



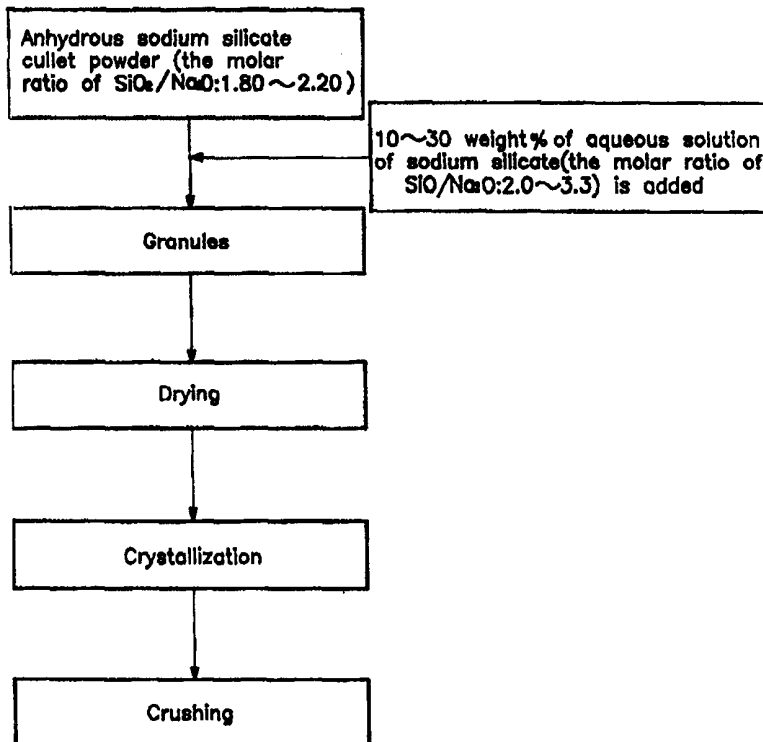
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(54) Title: A PROCESS FOR PREPARATION OF CRYSTALLINE LAYERED SODIUM DISILICATE

(57) Abstract

The present invention relates to a process for preparation of crystalline layered sodium disilicate and more particularly, to an improved process for preparation of crystalline layered sodium disilicate, being useful as a water softener or builder of detergent composition, which is fabricated in a simple manner by adding an aqueous solution of sodium silicate as a binder, to an Anhydrous sodium disilicate cullet powder used as a starting material, in a certain composition ratio, to give granules and thereafter charging the dried granules to a furnace for crystallization process. As a result, in comparison with the prior arts, the purity of the product is increased, the preparation process is simplified and the consumption of energy is remarkably reduced, whereas the cost of the product is reduced and also the deposition of reactant in a calcined device is improved.



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A PROCESS FOR PREPARATION OF CRYSTALLINE LAYERED SODIUM DISILICATE

BACKGROUND OF THE INVENTION

5 Field of the Invention

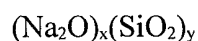
The present invention relates to a process for preparation of crystalline layered sodium disilicate and more particularly, to an improved process for preparation of crystalline layered sodium disilicate, being useful as a builder for detergent composition or water softener, which is fabricated in a simple manner by adding an aqueous solution of sodium silicate, a binder, to anhydrous sodium disilicate cullet
10 powder used as a starting material, in a certain composition ratio, to give granules and thereafter charging dried granules to a furnace for crystallization process. As a result, in comparison with the prior arts, the purity of the product is increased, the preparation process is simplified and the consumption of energy is remarkably
15 reduced, whereas the cost of the product is reduced and also the deposition of reactant in a calcined device is improved.

Description of the Prior Art

The term "cullet" as a starting material in the present invention, which has
20 been frequently used as a raw material in the field of preparation of an aqueous solution of sodium silicate, means a compound consisting of small mass or fragments of amorphous sodium silicate formulated in such a manner that silica and sodium carbonate are mixed in a suitable molar ratio [ratio of SiO_2 to Na_2O , i. e. , $(\text{SiO}_2/\text{Na}_2\text{O})$] and then, the mixture is heated and melted at a high temperature of about
25 $1,000 \sim 1,400^\circ\text{C}$ and cooled.

The layered sodium silicate is a crystalline silicate represented by the

following formula:



Wherein ,

y/x depends on the crystal structure, and has the value ranging between 2 ~ 11.

5 Among them, crystalline layered sodium disilicate represented by $\text{Na}_2\text{Si}_2\text{O}_5$ has been reported to be present in α -, β -, γ - and δ -type. Such crystalline layered sodium disilicate has been effectively used not only as a catalyst supporter, but also as a material in various chemical processes such as separation and refining processes, etc. due to its unique absorption property and ion-exchange capacity in
10 terms of structural characteristics. In particular, since δ -crystalline layered sodium disilicate has a higher binding capacity for ions such as Ca^{2+} and Mg^{2+} that represent hardness in water, it has been recently developed for various uses such as a water softener or a builder for detergent composition, etc.

