

DESCRIPTION

TITLE OF INVENTION: Alkali silicate aqueous solution and method for producing the same

TECHNICAL FIELD

[0001]

The present invention relates to an alkali silicate aqueous solution produced with plant ash (derived from plant) and a method for producing the same.

CROSS REFERENCE TO RELATED APPLICATIONS

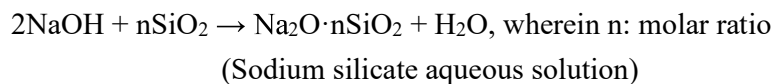
This application claims priority to Japan Patent Application No. 2022-062996, filed on Apr. 5, 2022, the entire description of which is incorporated herein by reference.

BACKGROUND ART

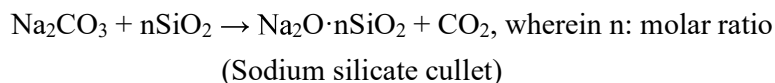
[0002]

Sodium silicate, also known as "water glass", is widely used as a raw material for wet process silica and synthetic zeolite in fields relating to e.g. a soil hardener for civil engineering and construction, detergents, fibers and pulp. Common and widely known methods of producing sodium silicate include a wet method (chemical formula A), in which a natural sand (e.g. silica sand, silica stone or silicate clay) with a high silica (SiO_2) component are dissolved in a sodium hydroxide solution, or a dry method (chemical formula B), in which a sand and a soda ash are mixed, placed in a melting furnace, taken out when it becomes a transparent body and cooled and solidified.

- Chemical formula A



- Chemical formula B



[0003]

The conventional wet process silica made from sodium silicate that is derived from sand has a high BET specific surface area and has pores of from micro to meso, and is therefore widely used in a wide variety of applications, e.g. a reinforcing filler for industrial rubbers, tires and silicone rubbers, a paper filler, a matting agent for paints, and an abrasive for toothpastes as well as an anti-blocking agent for films.

[0004]

In recent years, there has been an increasing demand to realize a society that is sustainable and renewable for protecting the global environment. Biomass technologies that do not use fossil fuels, such as a biomass boiler and a biomass power generation, are spreading in many regions as one of the specific measures to achieve that goal. Facilities using such technology often use plants with a high silica content (gramineous plant such as rice husk, rice straw, wheat straw, bagasse, and bamboo) as a fuel. However, these facilities face a problem of the disposal of combustion ash (plant ash) which has a high silica content.

[0005]

Accordingly, an attempt as a solution method for this problem has been made for a while now to produce a silicate aqueous solution containing alkali components by dissolving the plant ash (especially a rice husk ash) containing a large amount of silica component in a sodium hydroxide aqueous solution and to produce the wet process silica from the alkali silicate aqueous solution (e.g., Patent Literature 1 and Patent Literature 2).

[0006]

Note that the silicate aqueous solution made from the plant ash as a raw material usually contain potassium in addition to sodium as an alkali component. Therefore, in the following description, a silicate containing the alkali component is referred to as an “alkali silicate” instead of the commonly used designation “sodium silicate” ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$), unless the alkali component is specifically restricted to sodium. The meaning of the alkali silicate referred in the present invention and the present specification includes a sodium silicate.

[0007]

Patent Literature 1: JP 2007-510613 A

Patent Literature 2: JP 2007-522069 A

The entire descriptions in Patent Literatures 1 and 2 are incorporated herein by reference.

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0008]

It is not impossible to produce an alkali silicate aqueous solution from a rice husk ash or other plant ashes and to produce a wet process silica, based on known techniques such as Patent Literature 1 and Patent Literature 2.

[0009]

However, the alkali silicate aqueous solution derived from plant ash contains

more impurities and foreign matters that cause coloration than in that made from sand, and also the wet process silica made from the colored alkali silicate aqueous solution becomes only a low-quality wet process silica that is rich in impurities and foreign matters and colored (low whiteness). Therefore, the conventional wet process silica produced from the alkali silicate aqueous solution derived from plant ash can be used only in a limited application and usage, such as for use in inexpensive and universal applications, or for use of mixing a small amount of the alkali silicate aqueous solution derived from plant ash with an alkali silicate aqueous solution derived from sand.

[0010]

In case of the conventional alkali silicate derived from sand, it is possible to deal with the quality in impurities and the like by changing an origin place of sand according to a purpose of use since the quality of natural sand is homogeneous in each origin place. However, in case of using the plant ash, it is difficult to find a solution to the problems of impurities, foreign matters and coloration since the plant ash itself contains a large amount of impurities and foreign matters and is unstable in quality.

[0011]

For these reasons, the wet process silica made from the alkali silicate aqueous solution derived from plant ash are not as popular as expected.

[0012]

Furthermore, the methods of prior art, such as contacting with oxygen for a long time (Patent Literature 1) and combusting at a high temperature (Patent Literature 2), generate a large amount of carbon dioxide, consume a large amount of energy, and are not appropriate in terms of considerations for environmental issues in recent years.

[0013]

In addition, there is a demand from consumers who use the wet process silica, for a supply of a high-performance and high-quality wet process silica while using an environmentally friendly raw material (alkali silicate).

[0014]

The present invention has been made in view of the above problems, and an object of the present invention is to provide an alkali silicate aqueous solution derived from plant ash that enables to produce a wet process silica with a high quality having the same whiteness as that of the conventional alkali silicate aqueous solution derived from sand.

[0015]

The second object of the present invention is to provide a method for producing alkali silicate aqueous solution which enables to produce the alkali silicate aqueous

solution with such a sufficient quality.

SOLUTION TO PROBLEM

[0016]

The present inventors found that it is possible to produce a wet process silica with a high quality having the same whiteness as in case of the conventional alkali silicate aqueous solution derived from sand, by using an alkali silicate aqueous solution derived from plant ash having a high transmittance, as a raw material for producing the wet process silica, and they completed the present invention.

[0017]

The configuration of the present invention is as follows.

[1]

An alkali silicate aqueous solution having a ratio P_2O_5/SiO_2 of P_2O_5 concentration to SiO_2 concentration in mass% of 1.0×10^{-3} or more, SiO_2 concentration of 8.9 mass% to 16.7 mass%, and a transmittance (%T) through an optical path length 1 cm at a wavelength 500 nm of 65% or more.

[2]

The alkali silicate aqueous solution according to [1], having a ratio $SiO_2/(Na_2O+K_2O)$ of SiO_2 concentration to the concentration (Na_2O+K_2O) in mole% of 2.8 to 3.5.

[3]

The alkali silicate aqueous solution according to [1] or [2], having a ratio K_2O/Na_2O of K_2O concentration to Na_2O concentration in mole% of 0.03 to 0.30.

[4]

The alkali silicate aqueous solution according to any one of [1] to [3], wherein when the alkali silicate aqueous solution is filtered with a filter having an opening of 1 μm , the solid content captured on the filter is less than 100 mass-ppm with respect to the mass of the alkali silicate aqueous solution before the filtration.

[5]

The alkali silicate aqueous solution according to any one of [1] to [4], which is used as a raw material for wet process silica.

[6]

A method for producing alkali silicate aqueous solution, comprising subjecting a raw material alkali silicate aqueous solution obtained by mixing a plant ash containing a silica component, sodium hydroxide and water to one or both of a filtration treatment with a filter having an opening of less than 50 μm and an adsorption treatment with an

adsorbent to obtain the alkali silicate aqueous solution.

[7]

The method for producing alkali silicate aqueous solution according to [6], wherein the plant ash is a rice husk ash.

ADVANTAGEOUS EFFECT OF INVENTION

[0018]

The use of the alkali silicate aqueous solution derived from plant ash of the present invention as a raw material allows to produce a high-quality wet process silica having a whiteness comparable to that in the case of the conventional sodium silicate aqueous solution derived from sand.

[0019]

Furthermore, the producing method of the present invention can provide the alkali silicate aqueous solution derived from plant ash that allows to produce the high-quality wet process silica having a whiteness comparable to that in the case of the conventional alkali silicate aqueous solution derived from sand.

[0020]

In addition, the present invention allows to produce an environmentally friendly alkali silicate aqueous solution since plant ashes that would otherwise be discarded can be reused.

BRIEF DESCRIPTION OF DRAWINGS

[0021]

[Figure 1] FIG. 1 is an image showing filtration residues in coarse filtrations of alkali silicate aqueous solutions.

[Figure 2] FIG. 2 shows transmittance spectra of alkali silicate aqueous solutions (Example 4, Comparative Example 1, and Comparative Example 4) at a wavelength 200 nm to 800 nm.

[Figure 3] FIG. 3 shows transmittance spectra of alkali silicate aqueous solutions (Example 1, Example 5, and Reference Example 1) at a wavelength 200 nm to 800 nm.

[Figure 4] FIG. 4 shows a transmittance spectrum of an alkali silicate aqueous solution (Comparative Example 3) at a wavelength 200 nm to 800 nm.

