components						Unnecessary components					
	TREO + F	CeO ₂	La ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	F	SiO ₂	Al ₂ O ₃	CaO	(Si+Al+Ca)	(TREO+F)/(Si+Al+Ca)	Change ratio
Raw material (obtained by directly drying slurry)	90.24	55.40	27.30	3.30	0.39	3.85	3.93	0.39	0.53	4.85	18.6	-
80°C	93.75	57.00	27.20	3.48	N.D	6.07	2.11	0.14	0.19	2.44	38.4	2.1
90°C	95.16	58.10	27.50	3.65	N.D	5.91	2.22	0.11	0.18	2.51	37.9	2.0

[0077] [Table 7]

Sample	Representative diameter [μm]		
	D ₁₀	D ₅₀	D ₉₀
(Example 7)	0.85	2.55	5.02
80°C	0.79	2.21	4.91
90°C	0.74	2.16	4.87
Raw material (used slurry)	2.18	4.13	7.03

[0078] When the values of the (TREO + F)/(Si + Al + Ca) change ratio are compared, high values even compared to the data for Example 7 are obtained, which indicates that the removal effect for the unnecessary components is improved. However, as shown in Table 7, when the particle diameter distributions are compared, as the temperature for treatment is increased, the representative diameter becomes small and the particle diameter distribution shifts to the smaller diameter side. The reason for this is presumed that the treatment at an increased temperature advances the dissolution effect on the surfaces of the abrasive particles. This is presumed to also affect the polishing effect, and further, in view of the energy required for increasing the temperature for treatment, the treatment is desirably conducted at a temperature of 100°C or lower.

[0079] (Example 18) Treatment with another acid

Using, as a raw material, the used slurry discharged from a glass polishing process and comprised mainly of cerium oxide and lanthanum oxide, which is the same as that used in Example 4, the treatment test shown below was conducted.

[0080] 500 mL of the above-mentioned test raw material slurry, which had been well stirred so as to be in a uniform state, was placed in a glass beaker having a capacity of 2 L and further well stirred using a stirrer (rotational speed for stirring: 300 rpm). A concentrated H₂SO₄ having a concentration of 98% was added to the resultant slurry until the pH became 1.5. After adding H₂SO₄, the resultant slurry was further stirred at normal temperature (about 25°C) for 10 minutes, and then the stirring was stopped, followed by natural sedimentation for 20 minutes. The supernatant phase was removed using a tubular pump and the sediment phase was washed with pure water in the same manner as in Experiment 2, and the resultant solid material concentrated slurry was subjected to filtration, followed by drying under conditions in an atmosphere of air at 105°C. The results of the compositional analysis made on the obtained sample are shown in Table 8.

[0081] [Table 8]

Treatment conditions	Abrasive main components						Unnecessary components					
	TREO + F	CeO ₂	La ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	F	SiO ₂	Al ₂ O ₃	CaO	(Si+Al+Ca)	(TERO+F) /(Si+Al+Ca)	Change ratio
Raw material (obtained by directly drying slurry)	90.24	55.40	27.30	3.30	0.39	3.85	3.93	0.39	0.53	4.85	18.6	-
Example 18	92.96	59.50	25.40	3.44	N.D	4.62	2.47	0.10	0.22	2.80	33.2	1.8

[0082] In the present Example, like the other Examples, a removal effect for the unnecessary components was able to be obtained. However, the present Example has the following problems. The viscosity of the slurry is increased during the acid treatment, and it is difficult to remove the sulfur content derived from sulfuric acid. In the present Example, after the acid treatment, repulping washing using pure water was repeated three times until the slurry amount became 500 ml, but the content of sulfur which is undetectable in the raw material remained in an amount of 0.8%, and thus the washing was relatively difficult.

[0083] (Example 19)

The present Example shows an example of a treatment using a screw decanter. The results of XRF compositional analysis for the unused abrasive (virgin product) as a reference for the test and the abrasive used in a glass polishing process (used product) are shown in Table 9.