Typical processes for synthesis of δ -type crystalline layered sodium
15 disilicate are disclosed as follows:

The U. S. Patent No. 4,585,642 and the European Patent No. 293,640 comprise adjusting a molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ to 1.9 ~ 2. 5 using aqueous solutions of both sodium silicate and sodium hydroxide, dehydrating the mixed solution using a spray dryer, and then crystallizing the above dehydrated material at 550 ~ 800 °C.

20 However, such process has several recognized disadvantages in that a) an aqueous solution of sodium silicate, which is more expensive than anhydrous sodium silicate, is used, b) an enormous amount of energy is consumed to remove the large amount of moisture from an aqueous solution of sodium silicate, c) since dehydrated sodium silicate has very large bulk, the scale of crystallization device has to be big,
25 and d) the dust generated during the process causes the bag filter to be heavily loaded. Furthermore, in the early stage of crystallization in the above process, foaming

phenomenon occurs excessively owing to escape of the residual moisture, followed by sintering and contracting among particles. Thus, the resulting reactants are deposited inside the crystallization device, leading to difficulty in continuous process.

The Japanese Laid-open Patent No. Heisei 4-238809 disclosed that an aqueous
5 solution of sodium silicate with the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ adjusted to 1.9 ~ 3.2 is directly introduced into the heating section maintaining the temperature at 680 ~ 830 °C to crystallize, thus simplifying its preparing process. In the above process, however, there are problems that energy is consumed excessively because of generation of a large amount of vapor in the dehydrating process at high temperature,
10 the crystallization device corrodes easily and the reactant is deposited inside the apparatus when sudden shut-down occurs. Other disadvantages are such as a) easy corrosion of the crystallization device, and b) the deposition of reactant inside the apparatus associated owing to sudden shut-down.

The Japanese Laid-open Patent No. Heisei 3-93649 disclosed that after
15 anhydrous sodium silicate being prepared by adding part of an alumina constituent for improving water-resistance, it is pulverized and crystallized to improve layer-like structure. However, this method has also recognized a shortcoming in that a large amount of impurities are mixed, while particles are sintered to each other.

The following three processing steps in common were disclosed in some U. S.
20 Patent Nos. 4,585,642 and 5,211,930 and 5,268,156:

1) Heating and dissolution processing step: A large amount of water is first added to the cullet, followed by heating and dissolving the mixture to form an aqueous solution of sodium silicate (water content: 50 ~ 60 weight %);

2) Drying processing step: Sodium hydroxide is added to the aqueous solution
25 of sodium silicate to adjust a molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ to the desirable level, and water(50 ~ 60 weight %) contained from the above aqueous solution is dried at 140 °C

or higher using a spray dryer;

3) Crystallization processing step: The intermediate in powder form is charged into the furnace to effect crystallization at 600 ~ 800 °C.

The U. S. Patent No. 4,585,642 supplemented a process of adding δ -type
5 crystal seeds to prevent the final product from being mixed with multiple crystalline layered sodium disilicates.

The U. S. Patent No. 5,211,930 supplemented an recycle process to the final product to prevent products from depositing inside the calcined device.

The U. S. Patent No. 5,268,156 employed a method of increasing the bulk
10 density by pulverizing a powder-form intermediate to the particle size of about 1 ~ 50 μm so as to prevent products from depositing inside the calcined device and to inhibit the occurrence of dust.

However, along with complicated processing steps and need for complex equipment, these conventional methods have encountered the following shortcomings:

15 a) there is difficulty in maintaining the quality of a final product, b) a series of uneconomical high energy consuming processes (e. g., heating, drying and crystallizing) are required, thus demanding related complex devices, and c) several complicated processing steps increase difficulties in the preparation of a final product.

Therefore, the U. S. Patent No. 5,183,651 suggested another method of
20 reducing the number of necessary devices and energy costs by improving several complicated processing steps that the conventional methods have encountered hitherto. This method has been evaluated as an economical process, since α -crystalline layered sodium disilicate is obtained while several types of crystalline are not mixed. But in this method also there exist some recognized disadvantages in that a) a recycle
25 process of a final product is additionally necessary, and b) the final product cannot be used as a builder for water softener and detergent composition, since the majority of

the final product is composed of α -crystalline layered sodium disilicate and has quite lower binding capacity on the hardness constituents in water than δ -crystalline layered sodium disilicate has, as disclosed in the U. S. Patent No. 4,820,439 and Japanese Laid-open Patent No. Heisei 4-238809.