EMBODIMENTS OF INVENTION

[0022]

<Alkali silicate aqueous solution>

The alkali silicate aqueous solution of the present invention is an alkali silicate aqueous solution having a ratio P_2O_5/SiO_2 of P_2O_5 concentration to SiO_2 concentration in mass% of 1.0×10^{-3} or more, SiO_2 concentration of 8.9 mass% to 16.7 mass%, and a transmittance (%T) through an optical path length 1 cm at a wavelength 500 nm of 65% or more.

[0023]

The alkali silicate aqueous solution of the present invention is produced with a plant ash, which is a combustion ash of a plant containing a silica component. Plant ash contains a phosphorus component, and a phosphoric acid in oxide equivalent (P_2O_5) is a component inherent in plant ash. The alkali silicate aqueous solution of the present invention obtained by using the plant ash as a main silica source has the ratio of P_2O_5 concentration to SiO_2 concentration in mass% higher than that of the alkali silicate aqueous solution derived from sand, and the ratio P_2O_5/SiO_2 is 1.0×10^{-3} or more. Generally, the ratio P_2O_5/SiO_2 in the alkali silicate aqueous solution obtained by using only sand as a silica source is never 1.0×10^{-3} or more. Therefore, the presence of P_2O_5 based on the ratio P_2O_5/SiO_2 allows to determine that the alkali silicate aqueous solution is derived from plant ash (i.e., the plant ash is used in at least part of the silica source). The alkali silicate aqueous solution of the present invention may have the ratio P_2O_5/SiO_2 of 1.5×10^{-3} or more, 1.8×10^{-3} or more, or 2.0×10^{-3} or more. The upper limit of the ratio P_2O_5/SiO_2 is not particularly limited and depends on the type of plant ash, and is, for example, 20×10^{-3} or less. The ratio P_2O_5/SiO_2 is preferably 15×10^{-3} or less, more preferably 13×10^{-3} or less, and still more preferably 10×10^{-3} or less from the viewpoint of reducing impurities.

[0024]

The alkali silicate aqueous solution of the present invention has a transmittance (%T) through an optical path length 1 cm at a wavelength 500 nm of 65% or more.

[0025]

Normally, the plant ash contains a large amount of impurities or foreign matters. When the alkali silicate aqueous solution is produced by a conventional method with the plant ash containing a large amount of impurities or foreign matters, the impurities or foreign matters are mixed into the alkali silicate aqueous solution, and thus the transmittance (%T) decreases. The transmittance of the alkali silicate aqueous solution of the present invention is set to 65% or more by reducing the amount of impurities and foreign matters. The wet process silica having a high whiteness can be easily produced due to the transmittance of 65% or more. The alkali silicate aqueous solution of the present invention has a transmittance of preferably 70% or more, more preferably 80%

or more, and still more preferably 90% or more. In particular, when the transmittance is 80% or more, the wet process silica with a high whiteness of 90 or more can be easily produced.

[0026]

The transmittance (%T) refers to a measured value at a wavelength 500 nm measured by a spectrophotometer with a 10 mm square cell (standard type, optical path length 1 cm) made of borosilicate glass, using pure water as a comparative standard. The wavelength 500 nm is a wavelength near the border between blue and green in the visible-light wavelength (380 nm to 780 nm) and is easily correlated with the whiteness of silica.

[0027]

The alkali silicate aqueous solution of the present invention has SiO_2 concentration of 8.9 mass% to 16.7 mass%. Generally, the alkali silicate aqueous solution used as a raw material for wet process silica has SiO_2 concentration within the above range. Therefore, SiO_2 concentration within the above range allows the alkali silicate aqueous solution of the present invention to be easily used in the same applications as existing alkali silicate aqueous solutions.

[0028]

The alkali silicate aqueous solution of the present invention comprises a sodium component and a potassium component derived from plant ash. The alkali silicate aqueous solution of the present invention preferably has the ratio $\text{SiO}_2/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ of SiO_2 concentration to the concentration $(\text{Na}_2\text{O}+\text{K}_2\text{O})$ in mole% of 2.8 to 3.5. Generally, the alkali silicate aqueous solution used as a raw material for wet process silica has the molar ratio $\text{SiO}_2/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ (usually an amount of K_2O is very low) in the range of 2.8 to 3.5. Therefore, the molar ratio $\text{SiO}_2/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ within the above range allows the alkali silicate aqueous solution of the present invention to be easily used in the same applications as existing alkali silicate aqueous solutions.

[0029]

The alkali silicate aqueous solution of the present invention preferably has the ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ of K_2O concentration to Na_2O concentration in mole% of 0.03 to 0.30. The molar ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ of 0.30 or less reduces the quality stability problems in wet process silica, such as variations in neutralization reactions during neutralization synthesis of wet process silica. The molar ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ of 0.03 or more allows to easily adjust the molar ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$, for example, by mixing with another type of alkali silicate, such as an alkali silicate derived from sand. The molar ratio $\text{K}_2\text{O}/\text{Na}_2\text{O}$ is preferably in the range of 0.04 to 0.20, more preferably in the range of 0.05 to 0.15.

[0030]

The molar ratio K_2O/Na_2O in alkali silicate can be one of the criteria for determining whether the alkali silicate is derived from plant ash. Usually, the alkali silicate derived from sand has the molar ratio K_2O/Na_2O less than 0.01. Therefore, when the molar ratio K_2O/Na_2O is 0.01 or more, the alkali silicate aqueous solution can be considered to contain the plant ash in many cases, except where it is clear that K_2O concentration is adjusted to increase by a post-treatment.

[0031]

The total ($Na_2O + K_2O$) of Na_2O and K_2O concentrations can be, for example, 3.5 mass% to 5.0 mass%. Generally, the alkali silicate aqueous solution used as a raw material for wet process silica has the total concentration of $Na_2O + K_2O$ (usually an amount of K_2O is very low) in the range from 3.5 mass% to 5.0 mass%. Therefore, the total concentration of $Na_2O + K_2O$ within the above range allows the alkali silicate aqueous solution of the present invention to be easily used in the same applications as existing alkali silicate aqueous solutions.

[0032]

When the alkali silicate aqueous solution of the present invention is filtered by a filter having an opening (particle retention ability) of 1 μm , the solid content captured on the filter is preferably less than 100 mass-ppm with respect to the mass of the alkali silicate aqueous solution before the filtration. The solid content is preferably less than 90 mass-ppm, and more preferably less than 80 mass-ppm, with respect to the mass of the alkali silicate aqueous solution before the filtration. In particular, when the adsorption treatment and filtration described later are performed, the solid content may be less than 50 mass-ppm, preferably less than 40 mass-ppm, and more preferably less than 30 mass-ppm.

[0033]

The material of the filter to be used is not particularly limited as long as it has an opening of 1 μm . For example, the filtration is performed with a test filter paper (for example, Grade 5C, ADVANTEC Co., Ltd.), the filter paper is washed sufficiently with pure water and dried at 105°C for 2 hours. The mass% concentration of the undissolved residue can be determined by the following formula based on the mass of the solid content remaining on the filter paper (mass of the undissolved residue) and the mass of the alkali silicate aqueous solution subjected to the filtration.

[Mathematical formula 1]

Undissolved residue (mass-ppm)

$$= \frac{\text{Mass (g) of undissolved residue}}{\text{Total mass (g) of alkali silicate aqueous solution subjected to filtration}} \times 1,000,000$$

[0034]

According to experiments conducted by the present inventors, it was found that the problem of coloration in the conventional wet process silica derived from plant ash is caused by impurities and foreign matters in the alkali silicate aqueous solution derived from plant ash. That is, many impurities and foreign matters exist in the conventional alkali silicate aqueous solutions derived from plant ash, and the impurities and the foreign matters cloud and color the alkali silicate aqueous solutions. Then, as a result of producing the wet process silica with such an alkali silicate aqueous solution, the impurities and foreign matters are mixed into the wet process silica, resulting in a problem that the whiteness of the wet process silica decreases.

[0035]

As will be described later, the plant ash contains a carbon component remaining due to uncombustion, and insoluble foreign matters such as a graphite-based foreign matter and a glass silica component, and thus undissolved residues are easily generated in the alkali silicate aqueous solutions derived from plant ash. When the wet process silica is produced using, as a raw material, the alkali silicate aqueous solution containing a large amount of undissolved residues, a large amount of impurities and foreign matters are mixed into the wet process silica. For example, in matting applications, these foreign matters are scattered on the surface after coating to form protrusions, which degrade the matting performance and impair the aesthetic quality of appearance. In addition, the contamination of impurities and foreign matters into the wet process silica is not preferable even in applications such as industrial rubber, tire and toothpaste since the quality of the product is degraded. Therefore, the contamination of impurities and foreign matters into the wet process silica is suppressed by adjusting the mass% concentration of the undissolved residue in the alkali silicate aqueous solution in the above range, in order to obtain a wet process silica having a high whiteness.

[0036]

The alkali silicate aqueous solution of the present invention can be obtained by a method of the present invention for producing alkali silicate aqueous solution (a method for producing alkali silicate aqueous solution described later), in which one or both of

predetermined filtration treatment and adsorption treatment are performed. In addition, as shown in Examples, the alkali silicate aqueous solution of the present invention can be obtained also by a method for producing alkali silicate aqueous solution that comprises obtaining a plant ash with a high whiteness by the predetermined combustion process described in the present specification and mixing the plant ash, sodium hydroxide and water.