[0084] [Table 9]

	TREO	CeO ₂	La ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	F	SiO ₂	Al ₂ O ₃	BaO	ZnO
Virgin product	95.2	61.7	29.7	3.81	N.D.	3.68	0.13	0.11	N.D.	N.D.
Used product	80.9	53.8	24.9	2.26	N.D.	N.D.	11.6	1.53	4.85	0.23

[wt%]

[0085] The above-mentioned used abrasive and water were mixed together so that the concentration of the used abrasive is 10 wt% in terms of the dry weight, and the slurry was stirred for 10 minutes. While stirring, HCl having a concentration of 17.5% was added to the slurry to adjust the pH of the slurry to 1.3.

Screw decanter PTM015, manufactured by Tomoe Engineering Co., Ltd., was operated under conditions such that the centrifugal force was 1,500 G and the rotational speed difference between the main motor and the screw conveyor was 10 rpm, and the above-obtained used abrasive slurry was supplied to the screw decanter at a speed of 6.0 l/minute. At the outlet of the screw decanter, a dehydrated cake formed from concentrated solids and waste liquid were individually recovered. The dehydrated cake was dried in an atmosphere of air at a temperature of 100°C for 10 hours, and an XRF analysis for the obtained dry cake was made.

Further, the recovered dry cake and water were mixed together so that the concentration is 10 wt% in terms of the dry weight, and the slurry was repeatedly subjected to the above-mentioned series of the treatment with HCl and the treatment using a screw decanter. The cycle for the treatment was repeated 3 times. The results of the XRF analysis for the dry cake recovered in each cycle for the treatment made are shown in Table 10.

[0086] [Table 10]

Cycle for treatment	TREO	CeO ₂	La ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	F	SiO ₂	Al ₂ O ₃	BaO	ZnO
1st	85.3	52.5	29.2	3.04	0.52	N.D.	12.5	0.23	0.50	N.D.
2nd	85.1	53.4	28.5	2.73	0.45	2.16	10.8	0.23	0.38	N.D.
3rd	88.9	57.8	28.0	2.59	0.47	1.78	8.0	0.17	N.D.	N.D.

[wt%]

[0087] It is found that the repeated treatment using a screw decanter improves the removal effect for impurities, and the effect of recycling is obtained. By the repeated treatment, the total amount of TREO and fluorine, which are the effective components of the abrasive, contained in the recovered abrasive tends to increase.

INDUSTRIAL APPLICABILITY

[0088] By the present invention, an abrasive having polishing performance equivalent to that of an unused new abrasive can be recycled from abrasive waste by an easy method at high removal rate for the silicon component and aluminum component. Therefore, the present invention is industrially useful also from an economical point of view and from the viewpoint of protection of the environment.

CLAIMS

1. A method for recycling an abrasive from a used cerium oxide based abrasive for glass, wherein the method comprises the step of adjusting the pH of a slurry of a used cerium oxide based abrasive for glass to be within the range of from 0.5 to 3.0.
2. The method for recycling an abrasive according to claim 1, wherein hydrochloric acid or sulfuric acid is used as an agent for adjusting the pH.
3. The method for recycling an abrasive according to claim 1 or 2, wherein the temperature at adjusting the pH of the slurry of the used cerium oxide based abrasive for glass is 100°C or lower.
4. The method for recycling an abrasive according to any one of claims 1 to 3, wherein the method comprises the steps of: dispersing the used cerium oxide based abrasive for glass in water to obtain a slurry, adjusting the pH of the slurry to be within the range of from 0.5 to 3.0, and recovering an abrasive from the slurry.
5. The method for recycling an abrasive according to any one of claims 1 to 4, wherein, in the step of recovering an abrasive from the slurry, for separating and recovering the phase comprised mainly of the abrasive particles which have settled, the supernatant phase is removed while letting the abrasive particles remain in a settling state.