5 To overcome the aforementioned shortcomings, the inventor et al. have conducted intensive studies to improve and simplify complicated several processing steps and to mainly prepare qualified δ -crystalline layered sodium disilicate in high purity. As a result, the U. S. Patent No. 5,567,404 (Korean Laid-open Patent No. 95-31902) filed by the applicant of this patent suggested a novel process, wherein for
10 easier phase-transition into δ -type crystal, a small amount of water necessary for granulation is added to cullet powder, the starting material with a previously adjusted molar ratio to give granules, which is then charged to the furnace for crystallization thereof. In comparison with the prior arts, the purity of the product obtained, is increased, the whole process for preparation is drastically simplified, and the
15 consumption of energy is remarkably reduced, whereas cost of the product is reduced and also the deposition of reactant in the apparatus is reduced. According to this method, however, water used for preparation of cullet powder acts not only as a binder, but also as an indispensable factor for its phase-transition by hydration. In this respect, the preparing conditions for granules will become more complicated in
20 relation with the amount of water added. For example, if water is less added to cullet powder in terms of its characteristics, the process for preparation becomes difficult and the purity of the final product formed after crystallization becomes poor; in case of using too much water, the resulting slurry form cannot support the shape of granules qualified properly. Therefore, it is necessary that the amount of water
25 added be accurately adjusted for preparation of optimal granules.

From a process of preparing crystalline layered sodium disilicate based on the

U. S. Patent No. 5,567,404 (Korean Laid-open Patent No. 95-31902), the inventor et al. have understood that when an aqueous solution of sodium silicate is used instead of water as a binder in the process of granulating cullet powder, the amount of water may be easily adjusted due to binding capacity supported by solid constituents in a binder.

5 Thus, the present invention has been completed.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a process for preparation of crystalline layered sodium disilicate designed to simplify the complicated granulation
10 process and improve the purity of the final product.

The present invention relates to a process for preparation of crystalline layered sodium disilicate from crystallized granules, which are formed by adding a binder to anhydrous sodium silicate cullet powder; characterized in that it consists in adding an aqueous solution of sodium silicate as a binder instead of water to the anhydrous
15 sodium silicate powder.

Description of the Drawings

Fig. 1 is the schematic flow diagram showing the process of manufacturing crystalline layered sodium disilicate,

20 Fig. 2 shows the X-ray diffraction pattern of the sample prepared from example 1 according to the present invention.

Detailed Description of the Invention

The present invention is explained in more detail as set forth hereunder.

25 According to the present invention, anhydrous sodium disilicate cullet powder consisting of certain composition is prepared by adding an aqueous solution of sodium

silicate containing certain amount of water as a binder, and the addition of an aqueous solution of sodium silicate is one of the pivotal processes in the present invention, since it functions as a binder not only to easily control the size of granules in the process, but also to facilitate a hydration. Because an aqueous solution of sodium silicate in the present invention is used as a binder, the role of water and the process mechanism are entirely different from those of the prior arts in which water is simply added. More specifically, the use of an aqueous solution of sodium silicate in the present invention has the following advantages in that a) it contributes to the ease of granulation of pulverized cullet powder, b) water can be easily removed from the crystallization process, thus contributing to improvement of purity and disassembling due to formation of homogeneous crystalline and pore, and c) with the addition of very small amount, it may, on the contrary, give an mechanism to shorten the processing steps without any problems in the device or the physical properties of the final product.

Further, the majority of crystalline layered sodium disilicate, so prepared by the process of the present invention, has δ -type crystalline and thus can be in particular used as a water softener or detergent supplement.

The process for preparation of crystalline layered sodium disilicate according to the present invention is composed of the following three processing steps: a) silica and sodium carbonate are mixed, heated and melted to prepare anhydrous sodium disilicate cullet, b) an aqueous solution of sodium silicate is added to the cullet-pulverized powder to give granules, and c) the resulting granules are heated and calcined to effect crystallization.

Each processing step for preparation of crystalline layered sodium disilicate according to the present invention is explained in more detail as set forth hereunder.

The first processing step is that silica and sodium carbonate are mixed in a

molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ to 1.80 ~ 2.20, melted at 1,000 ~ 1,400 °C for 1 ~ 3 hours and cooled at room temperature to prepare the cullet. Since the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ is the most important factor to determine the crystal type of crystalline layered sodium disilicate, the above molar ratio should be maintained.

5 The second processing step: the cullet, so prepared in the above step, is pulverized to give powder having the particle size of 850 μm ($D_{50} \approx 300 \mu\text{m}$) or less and an aqueous solution of sodium silicate (solid contents: 15 ~ 40 weight %) in a molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ to 2.0 ~ 3.3 is added as a binder; then, the resulting mixture is granulated to give 1 ~ 50 mm diameter size of granules (bulk density: 1.1 ~ 1.6
10 g/cm^3).

If the particle size of the cullet powder is larger than 850 μm , longer retention time becomes inevitably necessary for granulation; further, much longer time is also required in infiltrating a high-temperature energy into the inside of the prepared granules during the crystallization, thus deteriorating the physical property of the final
15 product in the crystallization process.

Further, the bulk density of cullet powder is 0.5 ~ 0.6 g/cm^3 and its loss on ignition at 700 °C is 0.4 ~ 1.0 weight %.