[0037]

As a comparison, for example, the methods of Patent Literatures 1 and 2 do not perform purification treatments, such as the filtration treatment, on the obtained alkali silicate aqueous solution. Therefore, the conventional alkali silicate aqueous solution as described above is not transparent due to the presence of the impurities and foreign matters in plant ash, and thus it is not possible to produce a wet process silica with a high whiteness. This is demonstrated by the result of Comparative Example 3 described in Examples.

[0038]

<Method for producing alkali silicate aqueous solution>

The method of the present invention for producing alkali silicate aqueous solution comprises subjecting a raw material alkali silicate aqueous solution obtained by mixing a plant ash containing a silica component, sodium hydroxide and water to one or both of a filtration treatment with a filter having an opening of less than 50 μm and an adsorption treatment with an adsorbent to obtain the alkali silicate aqueous solution. This producing method allows to obtain the alkali silicate aqueous solution of the present invention described above.

[0039]

<Plant ash containing silica component>

The plant ash used in the production of the alkali silicate aqueous solution of the present invention is a combustion ash of a plant material containing a silica component. The type and part of the plant material are not particularly limited as long as they are a plant and a part containing the silica component. The plant containing the silica component includes, for example, a gramineous plant such as rice plant (rice straw, rice husk), wheat, sugarcane, and bamboo. The rice husk after threshing is most preferable because they are less contaminated, such as sludge adhesion, and are collected in a collection station and easily obtained.

[0040]

The quality of the plant ash used in the present invention is not particularly limited, but it is preferable to use a plant ash with a low content of a carbon component

and a high whiteness from the viewpoint of industrially efficiently producing the alkali silicate aqueous solution containing less impurities and foreign matters. The amount of carbon in the plant ash is preferably 2 mass% or less, and preferably 1 mass% or less. The lower limit of the amount of carbon in the plant ash is not particularly limited, and is practically 0.05 mass% or more, and may be 0.1 mass% or more. The plant ash preferably has a whiteness of 30 or more, more preferably 40 or more, and even more preferably 50 or more. The upper limit of the whiteness of the plant ash is not particularly limited, and is practically 90 or less, and may be 70 or less.

[0041]

It is preferable to use a combustion furnace capable of combusting plant materials at 550°C to 900°C while allowing it to flow, in order to obtain the plant ash with a high whiteness and low impurities and foreign matters as described above. The combustion temperature is more preferably 600°C to 800°C, even more preferably 650°C to 750°C.

[0042]

Here, the relationship between the above-described combustion method in which the plant material containing the silica component is combusted at 550°C to 900°C while allowing it to flow, and the impurities/foreign matters in the plant ash will be described. The present inventors investigated in detail the type of impurities and foreign matters in the plant ash and the cause of the occurrence thereof in order to produce the plant ash with a high whiteness. As a result, it was found that the plant material tends to become uncombusted and the water-soluble hydrocarbon component tends to remain in the plant ash when combusted at a temperature lower than 550°C or when the combustion is uneven due to insufficient material flow or the like. The water-soluble hydrocarbon component dissolves in the alkali silicate aqueous solution and are difficult to be removed by filtration, causing coloration of the aqueous solution. Furthermore, it was found that, when sufficient oxygen is not supplied during combustion, the hydrocarbon component in the plant material carbonizes to form the insoluble graphite-based foreign matter in the plant ash. In addition, it was found that, when the plant material was combusted at a combusting temperature over 700°C at once, a glass silica component was easily formed in the plant ash as the insoluble foreign matters. In this case, it was revealed that the silica component on the surface of the material was vitrified, which tends to cause a state of uncombustion and oxygen deficiency inside the material, and that the water-soluble hydrocarbon component and the insoluble graphite-based foreign matter are also easily generated. When an alkali silicate aqueous solution is produced with the plant ash obtained by the combustion under high temperature at once, the water-soluble

hydrocarbon component and the insoluble graphite-based foreign matter in addition to the glass silica component are mixed into the alkali silicate aqueous solution, and thus the quality of the alkali silicate aqueous solution is remarkably deteriorated. Moreover, it was confirmed that a certain amount of the impurities and foreign matters, such as the water-soluble hydrocarbon component, the insoluble graphite-based foreign matter and the glass silica component, are present in the plant ash even if they appear to be a white ash at first glance. In consideration of the above-described generation process of the impurities and foreign matters in the plant ash, it is effective for obtaining a plant ash with a high whiteness to uniformly combust the plant material under sufficient oxygen while suppressing the vitrification of the silica component by the above-described combustion method.

[0043]

The above combustion method preferably uses a combustion furnace for combustion of the plant material. The type of the combustion furnace is not particularly limited. As described above, in order to obtain the plant ash with a high whiteness and less impurities or foreign matters, it is preferable to use the combustion furnace provided with a flow device that flows the plant material during the combustion, wherein the combustion furnace is capable of combusting the plant material at 550°C to 900°C while allowing it to flow. For example, the combustion furnace may be a direct combustion furnace in which the plant material is combusted with oxygen, or a gasification combustion furnace in which the plant material is heated in an oxygen-free or low oxygen state to generate an organic gas, and then the material is combusted. When the plant ash contains a large amount of the graphite-based foreign matter, the carbon component may be removed, for example, by secondary combustion in the same combustion furnace while reusing the heat from the primary combustion.

Such a method makes the plant ash a better silica source for the alkali silicate aqueous solution of the present invention, since the quality of the plant ash is more stable.

[0044]

<Sodium hydroxide aqueous solution>

The producing method of the present invention may use known sodium hydroxide and water. In the manner mixing the sodium hydroxide aqueous solution and the plant ash, the concentration of the sodium hydroxide aqueous solution is not particularly limited, and a known one can be used. Generally, it is preferable to mix the sodium hydroxide aqueous solution having the highest possible concentration with the plant ash, and then dilute them with water so as to obtain the desired SiO₂ concentration from the viewpoint of the productivity of the alkali silicate aqueous solution. Meanwhile,

when the concentration of the sodium hydroxide aqueous solution is too high, the plant ash may be difficult to be fed into the sodium hydroxide aqueous solution since the plant ash has a very small apparent density. The concentration of the sodium hydroxide aqueous solution is practically 20 mass% or less, may be 15 mass% or less or 10 mass% or less from the viewpoint of facilitating mixing of the plant ash and the sodium hydroxide aqueous solution.

[0045]

<Detailed production conditions of alkali silicate aqueous solution>

The alkali silicate aqueous solution of the present invention is obtained by mixing the plant ash containing a silica component, sodium hydroxide and water. The order of mixing the plant ash, sodium hydroxide and water is not particularly limited. The plant ash and sodium hydroxide may be put in water simultaneously or separately, a mixture of the plant ash and sodium hydroxide may be put in water, the plant ash may be put in a sodium hydroxide aqueous solution in which sodium hydroxide is dissolved in water, and the sodium hydroxide may be put in an aqueous solution in which the plant ash is dissolved in water.

[0046]

The amounts and mixing ratios of the water, the sodium hydroxide, and the plant ash to be used can be appropriately adjusted according to conditions, such as the type of the plant ash, the target SiO_2 concentration of the alkali silicate aqueous solution, and the applications. Since the glass silica component is difficult to dissolve, it is not necessary to dissolve all of the silica components in the plant ash in the aqueous solution. If the method is such that approximately 90 mass% to 95 mass% of the silica component in the plant ash is dissolved, an alkali silicate aqueous solution can be produced with good productivity in terms of energy consumption and time.

[0047]

For example, assuming that 90% of the silica component contained in the plant ash is dissolved in an aqueous solution, when a mass of plant ash approximately 3 times the mass of sodium hydroxide in the aqueous solution is fed and dissolved, the ratio $\text{SiO}_2/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ of SiO_2 concentration to the concentration $(\text{Na}_2\text{O}+\text{K}_2\text{O})$ in mole% is easily adjusted to 2.8 to 3.5.

[0048]

In the producing method of the present invention, other conditions for mixing and dissolving the plant ash, sodium hydroxide and water are not particularly limited.

[0049]

The mixing and dissolving is performed, for example, in a dissolving tank

(container) with stirring and appropriately selecting from ranges of 60°C to 100°C and 1 hour to 5 hours under an ordinary pressure (atmospheric pressure) or an additional pressure.

[0050]

The producing method of the present invention comprises subjecting the raw material alkali silicate aqueous solution to one or both of the filtration treatment with the filter having an opening of less than 50 μm and the adsorption treatment with the adsorbent to obtain the alkali silicate aqueous solution. As described above, the conventional plant ash contains the graphite-based foreign matter, a foreign matter of the vitrified silica component, and impurities such as water-soluble hydrocarbon compounds. When these impurities and foreign matters are mixed into the alkali silicate aqueous solution and the wet process silica, they become colored. Therefore, it is not possible to obtain the wet process silica of the quality which the present invention aims, for example, only by conventionally dissolving the plant ash in the sodium hydroxide aqueous solution. The present invention allows to remove the impurities and foreign matters in the alkali silicate aqueous solution by performing one or both of the above-described filtration treatment and adsorption treatment on the raw material alkali silicate aqueous solution.