It is also preferred to maintain the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ to 2.0 ~ 3.3 in an aqueous solution of sodium silicate, being used as a binder designed for granulation of
20 cullet powder; if the molar ratio deviates said range, a lot of α - or β -type in crystalline phase is formed so that they may be present as impurities. Further, the solid contents in an aqueous solution of sodium silicate should be 15 ~ 40 weight %; if such solid contents are less than 15 weight %, a lot of water makes it difficult to properly control the granulation process and in case of exceeding 40 weight %, homogeneous addition of the solution on cullet powder becomes difficult due to its
25 higher viscosity.

An aqueous solution of sodium silicate having the above conditions is added in the range of 10 ~ 30 weight % per cullet powder; if the amount is added in less than 10 weight %, the granulation of powder becomes difficult and present in wet powder form, while in case of exceeding 30 weight %, the powder becomes a slurry form due to an excess of moisture, which makes it impossible to granulate cullet powder.

Said granules, so prepared, have 1 ~ 50 mm in diameter; if the size of granules is less than 1 mm in diameter, extremely small size of granule makes it difficult to maintain a certain retention time in a crystallization device and in case of exceeding 50 mm, some impurities may be formed due to the fact that a heat is not delivered into the inside of granules during the crystallization process. The bulk density of granules, so prepared, is in the range of 1.1 ~ 1.6g/cm³.

Further, the granulators according to the present invention can be selected from pan types, extruder types, disc types, and fluid layer types.

The third processing step is to obtain a desired product of the present invention, crystalline layered sodium disilicate, by drying, heating and calcining process of the granules, so formed as described in the above.

According to the present invention, granules are dried, prior to charging them into a continuous calcined device. As a result, there are the following advantages in that a) the adhesiveness of an aqueous solution of sodium silicate, being present at the surface of granules, may be removed to prevent granules from binding one another, b) it makes granules move easily, c) hydration induced by water within the inside of granules is facilitated so that the phase-transition in crystallization may be made available. However, if a drying temperature is extremely high, the purity of the final product may be affected by the formation of impurities. To handle this problem, it is preferred to perform the drying process at 80 ~ 200°C until the evaporation contents of the moisture become 0.2 ~ 1.0 weight %. The exhaust

gas which is discharged from a calcined device at next process can be used with the advantage as a heat source in the drying process to reduce energy consumption. The bulk density of granules, so dried, is maintained at $1.1 \sim 1.6 \text{ g/cm}^3$.

Said granules, so dried, are charged into the rotary furnace, the continuous
5 calcined device and crystallized at $650 \sim 770^\circ\text{C}$ for $0.1 \sim 1$ hour to obtain the material having a bulk density of $0.1 \sim 0.5 \text{ g/cm}^3$. Then, the said material is milled by a ball-mill. The crystalline shape depends on the crystallization conditions, therefore, δ -crystalline layered sodium disilicate having a high purity may be obtained, when the granules are crystallized under the above conditions.

10 As described in the foregoing, some characteristics related to the process of preparing crystalline layered sodium disilicate according to the present invention are summarized as follows:

First, the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ in cullet, which may affect the purity of a final product, is adjusted at $1.80 \sim 2.20$; a small amount of an aqueous solution of
15 sodium silicate necessary for the granulation is added to granulate and then the granules, so formed, are calcined. Through the preparing process remarkably simplified, the majority of the final product is composed of δ -type crystal and the product thus obtained can be effectively used as water softener or detergent supplement;

20 Second, since the present invention has economical benefits in that it makes it unnecessary to provide devices and heating energy designed to be used for some common process such as heating, dissolution, drying and recycle, whereby the time required for total preparation is markedly reduced and the production amount per unit may be expected to be enhanced;

25 Third, the use of an aqueous solution of sodium silicate as a binder makes it easier to control the granulation process; and by the drying process to dry the surface

of prepared granules, any possible problems in the storage and delivery of granules may be prevented; homogenous crystallization of granules within a calcined device, by charging into the furnace the granule-type materials having the minimum moisture necessary for phase transition, is enabled; the deposition of reactant in the furnace
5 does not occur; local sinter may be prevented so that the disassembling properties are favorable; in particular, the final product, mainly comprising δ -crystalline layered sodium disilicate in high purity, may be obtained and it may be effectively used for both detergent composition and water softener.

Crystalline layered sodium disilicate of the present invention, so prepared by
10 the above process for preparation, has proven to be superior to that of well known methods in that the former has calcium ion binding capacity of 98 ~ 108 mg Ca^{2+}/g and magnesium ion binding capacity of 78 ~ 86 mg Mg^{2+}/g at the temperature of 25 °C. Further, the majority of crystalline phase according to the present invention has proven to be δ -type.

15 The present invention is explained in more detail by the following examples, but the claims are not limited to these examples.

EXAMPLE 1

600.0g of silica (Cape Capentery, Australia), dried at 120 °C for 5 hours and
20 531.9g of sodium carbonate (Solvey Co., Sweden), dried at 350 °C for 5 hours, were accurately weighed and pulverized/mixed by a ball-mill (material: alumina, capacity: 3.6 l, ball: ϕ 20 mm) for 1 hour. The mixture of about 1 kg was charged to an alumina crucible, and heated for melting in an electric furnace (Thermoline, U. S. A, Model No. 46200) at 1,200 °C for 2 hours. After cooling it to room temperature,
25 about 700g of transparent cullet mass was obtained. It was ascertained by an analysis method of liquid-phase sodium silicate (KS-M-1415) that the molar ratio of

SiO₂/Na₂O was 2.03. The cullet mass was first pulverized into small pieces by a jaw crusher (Daegabunche Co., Korea), further pulverized by a ball-mill (material: alumina, capacity: 3.6 ℓ, ball: $\varnothing$ 20 mm) for 3 hours and distributed. The cullet powder (bulk density: 0.5 ~ 0.6 g/cm³) having the particle size of 850 μ m (D₅₀: $\approx$ 300 μ m) or less was prepared, while its loss on ignition at 700°C was 0.40 weight %. 500g of cullet powder, accurately weighed, was placed on a disk-type granulator (Yungjin Machine, Korea) and rotated at 15 rpm. Then, a small amount of an aqueous solution of sodium silicate (solid contents: 30 weight %, Shinheung Kyusan, Korea) having a molar ratio of SiO₂/Na₂O (2.26) was added to the granulator dropwise to form granules until the amount of sodium silicate was about 18 weight % and spherical granules were obtained with the average diameter of about 17 mm.

The granules, so formed, were dried for 30 minutes in a fan-type dryer maintained at 120°C (moisture evaporation: 0.5 weight %, bulk density: 1.31 g/cm³), charged to the rotary furnace (Lindberg Co., U. S. A., Model No. 54579) maintained at 725°C in the air and crystallized for 20 minutes (angle of inclination: 0.5° , rotation: 8 rpm). During the above process, the resulting materials did not adhere within the device. While maintaining the initial shape of granules, 498g of white porous crystalline layered sodium disilicate having the expanded bulk density of about 0.26 g/cm³ was obtained.

EXAMPLE 2

500g of cullet powder, so collected by treating under the same conditions as Example 1, was charged to a disc-type granulator and rotated at 15 rpm. With the addition of 18 weight % of an aqueous solution of sodium silicate (contents of solid constituents: 30 weight %, Sinheung Kyusan Co.) having the molar ratio of SiO₂/Na₂O on 3.20, granules were prepared under the same conditions as Example 1.

The next process was carried out by the same conditions as Example 1 so that crystalline layered sodium disilicate was obtained.

COMPARATIVE EXAMPLE 1

5 The cullet powder, so collected by the same conditions as Example 1, was crystallized and disassembled without granulation process so that crystalline layered sodium disilicate was prepared. In the process of preparation, some product was melted and adhered to the inside of calcined device; there were a lot of dusts during the addition of raw materials; and the disassembling of the product was poor due to
10 sinter.

COMPARATIVE EXAMPLE 2

By the same procedure as described in Example 1, the cullet (molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$: 2. 50) obtained from accurately weighed 600g of silica and 432.0g of
15 sodium carbonate, respectively, was treated by the same procedure as described in Example 1 so that crystalline layered sodium disilicate was prepared.

COMPARATIVE EXAMPLE 3

By the same procedure as described in Example 1, the reaction was carried out.
20 125g of water instead of the aqueous solution of sodium silicate was added to 500g of cullet powder, so formed, to give some granules. By the same conditions as described in Example 1, the granules were crystallized and disassembled to prepare crystalline layered sodium disilicate.

25 EXPERIMENTAL EXAMPLE 1 : MEASUREMENT OF BINDING CAPACITY WITH HARDNESS CONSTITUENTS

Each of the final product, so prepared from Example 1, 2 and Comparative example 1 through 3, was disassembled by a ball-mill for 30 minutes and distributed to the particle size of $43 \sim 104 \mu\text{m}$ and Ca^{2+} and Mg^{2+} binding capacities were measured with the following methods and the results are shown in the following table

5 1.

(1) Measurement of Ca^{2+} binding capacity

About 1. 0g of the sample was weighed and charged to an agitator maintained at 25°C . With the addition of 1,000 ml of hard water (aqueous solution of Ca^{2+} ,

hardness: 200 mg Ca^{2+}/ℓ), stirred for 15 minutes and filtered off immediately.

10 Then, 25 ml of the remaining solution was accurately weighed and charged to 100 ml of Erlenmeyer flask. With the addition of 2 ~ 3 ml of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer

solution (pH 10), E. B. T indicator was added to the mixture, and then titrated with 0.01M EDTA standard solution. Thus, Ca^{2+} binding capacity was calculated by

the following equation.