[0051]

The opening of the filter used in the filtration treatment is less than 50 μm in order to remove the insoluble foreign matters. The opening of the filter is preferably 40 μm or less, more preferably 30 μm or less, and still more preferably 20 μm or less from the viewpoint of more sufficiently removing the foreign matters. The filterability (productivity) is significantly deteriorated when the opening of the filter is 10 μm or less, so the opening of the filter may be appropriately selected in consideration of the productivity and quality. The material of the filter is not particularly limited, and various filters such as filter paper, filter cloth, and membrane filter can be used. The filtration treatment with the filter having an opening of less than 50 μm may be performed a plurality of times from the viewpoint of more sufficiently removing the foreign matters. In the case where the filtration treatment is performed a plurality of times, it is common practice to perform in descending order of the opening.

[0052]

Furthermore, the producing method of the present invention may perform a filtration treatment with a filter having an opening of 50 μm or more before performing the filtration process with the filter having an opening of less than 50 μm . The filtration treatment with the filter having an opening of 50 μm or more can be appropriately performed as necessary, for example, when there are many undissolved coarse particles.

[0053]

The adsorption treatment can remove water-soluble impurities that are difficult to be removed by the filtration treatment.

[0054]

The presence or absence of the adsorption treatment is appropriately determined according to the amount and type of impurities in the alkali silicate aqueous solution. For example, the alkali silicate aqueous solution having the above-described transmittance (%T) of less than 10% at a wavelength 500 nm is preferably subjected to both the filtration and adsorption treatments.

[0055]

In contrast, when the transmittance (%T) of 65% or more can be achieved after any one of the treatments (for example, when there are few impurities or foreign matters in the plant ash), only one of the filtration and adsorption treatments may be used. Specifically, when it is sufficient to remove insoluble foreign matters, only filtration may be performed, and when it is sufficient to remove water-soluble impurities, only adsorption treatment may be performed. Moreover, one or both of the filtration and the adsorption treatment may be performed on the alkali silicate aqueous solution having a transmittance (%T) of 65% or more in order to further improve the transmittance thereof, and the filtration may be performed again following the adsorption treatment after filtration, in order to remove the remaining adsorbent.

[0056]

The adsorbent used in the adsorption treatment is not particularly limited, and a known adsorbent can be used. Examples of the adsorbent include diatomaceous earth, clay minerals, activated carbon, zeolite, silica gel, and activated alumina. The adsorbent is preferably an activated carbon. The time of the adsorption treatment can be appropriately adjusted according to the amount of impurities and foreign matters in the alkali silicate aqueous solution, and is, for example, 12 hours to 40 hours, and preferably 15 hours to 30 hours. The amount of the adsorbent used in the adsorption treatment can be appropriately adjusted according to the amount of impurities in the alkali silicate aqueous solution, and is, for example, 5 g to 20 g per 1,000 g of the alkali silicate aqueous solution, and may be 8 g to 15 g.

[0057]

Since the silica component and the alkali component in the plant ash are not constant, K_2O and SiO_2 concentrations in the alkali silicate aqueous solution tends to vary. Therefore, the final concentration adjustment and an adjustment of each molar ratio are performed as necessary, after one or both of the filtration treatment and the adsorption

treatment is performed. SiO_2 mass% can be adjusted by a water-dilution or adding an additional silica material (e.g. commercially available silica powder). The ratio $\text{SiO}_2/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ of SiO_2 concentration to the concentration $(\text{Na}_2\text{O}+\text{K}_2\text{O})$ in mole% can be adjusted by adding sodium hydroxide.

[0058]

<Other conditions of alkali silicate aqueous solution>

In the alkali silicate aqueous solution of the present invention, a silica material derived from sand (silica sand, silica stone, silicate clay, etc.) may be used as a part of the silica source. When the quality of the wet process silica is emphasized, the proportion of the silica material derived from sand can be increased, and when the environmentally friendly (recycling of plant ash) is emphasized, the proportion of the plant ash can be increased. It is preferable to use as much plant ash as possible from the viewpoint of environmentally friendly. The proportion of plant ash in the silica source is preferably 60 mass% or more, more preferably 80 mass% or more, and still more preferably 90 mass% or more. The preparation of the raw material alkali silicate aqueous solution may not use the silica material derived from sand as the silica source, and the amount of plant ash may be 100 mass%.

[0059]

The silica material derived from sand may be added as part of the silica source in preparing the alkali silicate aqueous solution. Also, the silica material derived from sand may be used in a manner in which the alkali silicate aqueous solution derived from plant ash and the sodium silicate aqueous solution derived from sand are separately prepared and mixed before the aqueous solution is used.

[0060]

The alkali silicate aqueous solution of the present invention may contain an additive as necessary. The additive is not particularly limited, and known additives can be used. For example, an aluminium oxide (Al_2O_3) source such as sodium aluminate may be added. The wet process silica produced from the alkali silicate aqueous solution containing such an additive has an effect of improving the reinforcing performance as a reinforcing agent for silicone rubber, industrial rubber, and tire.

[0061]

As described above, according to the producing method of the present invention, impurities and foreign matters in the plant ash, such as the graphite-based foreign matter, the foreign matter of the vitrified silica component, and the water-soluble hydrocarbon compounds, can be sufficiently removed from the alkali silicate aqueous solution. As a result, it is possible to provide the alkali silicate aqueous solution derived from plant ash

that allows to produce a high-quality wet process silica having a whiteness comparable to that in the case of the conventional alkali silicate aqueous solution derived from sand.

[0062]

In addition, the present invention allows to provide an environmentally friendly alkali silicate aqueous solution since plant ashes that would otherwise be discarded can be reused. Moreover, the alkali silicate aqueous solution obtained by the producing method of the present invention has a small content of impurities and foreign matters and thus allows to produce the high-quality wet process silica.

[0063]

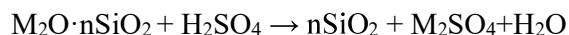
<Use application of alkali silicate aqueous solution>

The alkali silicate aqueous solution of the present invention can be used as a raw material for producing the wet process silica. Although the alkali silicate aqueous solution of the present invention is derived from plant ash, the transmittance (%T) is 65% or more, and the content of impurities and foreign matters causing coloration is small. The use of the alkali silicate aqueous solution of the present invention as a raw material allows to produce a high-quality wet process silica having a whiteness comparable to that in the case of the conventional alkali silicate aqueous solution derived from sand, despite being produced with the plant ash. In addition, the alkali silicate aqueous solution of the present invention has a small content of impurities and foreign matters and thus allows to produce the high-quality wet process silica with little impurities and foreign matters.

[0064]

The type of the wet process silica produced using the alkali silicate aqueous solution of the present invention as a raw material is not particularly limited, and may be, for example, a precipitated silica (white carbon) or a gel-process silica. This is because all processes to deposit silica from alkali silicate aqueous solution for wet process silica show basically the same tendency. An example of the process for synthesizing wet process silica is shown below (Chemical Formula C).

-Chemical Formula C (example of synthesis process of wet process silica)



Here, M represents an alkali containing sodium and potassium, and n represents a molar ratio.

[0065]

The wet process silica produced using the alkali silicate aqueous solution of the present invention as a raw material has high whiteness and low foreign matter, and therefore has sufficient reinforcing properties as a reinforcing filler for industrial rubber and tire. Furthermore, it can be used in applications that emphasize transparency and

whiteness, such as a reinforcing filler for silicone rubbers, a paper filler (anti-bleed-through agent), a matting agent for paints, an abrasive such as for toothpastes, and an anti-blocking agent for films, as well as known alkali silicate aqueous solutions derived from sand.

[0066]

Furthermore, the alkali silicate aqueous solution of the present invention can be used also in known applications other than the wet process silica, for example, a raw material for synthetic zeolite, a soil hardener for civil engineering and construction as well as an additive for detergents, fibers and pulp, since the alkali silicate aqueous solution of the present invention has low impurities and foreign matters. The use of alkali silicate aqueous solutions of the present invention reduces the problem of contamination caused by the foreign matters in materials and products as described above, compared to the conventional alkali silicate aqueous solutions derived from plant ash.

EXAMPLES

[0067]

Specific examples will be described below. However, it is not intended to be limited thereto.

[0068]

<Combustion conditions of plant ash>

The plant materials used to produce the plant ash were rice husk and rice straw. The rice husk and rice straw were thoroughly dried at 125°C for 2 hours. A 500 g of rice husk (apparent density: about 110 g/L) or a 250 g of rice straw that is cut into about 10 cm was put into a 2 mm thick stainless-steel sagger (300 mm × 300 mm × 115 mm (height)) with an air hole and a lid, and this was stacked in two stacks and burned in a tabletop muffle furnace (model: KDF S100G, DENKEN Co., Ltd.) under an air atmosphere. Since only about 200 g of plant ash can be obtained at most at one time, the combustion process was performed several times under the same conditions until the required amount of plant ash was obtained, and finally mixed. In addition, in case of the combustion at 900°C, a mullite sagger (outer size 210 mm × 210 mm × 70 mm (height), inner size 194 mm × 194 mm × 56 mm (height)) with an air hole and a lid was used instead of the stainless-steel sagger.