15
$$\text{Ca}^{2+} \text{ binding capacity (mg } \text{Ca}^{2+} / \text{g}) = (12.5 - (t \times f)) / w \times 200 / 12.5$$

Wherein,

t, is consumed amount of EDTA (ml),

w, is a sample weight (g),

20 f, is a factor of used EDTA solution.

(2) Measurement of Mg^{2+} binding capacity

About 1. 0g of the sample was weighed and charged to an agitator maintained at 25°C . With the addition of 1,000 ml of hard water (aqueous solution of Mg^{2+} ,

25 hardness: 120 mg Mg^{2+}/ℓ), stirred for 15 minutes and filtered off immediately.

Then, 25 ml of the remaining solution was accurately weighed and charged to 100

ml of Erlenmeyer flask. With the addition of potassium cyanide solution (10%)
 0.5 ml, several drops of hydroxyl ammonium chloride solution (10%) and 2 ~ 3 ml
 of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution (pH 10), E. B. T indicator was further added to the
 mixture, titrated with 0.01M EDTA standard solution. Thus, Mg^{2+} binding
 5 capacity was calculated by the following equation.

$$\text{Mg}^{2+} \text{ binding capacity (mg } \text{Mg}^{2+} / \text{g}) = (12.5 - (t \times f)) / w \times 120 / 12.5$$

Wherein,

10 t, is consumed amount of EDTA (ml),

w, is a sample weight (g),

f, is a factor of used EDTA solution.

Table 1.

Item	Molar ratio of SiO ₂ /Na ₂ O		Ca ²⁺ binding amount (mgCa ²⁺ /g)	Mg ²⁺ binding amount (mgMg ²⁺ /g)	X-ray Diffraction
	Cullet	Aqueous solution of Sodium Silicate			
Example 1	2. 03	2. 26	108. 6	86. 5	δ - Na ₂ Si ₂ O ₅
Example 2	2. 03	3. 20	98. 7	78. 7	δ - Na ₂ Si ₂ O ₅
Comparative Example 1	2. 03	-	65. 7	56. 5	Mixture of α , β , δ - Na ₂ Si ₂ O ₅
Comparative Example 2	2. 50	2. 26	62. 4	51. 7	Mixture of α , β , δ - Na ₂ Si ₂ O ₅
Comparative Example 3	2. 03	-	97. 6	76. 9	δ - Na ₂ Si ₂ O ₅

As shown in the above table 1, it was revealed that the final products of Examples 1 ~ 2 according to the present invention have excellent binding capacity with hardness constituents and its crystalline phase is mainly composed of δ -Na₂Si₂O₅. In comparison, the final products belonging to Comparative example 1 and 2 have poor binding capacity with hardness constituents and α - or β -type impurities were included in addition to δ -type. Further, in case of Comparative example 3 using water as a binder, the physical property was somewhat poorer than Example 1 and the granulation process was more complicated than Example 1 and 2.

EXPERIMENTAL EXAMPLE 2 : X-RAY DIFFRACTION ANALYSIS

The product, so prepared from Example 1, was pulverized by a ball-mill for 30 minutes and distributed to the particle size of 43 ~ 104 μ m. Then, the degree of crystallization was investigated using X-ray diffraction analyzer (Rigakusa, Japan,

D/MAX-3B) under the following test conditions: a) material: CuK α target and Ni filter, b) output: 15 mA, 35 kV, c) diffraction angle: $5 \sim 50^\circ$, and d) relative intensity in the count range of 5,000 cps.

In line with such X-ray diffraction analysis, the relative intensity of δ -
5 crystalline layered sodium disilicate, defined in JCPDS (Joint Committee on Powder Diffraction Standard, U. S. A., 22-1396), was shown in the following table 2. Further, the X-ray diffraction characteristics of crystalline layered sodium disilicate, so prepared from Example 1 of the present invention, were shown in the following table 3 and Fig. 2, respectively.

Table 2.

D-SPACE (10^{-8}cm)	Relative intensity
6.88 (± 0.06)	0 ~ 24
4.90 (± 0.05)	0 ~ 24
3.93 (± 0.07)	75 ~ 100
3.78 (± 0.05)	50 ~ 74
3.44 (± 0.05)	0 ~ 24
3.02 (± 0.06)	25 ~ 49
2.72 (± 0.05)	0 ~ 24
2.53 (± 0.06)	0 ~ 24
2.42 (± 0.06)	25 ~ 49
2.09 (± 0.05)	0 ~ 24
1.98 (± 0.07)	0 ~ 24
1.84 (± 0.05)	0 ~ 24

Table 3.

2θ	D-SPACE (10^{-8}cm)	Relative intensity
12.79	6.91	5
14.59	6.07	12
17.98	4.93	13
21.10	4.21	13
22.36	3.97	100
22.97	3.87	7
23.45	3.79	40
24.45	3.64	10
25.80	3.45	10
26.87	3.31	13
28.74	3.10	7
29.50	3.02	20
30.71	2.91	9
31.41	2.84	14
32.79	2.73	6
34.92	2.56	7
35.29	2.54	6
35.96	2.49	11
37.01	2.42	37
43.07	2.10	17
43.73	2.07	5
44.53	2.01	4
47.27	1.92	5

48.24	1.87	7
48.92	1.86	5
49.81	1.83	5
49.16	1.82	7

As shown in the above table 3, it was revealed that the final product is mainly composed of δ -type crystal, since X-ray diffraction values of crystalline layered sodium disilicate, so prepared by the procedures as described in the Examples of the present invention, concur to main D-SPACE values (e. g., 2. 42, 3. 78, 3.93 and 6.88), as shown in the above table 2.

As explained above, the process of preparing crystalline layered sodium disilicate according to the present invention has the following advantages:

that, as adjusting the composition of cullet powder to some specific range, the final product is mainly composed of δ -type layered crystalline; after preparing the cullet powder having a certain particle size, an aqueous solution of sodium silicate is added to easily modulate the size of granules; the granules, so prepared, is dried so as to prevent any problems associated with the granulation process; crystalline layered sodium disilicate with excellent physical properties can be easily obtained when granules are crystallized.

CLAIMS

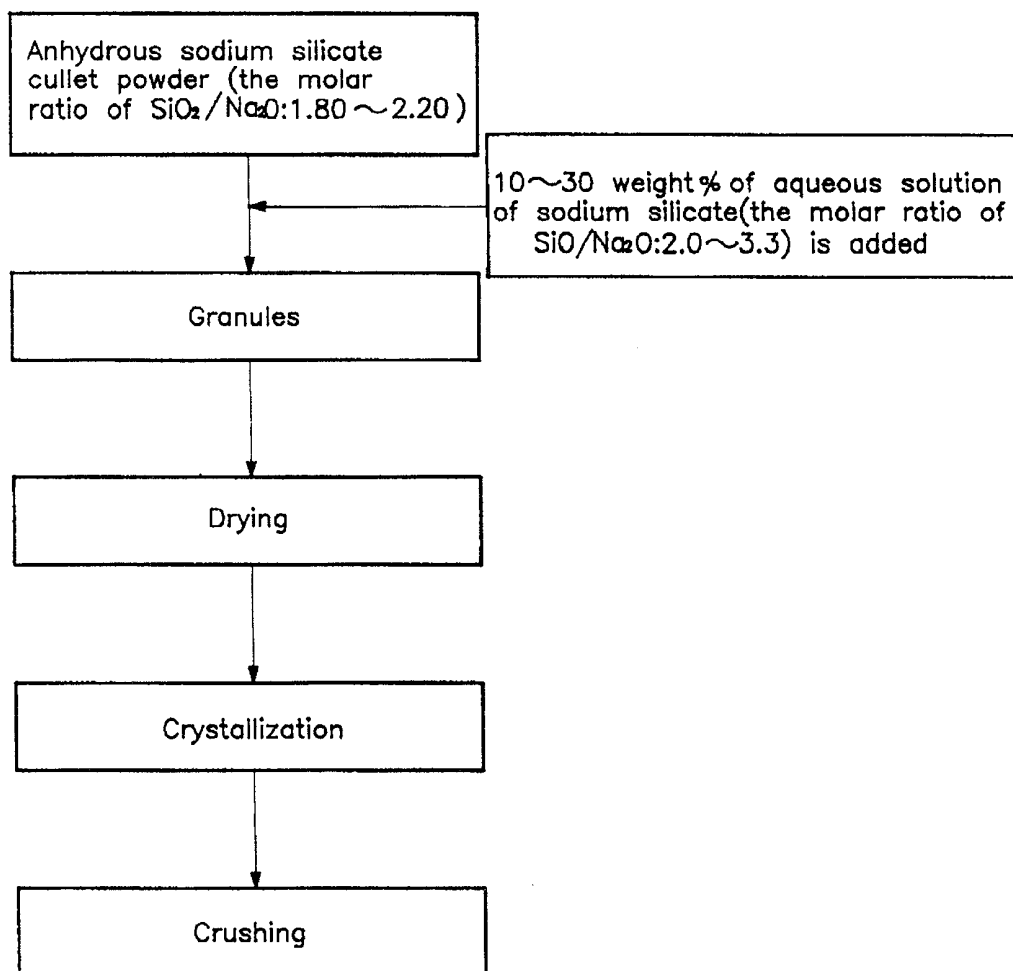
What is claimed is:

1. A process for preparation of crystalline layered sodium disilicate formulated in such a manner that a binder is added to anhydrous sodium silicate cullet powder to form granules and then, the granules are subjected to crystallization,
5 characterized wherein said binder is an aqueous solution of sodium silicate.
2. The process according to claim 1, characterized wherein said aqueous solution of sodium silicate is molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ in 2. 0 ~ 3. 3 and 15 ~ 40
10 weight % of solid contents.
3. The process according to claim 1 or 2, characterized wherein 10 ~ 30 weight % of said aqueous solution of sodium silicate is added to anhydrous sodium silicate cullet powder.
- 15 4. The process according to claim 1, characterized wherein said anhydrous sodium silicate cullet powder has a molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ in 1. 80 ~ 2. 20 and particle size of 850 μm (D_{50} : $\approx$ 300 μm) or less.
- 20 5. The process according to claim 1, characterized wherein said granules have 1 ~ 50 μm diameter.
6. The process according to claim 1, characterized wherein said crystallization process is carried out by heating and calcining the granules at 650 ~ 770 $^{\circ}\text{C}$ for
25 0. 1 ~ 1 hour.