[0069]

Six types of plant ashes, Ash a to Ash f, were obtained by the above method. The combustion condition of each sample is shown in Table 1 below. In Table 1, the combustion condition where a plurality of combustion processes are shown represents

performing pre-combustion (one or more) at 500°C, stirring the removed ash, and then performing the following combustion process. For example, the combustion condition of Ash b "500°C, 2 hr, 600°C, 2 hr" in Table 1 represents performing one pre-combustion at 500°C for 2 hours and then performing a combustion process at 600°C for 2 hours. Plant Ash f is an ash obtained by combusting a rice husk at 700°C for 2 hours without flowing the material in an air-rich state according to the method described in Patent Literature 1.

[0070]

<Analysis of plant ash>

●Whiteness of plant ash

The measurement was performed with a whiteness meter (model: NW-12, NIPPON DENSHOKU INDUSTRIES Co., Ltd.).

[0071]

●Carbon content in plant ash (mass%)

The carbon content was measured with a carbon analyzer (model: CS744, LECO JAPAN Co., Ltd.) by an oxygen stream combustion-non dispersive infrared absorption method, in which the sample was heat-treated at a temperature of 1,350°C, an oxygen inflow pressure of 0.24 MPa, and a measurement time of 50 seconds, and CO and CO₂ gases were quantified with an infrared detector (NDIR) in the analyzer. The plant ash was dried for 2 hours at 105°C as a pretreatment.

[0072]

●Composition of inorganic components other than carbon in plant ash (mass%)

Qualitative analysis was first performed for elements other than carbon with a scanning X-ray fluorescence analyzer (model: ZSX PrimusII, RIGAKU Co., Ltd.) to confirm the types of inorganic impurities detected. Subsequently, quantitative analysis of the detected inorganic impurities was performed. The measurement sample was prepared by placing the plant ash in a ring-shaped mold and performing pressure molding. The concentration (mass%) in the quantified inorganic composition (excluding carbon) was obtained by converting in oxide equivalent by an analysis software provided with the analyzer.

[0073]

●Ashing rate (mass%)

The mass% of the combusted ash after combustion was measured with respect to the mass of the plant, such as rice husk, after being sufficiently dried at 125°C for 2 hours.

[Mathematical formula 2]

$$\text{Ashing rate (mass\%)} = \frac{\text{Mass (g) of plant ash}}{\text{Mass (g) of plant before combustion}} \times 100$$

[0074]

● Apparent density of plant ash (bulk specific gravity) (g/L)

The apparent density of the plant ash was determined according to JIS K5101-12-1:2004 (Test methods for pigments - Apparent density or apparent specific volume - Loose packing method) with dedicated measuring instruments (a sieve having an opening of 0.5 mm, a funnel, a cylinder receiver with a capacity of 30 mL, a receiver stand, and a funnel stand). The sample (plant ash) was dropped over the sieve into the funnel with a brush, and the heap portion of the sample that had accumulated in a heap on the receiver was scraped off with a spatula, and then the mass of the sample was measured. The apparent density (bulk specific gravity) of the plant ash in a unit of g/L was calculated on the basis of the mass by the following formula.

[Mathematical formula 3]

$$\text{Apparent density (bulk specific gravity) (g/L)} = \frac{\text{Mass (g) of cylinder sample}}{30 \text{ (mL)}} \times 1000$$

[0075]

● Bulk density of plant ash (apparent specific gravity) (g/mL)

The bulk density of the plant ash was measured according to the section "7.8 Bulk Density" in JIS K6220-1:2015 (Rubber compounding ingredients-Organic chemicals-Test methods- Part 1: General) with dedicated measuring instruments (a cylinder with an internal diameter of 22.00 ± 0.05 mm and an inner depth of 100 mm, and a piston with an outer diameter of 21.80 ± 0.05 mm, a length of 115 mm, a mass of 190 g, and an internal cavity, which are made from a general steel). The piston was naturally dropped into the cylinder before the sample (plant ash) was put in, and the height of the piston protruding from the top of the cylinder was measured. Then, the weighed sample of about 1 g was placed in the cylinder, the piston was gently dropped over 5 seconds, the side wall of the cylinder was gently tapped with a piece of wood to make the piston fit well, and the height of the piston protruding from the top of the cylinder was measured. The bulk density (apparent specific gravity) in a unit of g/mL was calculated by the following equation with the change in the height of the piston protruding from the top of the cylinder and the bottom area in the cylinder.

[Mathematical formula 4]

Bulk density (apparent specific gravity) (g/mL)

$$= \frac{\text{Mass (g) of cylinder sample}}{\text{Change (cm) in piston height} \times \text{Bottom area (cm}^2\text{) in cylinder}}$$

[0076]

The content of carbon in the plant ash and the composition of the inorganic components other than carbon in each sample are as shown in Table 1.

[0077]

Combustion conditions and contained components of Ash a to Ash f:

[Table 1]

Plant ash		a	b	c	d	e	f
Plant (site)		Rice husk	Rice husk	Rice husk	Rice husk	Rice straw	Rice husk
Combustion condition (1 to 3 combustions)		500°C, 2hr	500°C, 2hr; 600°C, 2hr	500°C, 2hr; 700°C, 2hr	500°C, 2hr; 500°C, 2hr; 900°C, 2hr	500°C, 2hr; 500°C, 2hr	700°C, 2hr; Excess oxygen
Ashing rate mass%		24.1	19.2	19.5	19.1	17.4	26.2
Whiteness		20	43	44	49	26	5
Apparent density g/L		167	176	151	250	89	116
Bulk density g/mL		0.23	0.20	0.18	0.27	0.13	0.14
Ash composition mass%	Carbon content	7.56	0.191	0.137	0.000	1.43	28.1
	SiO ₂	85.97	93.12	93.37	91.7	75.90	66.00
	P ₂ O ₅	0.722	0.738	0.619	0.642	1.78	0.834
	Na ₂ O	0.231	0.220	0.263	0.193	0.276	0.152
	K ₂ O	3.559	3.73	3.49	2.80	11.53	3.178
	MgO	0.314	0.358	0.318	0.269	1.61	0.313
	CaO	0.690	0.673	0.664	0.609	2.57	0.641
	MnO	0.194	0.196	0.201	0.244	0.468	0.171

	ZnO	0.017	0.019	0.017	0.018	0.032	0.016
	Al ₂ O ₃	0.032	0.054	0.040	0.059	1.42	0.036
	Fe ₂ O ₃	0.060	0.110	0.322	2.23	0.881	0.068
	SO ₃	0.257	0.289	0.236	0.217	0.812	0.169
	Cl	0.363	0.291	0.230	0.051	1.143	0.333

[0078]

<Preparing method for alkali silicate aqueous solution>

●Primary treatment (mixing and filtering of materials)

A 1,740 g of sodium hydroxide aqueous solution adjusted to 5.8 mass% was charged into a 3 L stainless-steel container equipped with a stirrer, and heated to 85°C. Subsequently, a 300 g of plant ash was charged into the sample solution with continuous stirring and was dissolved over 2 hours while maintaining the temperature at 85°C, and the sample solution was cooled down to room temperature. Here, the target SiO₂ concentration was set at 12.0 mass% assuming that 90% of SiO₂ contained in the plant ash was dissolved in the sodium hydroxide aqueous solution. A magnetic buchner funnel (nutche) with 150 mm Φ was attached to a suction filtration bottle with a capacity of 3 L, and the sample solution was coarsely filtered through a polyester plain weave filter cloth (an opening of about 50 μm x 400 μm) with suction to remove an undissolved residue. As a result, an alkali silicate aqueous solution after the primary treatment was obtained.

[0079]

The undissolved residue was confirmed in all plant ashes, the amount of which was 10 to 20 mass% on a wet basis. This amount corresponds to about 1 to 4 mass% in terms of solid content after drying. FIG. 1 is a photograph of the undissolved residues of Plant Ash a to Plant Ash d and Plant Ash f. It is difficult to quantitatively evaluate the amount of undissolved residue due to the contained water, but it was not possible to confirm the correlation between the total amount of undissolved residue and the final combustion temperature. In contrast, the colors of the undissolved residues differed depending on the final combustion temperature. Specifically, the residue of Plant Ash d combusted at 900°C was a light yellow to white colored residue composed mainly of undissolved glass, the residues of the other were gray to black colored residues, and the lower the final combustion temperature, the darker black the undissolved residues were. Note that, when the alkali silicate aqueous solution was not obtained in the required amount after the above-mentioned filtration, the process was repeated a plurality of times under the same conditions, and finally mixed to obtain the sample.

[0080]

●Measurement of alkali concentration and SiO₂ concentration (simple measurement for adjusting concentration)

For the alkali silicate aqueous solution after the primary treatment, the alkali concentration (mass% concentration of Na₂O+K₂O) and SiO₂ concentration (mass% concentration) were measured by the titration method described below.

[0081]

Alkali concentration:

A conical beaker with a capacity of 300 mL was charged with about 2 g of the sample weighed to 1 mg unit and about 100 mL of distilled water, 2 or 3 drops of methyl orange (0.1 mass% aqueous solution) as an indicator were added to the sample solution, and the titration was performed with 1N-HCl using a 50 mL burette. The point at which orange color was observed in one drop was set as an endpoint, and the alkali concentration was determined from the consumption of 1N-HCl at that time by the following equation.

[Mathematical formula 5]

$$\text{Alkali concentration (mass\%)} = \frac{\text{Consumption of 1N-HCl (mL)} \times 0.031}{\text{Weight (g) of sample}} \times 100$$

[0082]

SiO₂ concentration:

To the above alkali concentration titration endpoint solution was added with a 5.0 g of sodium fluoride and was shaken well. Thereafter, an about 0.5 mL of methyl red xylene anole FF indicator was added to the sample solution and titrated with 1N-HCl. A further 2.0 mL of 1N-HCl was added when the solution turned red, and the titration volume a (mL) was recorded. Here, the methyl red xylene anole FF indicator is a dissolution of a 0.8 g of methyl red and a 0.2 g of xylene anole FF in a 1,000 mL of ethanol.

[0083]

Next, a reverse titration was performed with 1N-NaOH using a 10 mL burette, and the endpoint was determined when the color of the sample solution turned brownish-orange and pH was in the range of 5.8 to 6.0. The titration volume b (mL) was recorded, and SiO₂ concentration was determined by the following equation.

[Mathematical formula 6]

$$\text{SiO}_2 \text{ (mass\%)} = \frac{(a \text{ mL} - b \text{ mL}) \times 0.01502}{\text{Weight (g) of sample}} \times 100$$

[0084]

●Secondary treatment of alkali silicate aqueous solution (as necessary)

Based on the results of the above titration method, one or both of a wet process silica and water was added to fine-adjust components so that SiO₂ concentration in oxide equivalent approaches the target SiO₂ concentration of 12.0 mass% (additional dissolution or additional heat dissolution). In the present example and the comparative example, the secondary treatment was performed on the alkali silicate aqueous solution obtained with Plant Ash d, Plant Ash e, and Plant Ash f, respectively. To the alkali silicate aqueous solution derived from Plant Ash d was added with only a wet process silica (silica purity: about 93 mass%, Nipsil LP, TOSOH SILICA Co., Ltd.), and SiO₂ concentration was adjusted by heat dissolution. To the alkali silicate aqueous solution derived from Plant Ash e was added with water and the mentioned wet process silica, and SiO₂ concentration was adjusted by heat dissolution. To the alkali silicate aqueous solution derived from Plant Ash f was added with only the mentioned wet process silica, and SiO₂ concentration was adjusted by heat dissolution. Plant Ash f is an ash obtained by combusting a rice husk at 700°C for 2 hours without flowing the material in an air-rich state according to the method described in Patent Literature 1. In the case of Plant Ash f, the surface part of the rice husk is vitrified first, and most of the vitrified component is removed as residue from the coarse filtration during the primary treatment. Therefore, a larger amount of wet process silica was required to adjust SiO₂ concentration as compared to Plant Ash d and Plant Ash e.

[0085]

The sample solution subjected to the primary treatment and, as necessary, the secondary treatment was used as a raw solution for the alkali silicate aqueous solution used in Examples or Comparative examples. In the following description, the raw solution obtained with Plant Ash a is referred to as "Alkali Silicate a", and similarly, the raw solutions obtained with Plant Ash b to Plant Ash f are referred to as "Alkali Silicate b" to "Alkali Silicate f", respectively.

[0086]

In addition, as Reference Example 1, an alkali silicate aqueous solution was produced using a commercially available silica sand as a raw material by the following method.

Sodium silicate aqueous solution derived from silica sand:

A pressure container (autoclave) with a capacity of 5 L was charged with a 3,000 g of water, and a 1,500 g of commercially available sodium silicate cullet (medium molar grade, Na₂O: 24.51%, SiO₂: 75.44%, purity: 99.9% or more, TOKUYAMA Co., Ltd.) produced from silica sand as a raw material was dissolved under the conditions of pressure 0.7 MPa and temperature 160°C for 60 minutes. A 2,000 g of sodium silicate aqueous solution was taken from the container, diluted twice with water and cooled to room temperature. Thereafter, a magnetic buchner funnel (nutche) with 150 mm Φ was attached to a suction filtration bottle with a capacity of 5 L, and a coarse filtration was performed through a polyester plain weave filter cloth (an opening of about 50 μm x 400 μm) with suction. The undissolved residue component was removed by the coarse filtration to obtain an aqueous solution of silicate soda (alkali silicate) derived from silica sand.

[0087]

<Examples and comparative examples of alkali silicate aqueous solutions>

Alkali Silicate a to Alkali Silicate f were prepared with Plant Ash a to Plant Ash f, respectively, and alkali silicate aqueous solutions of Examples 1 to 3 and Comparative Examples 1 to 3 were obtained. The following measurement was performed on each aqueous solution, as well as on the alkali silicate aqueous solution of Reference Example 1.

[0088]

●Composition analysis and impurity measurement

The alkali silicate aqueous solution sample extracted through a syringe with a membrane filter having an opening of 1 μm was diluted with pure water. Quantitative analysis (unit: mass%) of the sample was performed with a high resolution ICP optical emission spectrometer (model: PS3520DDII, HITACHI HIGH-TECH SCIENCE Co., Ltd.) based on the standard solution for calibration curve for each element. The dilution ratio was 10,000 times (standard solution for calibration curve: 20 mass-ppm) for the quantitative analysis of SiO₂, Na₂O and K₂O, and 1,000 times (standard solution for calibration curve: 10 mass-ppm) for the quantitative analysis of P₂O₅, CaO, MgO, Al₂O₃, Fe₂O₃, MnO.

[0089]

●Molar ratio

SiO₂, Na₂O and K₂O mass concentrations measured above were converted to molar amounts, and then the molar ratio SiO₂/ (Na₂O+K₂O) and the molar ratio K₂O/Na₂O were determined. Specifically, the molar masses of the components were

60.08 (SiO₂), 61.98 (Na₂O) and 94.19 (K₂O), and the molar ratios were calculated by the following equation, respectively.

[Mathematical formula 7]

$$\text{Molar ratio } \frac{\text{SiO}_2}{(\text{Na}_2\text{O} + \text{K}_2\text{O})} = \frac{\frac{\text{SiO}_2 (\text{mass}\%)}{60.08}}{\frac{\text{Na}_2\text{O} (\text{mass}\%)}{61.98} + \frac{\text{K}_2\text{O} (\text{mass}\%)}{94.19}}$$

$$\text{Molar ratio } \frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} = \frac{\frac{\text{K}_2\text{O} (\text{mass}\%)}{94.19}}{\frac{\text{Na}_2\text{O} (\text{mass}\%)}{61.98}} = \frac{\text{K}_2\text{O} (\text{mass}\%)}{\text{Na}_2\text{O} (\text{mass}\%)} \times 0.6580$$

[0090]

●Measurement of transmittance (%T) of alkali silicate aqueous solution

The transmittance at a wavelength from 200 nm to 800 nm was measured with a commercially available ultraviolet-visible spectrophotometer (model: V-730, JASCO Co., Ltd.). The measurement was performed with a standard spectrophotometric cell (model: S10-G-10, GL SCIENCE Co., Ltd.) which is made of borosilicate glass and has an optical path length of 10 mm, and a measured value with pure water was used as a comparative standard. The transmittance (%T) at a wavelength 500 nm (near the border between blue and green), in which the coloration is easily visually recognized in the visible light wavelength (wavelength 380 nm to 780 nm), was defined as the transmittance (%T) of the alkali silicate aqueous solution.

[0091]

●Measurement of undissolved residue (mass-ppm) of alkali silicate aqueous solution

The undissolved residue of the alkali silicate aqueous solution (a solid content captured on the filter by the filtration with the filter having an opening of 1 μm), which is used as a raw material for wet process silica, was measured. A magnetic buchner funnel (nutche) with 110 mm Φ was attached to a suction filtration bottle with a capacity of 2 L, and an 1,000 g of alkali silicate aqueous solution was subjected to a suction-filtration through a filter paper (Grade 5C, ADVANTEC Co., Ltd.) with an opening of 1 μm. After filtration, it was washed with another 1,000 g of pure water and dried in a box dryer at 105°C for 2 hours. Thereafter, the mass of the solid content captured on the filter paper was determined, and the concentration in mass-ppm of the undissolved residue was determined by the following equation.