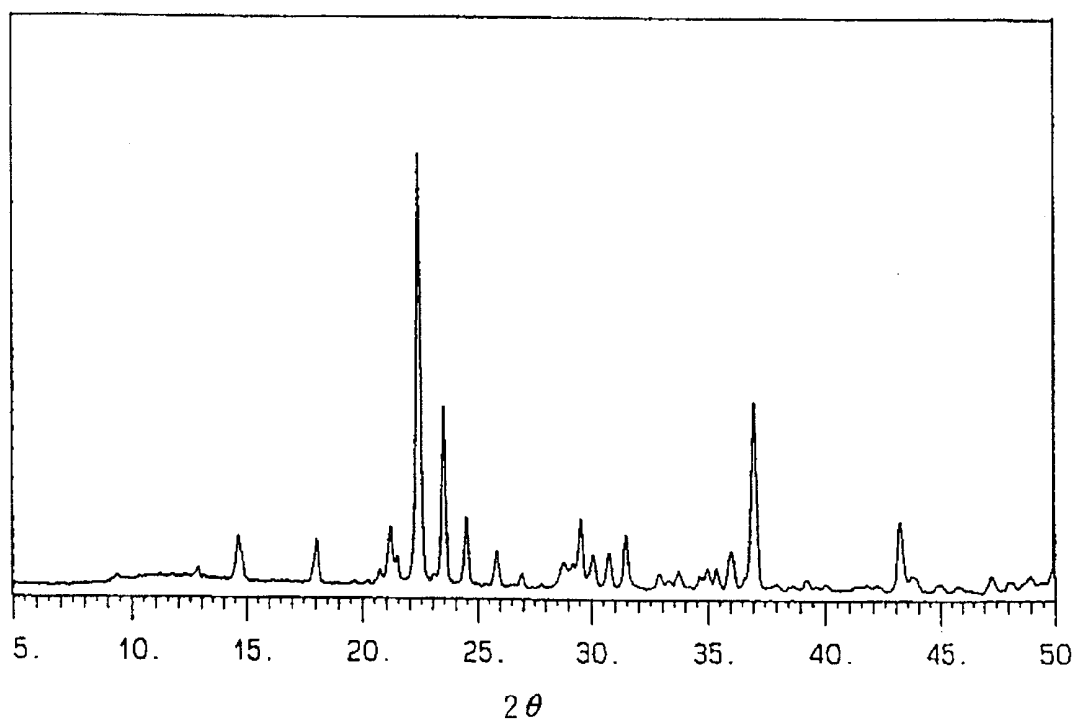
7. Crystalline layered sodium disilicate, having that calcium ion binding capacity and magnesium ion binding capacity are 98 ~ 108 mg Ca^{2+} /g and 78 ~ 86 mg Mg^{2+} /g respectively at the temperature of 25°C and that crystalline phase is δ -crystalline form, prepared by the preparation process as defined in claim 1.

1/2

Fig.1



2/2
Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 97/00269

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 01 B 33/32

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 01 B 33/32; B 01 J 2/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

Questel WPIL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 745 559 A1 (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY) 25 May 1996 (25.05.96), claims.	1
A	Database WPIL no. 97-294626, Derwent Publications Ltd., London, GB, & JP 09-110416 A (TOKUYAMA SODA KK), abstract. -----	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 April 1998 (15.04.98)

Date of mailing of the international search report

11 May 1998 (11.05.98)

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EP 0 745 559 A1 describes the preparation of sodium disilicate comprised pulverising cullet powder with a silica to sodium oxide molar ratio of 1.8-2.2: 1 to 40-200 μm particle size and adding 10-30 wt.% water. The obtained mixture is granulated to 1-50 mm size and calcined and crushed to obtain a sodium disilicate with a layered structure. The granules are pref. calcined at 650-770 deg.C for 20 mins. to 1 hr. The composition is used as a H₂O softener or detergent builder.

Database AN-Nr. 97-294626 = JP 09-110416 A describes a cullet of alkaline silicate is dissolved into water in the co-existence of calcium silicate (as seeds) to form an aqueous solution which is filtered. Preferably, dissolution of the alkaline silicate into water is at 100-250 deg.C. The method prepares aqueous solution of alkaline silicate without turbidity using low filtering resistance so that preparation time is reduced.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 97/00269

Im Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1 745559	04-12-96	JP A2 9002814	07-01-97