[Mathematical formula 8]

Undissolved residue (mass-ppm)

$$= \frac{\text{Mass (g) of undissolved residue}}{\text{Total mass (g) of alkali silicate aqueous solution subjected to filtration}} \times 1,000,000$$

[0092]

●Specific gravity of alkali silicate aqueous solution (reference value)

The alkali silicate aqueous solution adjusted to 20 ± 0.5 °C was placed in a measuring cylinder of 250 mL, a specific gravity meter (hydrometer) was inserted, and the scale was read at the point of rest.

[0093]

<Production and physical property evaluation of wet process silica>

Since all processes to deposit silica from alkali silicate aqueous solution for wet process silica show basically the same tendency, precipitated silicas among wet process silica were produced by the following method with Alkali Silicate a to Alkali Silicate f, respectively, and its physical properties were confirmed (Examples 1 to 3, Comparative Examples 1 to 3). In addition, a precipitated silica was produced with the sodium silicate aqueous solution derived from silica sand, and the quality was confirmed as Reference Example 1. The sodium silicate cullet and its aqueous solution in Reference Example 1 contain almost no impurities, and are widely used as a raw material for a high-quality wet process silica with a high whiteness. The physical properties are shown in Table 2 below.

[0094]

●Production of wet process silica

A 495 mL of warm water and a 36 mL of the alkali silicate aqueous solution to be tested were charged into a 2 L stainless-steel container equipped with a stirrer at pH of 11.8 ± 0.2 , and the temperature was raised to 75°C. A 366 mL of the alkali silicate aqueous solution and about 108 mL of 20 mass% dilute sulfuric acid were dropped at a constant flow rate over 60 minutes while maintaining the temperature and pH with continuous stirring. The dropping of the alkali silicate aqueous solution was then stopped, and when pH reached 3, the dropping of the dilute sulfuric acid was also stopped to finish the neutralization reaction. A magnetic buchner funnel (nutche) with 150 mm Φ was attached to a suction filtration bottle with a capacity of 2 L, and the sample solution was subjected to a suction-filtration through a filter paper (Grade 5A, ADVANTEC Co., Ltd.) with an opening of 8 μm , further washed with a 600 mL of pure water, and dried at 125°C for 8 hours to obtain the wet process silica (precipitated silica).

[0095]

●Whiteness of wet process silica

The resulting wet process silica powder was gently reground in a mortar for about 3 minutes, and then the whiteness of the wet process silica was measured by the same method as for the whiteness measurement of plant ash. When the whiteness of the wet process silica is 85 or more, the alkali silicate aqueous solution that is the raw material for it is evaluated as GOOD because the quality of high performance wet process silica is satisfied. When the whiteness of the wet process silica is less than 85, the wet process silica is considered to be a colored product (discolored product), and the alkali silicate aqueous solution that is the raw material for it is evaluated as NG.

[0096]

●BET specific surface area of wet process silica (reference value)

BET specific surface area of the wet process silica powder was measured by a one-point method with a fully automated specific surface area measurement device (model: Macsorb HMmodel-1210, MOUNTECH Co., Ltd.).

[0097]

●Amount of carbon in wet process silica (reference value)

The amount of carbon in the wet process silica was measured by the same method as in the case of measuring the amount of carbon in the plant ash.

[0098]

The analysis results of Examples 1 to 3, Comparative Examples 1 to 3, and Reference Example 1 are shown in Table 2 below.

[Table 2]

		Com. Ex. 1	Ex. 1	Ex. 2	Ex. 3	Com. Ex. 2	Com. Ex. 3	Ref. Ex. 1
Sample		a	b	c	d	e	f	Silica sand
ICP mass%	SiO ₂	11.45	11.96	12.06	11.38	11.67	11.98	12.57
	P ₂ O ₅	0.086	0.094	0.087	0.054	0.198	0.054	0.001
	Na ₂ O	3.333	3.327	3.526	3.756	3.250	3.664	4.040
	K ₂ O	0.457	0.403	0.544	0.494	1.403	0.316	0.000
	CaO	0.002	0.002	0.002	0.001	0.002	0.001	0.000
	Al ₂ O ₃	0.002	0.002	0.003	0.004	0.008	0.001	0.007
	Fe ₂ O ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.002

	MnO	0.000	0.000	0.000	0.001	0.001	0.001	0.000
	MgO	0.000	0.000	0.000	0.001	0.002	0.001	0.000
P ₂ O ₅ /SiO ₂ Concentration ratio ($\times 10^{-3}$)		7.51	7.86	7.21	4.75	16.97	4.51	0.08
Na ₂ O+K ₂ O mass%		3.79	3.73	4.07	4.25	4.65	3.98	4.04
SiO ₂ / (Na ₂ O+K ₂ O) Molar ratio		3.25	3.43	3.20	2.87	2.88	3.19	3.20
K ₂ O/Na ₂ O Molar ratio		0.090	0.080	0.102	0.091	0.284	0.057	0.000
Specific gravity		1.147	1.149	1.150	1.149	1.148	1.146	1.146
Transmittance (@ 500 nm) %T		4.4	65.7	85.8	86.2	22.6	55.4	99.5
Filtration residue (1 μ m) mass-ppm		410	89	82	0	399	115	0
Wet process silica	Whiteness	58	85	91	89	62	73	97
	(Evaluation)	NG	GOOD	GOOD	GOOD	NG	NG	GOOD
	BET m ² /g	249	257	254	248	242	239	245
	Carbon mass%	0.077	0.019	0.011	0.013	0.055	0.048	0.001

[0099]

<Examples and Comparative Examples in which alkali silicate aqueous solution subjected to filtration and adsorption treatments and alkali silicate aqueous solution derived from sand were mixed>

As described below, one or both of the filtration and adsorption treatments were performed on Alkali Silicate a and Alkali Silicate b to evaluate the effect on the quality of the wet process silica (Example 4, Example 5 and Comparative Example 4 of the alkali silicate aqueous solutions). Furthermore, the quality of the mixture of the alkali silicate aqueous solution derived from plant ash and the alkali silicate aqueous solution derived

from sand was confirmed (Examples 6 to 8 of the alkali silicate aqueous solution).

[0100]

< Comparative Example 4>

A magnetic buchner funnel (nutche) with 110 mm Φ was attached to a suction filtration bottle with a capacity of 3 L, and Alkali Silicate a (about 2,000 g) was subjected to only a filtration through a filter paper (an opening of 1 μ m, Grade 5C, ADVANTEC Co., Ltd.) with suction. Hereinafter, the filtration by this filter paper is referred to as "5C filtration". That is, in Comparative Example 4, Alkali Silicate a of Comparative Example 1 was subjected to 5C filtration to remove solid foreign matters present in the alkali silicate aqueous solution. In addition, a wet process silica was produced using Alkali Silicate a as a raw material after 5C filtration, and its qualities were analyzed.

[0101]

< Example 4>

A 20 g of commercially available powdered activated carbon was added to Alkali Silicate a (about 2,000 g), and the sample was left standing for 24 hours to perform the adsorption treatment of the components. Thereafter, a magnetic buchner funnel (nutche) with 150 mm Φ was attached to a suction filtration bottle with a capacity of 3 L, and the sample was subjected to 5C filtration. That is, in Example 4, Alkali Silicate a of Comparative Example 1 was subjected to the adsorption treatment to adsorb and remove impurities in the aqueous solution, and 5C filtration was performed to remove solid foreign matters present in the alkali silicate aqueous solution. In addition, a wet process silica was produced using Alkali Silicate a as a raw material after 5C filtration, and its quality was analyzed.

[0102]

< Example 5>

A magnetic buchner funnel (nutche) with 110 mm Φ was attached to a suction filtration bottle with a capacity of 3 L, and Alkali Silicate b (about 2,000 g) was subjected to 5C filtration. In addition, a wet process silica was produced using Alkali Silicate b as a raw material after 5C filtration, and its qualities were analyzed.

[0103]

<Example 6 to Example 8>

Alkali silicate aqueous solutions were produced by mixing the alkali silicate aqueous solution after 5C filtration obtained in Example 5 and the alkali silicate aqueous solution of Reference Example 1 at 4:6 (Example 6: 40 mass% of the aqueous solution derived from plant ash; the same applies hereafter), 6:4 (Example 7), and 8:2 (Example 8), respectively. In addition, wet process silicas were produced using the alkali silicate

aqueous solutions as raw materials, and their qualities were analyzed.

[0104]

The analysis results of Comparative Example 4 and Examples 4 to 8 are shown in Table 3 below.

[Table 3]

		Com. Ex. 4	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Sample		a	a	b	Ex. 5 : Ref. Ex. 1		
Sample preparation		5C filtration	Adsorpti on + 5C filtration	5C filtration	4:6	6:4	8:2
ICP mass%	SiO ₂	11.45	11.45	11.96	12.33	12.20	12.08
	P ₂ O ₅	0.086	0.086	0.094	0.040	0.059	0.076
	Na ₂ O	3.333	3.333	3.327	3.713	3.552	3.470
	K ₂ O	0.457	0.457	0.403	0.161	0.242	0.326
	CaO	0.002	0.002	0.002	0.001	0.001	0.002
	Al ₂ O ₃	0.002	0.002	0.002	0.006	0.004	0.004
	Fe ₂ O ₃	0.000	0.000	0.000	0.001	0.001	0.001
	MnO	0.000	0.000	0.000	0.001	0.000	0.001
	MgO	0.000	0.000	0.000	0.000	0.000	0.000
P ₂ O ₅ /SiO ₂ Concentration ratio ($\times 10^{-3}$)		7.51	7.51	7.86	3.24	4.84	6.29
Na ₂ O+K ₂ O mass%		3.79	3.79	3.73	3.87	3.79	3.80
SiO ₂ / (Na ₂ O+K ₂ O) Molar ratio		3.25	3.25	3.43	3.33	3.39	3.38
K ₂ O/Na ₂ O Molar ratio		0.090	0.090	0.080	0.029	0.045	0.063
Specific gravity		1.148	1.148	1.149	1.146	1.147	1.147

Transmittance (@ 500 nm) %T		32.8	94.5	94.4	97.6	96.4	95.2
Filtration residue (1 μ m) mass-ppm		81	12	27	11	18	23
Wet process silica	Whiteness	75	94	91	95	94	92
	(Evaluation)	NG	GOOD	GOOD	GOOD	GOOD	GOOD
	BET m ² /g	248	238	242	248	254	250
	Carbon mass%	0.0288	0.0122	0.0133	0.0104	0.0101	0.0018

[0105]

<Explanation of results>

From the results of Plant Ash b to Plant Ash d shown in Table 1, it can be seen that the pre-combustion and sufficient combustion of the plant material reduce the amount of carbon-containing impurities in the plant ash due to non-combustion. In contrast, from the results of Plant Ash a and Plant Ash e, it can be seen that a large amount of carbon-containing impurities remain due to the insufficient combustion temperature. Furthermore, from the result of Plant Ash f, it can be seen that a large amount of carbon-containing impurities remain even in the case of the combustion at a high temperature without the pre-combustion. This is considered that the surface of the plant material is vitrified by the high-temperature combustion, resulting in a noncombustible state inside the material due to insufficient oxygen supply and other reasons.

[0106]

The results of Examples 1 to 3 shown in Table 2 indicate that when the alkali silicate aqueous solution is produced with the plant ash that obtained by performing the pre-combustion and sufficiently combusting the sample, the filtration residue is low and the transmittance is high even without the filtration and adsorption treatments of the alkali silicate aqueous solution, so it can be seen that the amounts of the insoluble foreign matter and the water-soluble carbon compound in the alkali silicate aqueous solution are low. Furthermore, it can be seen that when the wet process silica is produced using such a plant ash as a raw material, impurities in the wet process silica are also reduced, and a wet process silica with a sufficient whiteness can be obtained. In contrast, the results of Comparative Example 1, Comparative Example 2, and Comparative Example 3 show that

when the alkali silicate aqueous solutions are produced with the plant ash that obtained at insufficient combustion temperature or the plant ash that obtained by just simply high temperature combustion, a large amount of carbon-containing impurities remain. Furthermore, it can be seen that when the wet process silica is produced using such a plant ash as a raw material, impurities in the wet process silica are also increased, and a wet process silica with a sufficient whiteness cannot be obtained.

[0107]

The results of Comparative Example 4, Example 4, and Example 5 shown in Table 3 indicate that the quality of the alkali silicate aqueous solution is remarkably improved by performing one or both of the filtration and adsorption treatments on the alkali silicate aqueous solution.

[0108]

In particular, the comparison of Comparative Example 1, Comparative Example 4, and Example 4 shows that the quality of alkali silicate aqueous solutions of insufficient quality can be improved by the adsorption and filtration treatments to the extent that it is possible to produce a wet process silica with a whiteness of more than 90.

[0109]

FIG. 2 shows transmittance spectra (wavelength 200 nm to 800 nm) of alkali silicate aqueous solutions in Comparative Example 1, Comparative Example 4, and Example 4. It is shown that the higher the transmittance (%T) at a wavelength 500 nm, the higher the transparency. The transmittance of Alkali Silicate a of Comparative Example 1 (Plant Ash a combusted at 500°C, only the primary treatment was performed) at a wavelength 500 nm was 4.4%, and the whiteness of the precipitated silica produced using Alkali Silicate a as a raw material was 58. In Comparative Example 4, where 5C filtration was performed on Alkali Silicate a, although the colored components dissolved and remained in the alkali silicate aqueous solution, the transmittance at a wavelength 500 nm was improved to 32.8%. The whiteness of the wet process silica using the alkali silicate aqueous solution of Comparative Example 4 as a raw material was also improved to 75, but the quality of the wet process silica was insufficient. In contrast, in Example 4, where the adsorption treatment and 5C filtration were performed on Alkali Silicate a, the transmittance at a wavelength 500 nm was improved to 94.5%, and the whiteness of the wet process silica was also improved to 94, resulting in a wet process silica having sufficient quality.

[0110]

FIG. 3 shows transmittance spectra (wavelength 200 nm to 800 nm) of the alkali silicate aqueous solutions in Example 1, Example 5, and Reference Example 1. In

Example 1, Alkali Silicate b was produced with Plant Ash b, which was combusted at a final temperature of 600°C, and then it was used as a raw material to produce the wet process silica. In Example 5, Alkali Silicate b was subjected to 5C filtration, and then it was used as a raw material to produce the wet process silica. In Reference Example 1, the wet process silica was produced with the alkali silicate aqueous solution derived from silica sand.

[0111]

Although Alkali Silicate b includes the filtration residue as a solid foreign matter of 0.41 mass%, the colored components dissolved in the alkali silicate aqueous solution were hardly confirmed by the naked eye, and the transmittance at a wavelength 500 nm was 65.7%. The whiteness of the wet process silica produced using Alkali Silicate b as a raw material was 85, which was sufficient whiteness as a highly functional wet process silica. In Example 5, where 5C filtration was performed on Alkali Silicate b, the transmittance at a wavelength 500 nm was improved to 94.4%, and the whiteness of the precipitated silica was also improved to 91. This quality was comparable to the whiteness of wet process silica produced using the alkali silicate aqueous solution derived from sand as a raw material.

[0112]

The quality of the alkali silicate aqueous solution derived from plant ash may not be comparable to the quality of the alkali silicate aqueous solution derived from sand as in Reference Example 1. In such a case, it is also possible to further improve the quality of the alkali silicate aqueous solution derived from plant ash by mixing with an alkali silicate aqueous solution derived from sand as necessary (Examples 6 to 8).

[0113]

FIG. 4 shows a transmittance spectrum (wavelength 200 nm to 800 nm) of the alkali silicate aqueous solution in Comparative Example 3. The transmittance at a wavelength 500 nm of the alkali silicate aqueous solution derived from Plant Ash f, which was prepared according to the method described in Patent Literature 1, was 55.4%, and the whiteness of the wet process silica produced using it as a raw material was 73, indicating that a wet process silica with a sufficiently whiteness could not be obtained.

INDUSTRIAL APPLICABILITY

[0114]

The wet process silica synthesized using the alkali silicate aqueous solution of the present invention as a raw material can have a high reinforcing properties for industrial rubbers and tires, and also can be used as a reinforcing filler for silicone rubbers,

a paper filler (anti-bleed-through agent), a matting agent for paints, an abrasive such as for toothpastes, an anti-blocking agent for films and the like, which emphasize transparency and whiteness, (similar to the conventional alkali silicate aqueous solution derived from sand), and is therefore useful as an environmentally friendly alkali silicate aqueous solution.

CLAIMS

1. An alkali silicate aqueous solution having a ratio P_2O_5/SiO_2 of P_2O_5 concentration to SiO_2 concentration in mass% of 1.0×10^{-3} or more, SiO_2 concentration of 8.9 mass% to 16.7 mass%, and a transmittance (%T) through an optical path length 1 cm at a wavelength 500 nm of 65% or more.
2. The alkali silicate aqueous solution as claimed in claim 1, having a ratio $SiO_2/(Na_2O+K_2O)$ of SiO_2 concentration to the concentration (Na_2O+K_2O) in mole% of 2.8 to 3.5.
3. The alkali silicate aqueous solution as claimed in claim 1 or 2, having a ratio K_2O/Na_2O of K_2O concentration to Na_2O concentration in mole% of 0.03 to 0.30.
4. An alkali silicate aqueous solution as claimed in claim 1 or 2, wherein when the alkali silicate aqueous solution is filtered with a filter having an opening of 1 μm , the solid content captured on the filter is less than 100 mass-ppm with respect to the mass of the alkali silicate aqueous solution before the filtration.
5. The alkali silicate aqueous solution as claimed in claim 1 or 2, which is used as a raw material for wet process silica.
6. A method for producing alkali silicate aqueous solution, comprising subjecting a raw material alkali silicate aqueous solution obtained by mixing a plant ash containing a silica component, sodium hydroxide and water to one or both of a filtration treatment with a filter having an opening of less than 50 μm and an adsorption treatment with an adsorbent to obtain the alkali silicate aqueous solution.
7. The method for producing alkali silicate aqueous solution as claimed in claim 6, wherein the plant ash is a rice husk ash.