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AUSTRALIAN PATENT OFFICE SEC. 104

PATENT REQUEST: STANDARD PATENT

We, CARL-ZEISS STIFTUNG trading as SCHOTT GLASWERKE, being the person(s) identified below as the Applicant, request the grant of a standard patent to the person identified below as the Nominated Person, for an invention described in the accompanying complete specification.

Full application details follow.

Applicant:	CARL-ZEISS STIFTUNG trading as SCHOTT GLASWERKE
Address:	of Hattenbergstrasse 10, Postfach 2480, D-6500 Mainz 1, Federal Republic of Germany
Nominated Person:	CARL-ZEISS STIFTUNG trading as SCHOTT GLASWERKE
Address:	of Hattenbergstrasse 10, Postfach 2480, D-6500 Mainz 1, Federal Republic of Germany
Invention Title:	"Process for the preparation of very fine glass powder of high purity (mean particle size ≤ to 10 µm)"
Name(s) of Actual Inventor(s):	Dr. Hartmut Paschke; Johann Daimer; Richard Haring
Address for service is:	F.B. RICE & CO., 28A Montague St, Balmain N.S.W. 2041
Attorney Code:	RI

BASIC CONVENTION APPLICATION(S) DETAILS

Application No	Country	Country Code	Date of Application
P4100604.6	Federal Republic of Germany	DE	11 January 1991

We are not an eligible person described in Section 33 - 36 of the Act.

Dated this 18 day of May 1992

CARL-ZEISS STIFTUNG trading as SCHOTT GLASWERKE

By: _____
Registered Patent Attorney

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P/00/008
Section 29 (1)
Regulation 3.1(2)

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

I/We CARL-ZEISS-STIFTUNG trading as

*being authorised by SCHOTT GLASWERKE

of Hattenbergstrasse 10 Postfach 24 80 D 6500 Mainz 1

FEDERAL REPUBLIC OF GERMANY

the applicant in respect of an application for a patent for an invention entitled PROCESS FOR THE PREPARATION OF VERY FINE GLASS POWDER OF HIGH PURITY (MEAN PARTICLE SIZE ≤10 µm)

filed under Australian Application No. _____, state the following:-

Part 1 - Must be completed for all applications.
The person(s) nominated for the grant of the patent:

~~[ ] *is/*are the actual inventor(s)~~

or

[X] has, for the following reasons, gained entitlement from the actual inventor(s):

The nominated person is the assignee of the invention from the actual inventors

Part 2 - Must be completed if the application is a Convention application.
The person~~(s)~~ nominated for the grant of the patent *is/~~*are:~~

[X] the applicant(s) of the basic application(s) listed on the patent request form

or

~~[ ] entitled to rely on the basic application(s) listed on the patent request form by reason of the following:~~

~~*Part 3 - must be completed if the application was made under the PCT and claims priority.~~*
The person(s) nominated for the grant of the patent *is/*are:

[ ] the applicant(s) of the application(s) listed in the declaration under Article 8 of the PCT

or

[ ] entitled to rely on the application(s) listed in the declaration under Article 8 of the PCT by reason of the following:-

(continued over)

Part 4 - Must be completed if the application is a Convention application, or the application was made under the PCT and the applicant made a declaration under Article 8 of the PCT in respect of the basic application.

[X] The basic application~~(s)~~ *listed on the patent request form/~~*referred to in the declaration under Article 8 of the PCT~~ *is/~~*are~~ the application~~(s)~~ first made in a Convention country in respect of the invention.

CARL-ZEISS-STIFTUNG trading as
SCHOTT GLASWERKE
ppa. i.V.

Signed: _____ **Date:** Mainz, den 17.01.1992

(Dr. Lange) (Dr. Amrhein)

Status: _____

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-10035/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 637279

(54) Title
PROCESS FOR THE PREPARATION OF VERY FINE GLASS POWDER OF HIGH PURITY (MEAN PARTICLE SIZE IS LESS THAN OR EQUAL TO 10 MICRON)

(51)[5] International Patent Classification(s)
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(56) Prior Art Documents
US 4131238
AU 571108 46770/85 B02C 19/18 23/36
AU 35335/78 B01F 5/00 13/10 B02C 13/09 17/16 23/36

(57) Claim

1. Process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of $\leq$ 10µm by wet-grinding in the presence of grinding elements, characterised in that glass powder having a maximum particle size of $\leq$ 300µm is ground to the desired particle size in a stirred mill by means of grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder, in the presence of a grinding liquid comprising water or mixtures of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule, the grinding slurry is then frozen, and the grinding liquid is subsequently removed from the grinding slurry by freeze-drying.

637279

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CARL-ZEISS STIFTUNG trading as
SCHOTT GLASWERKE

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Invention Title:

PROCESS FOR THE PREPARATION OF VERY FINE GLASS POWDER OF HIGH PURITY (MEAN PARTICLE SIZE ≤10 µm)

The following statement is a full description of this invention including the best method of performing it known to us:-

Process for the preparation of very fine glass powder of high purity (mean particle size ≤ 10 μm).

The invention relates to a process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of ≤ 10 μm by wet-grinding in the presence of grinding elements.

High-purity glass powders are required, in particular, as fillers for plastics employed in the dental sector, for example dental fillings. For glass powders of this type, mean particle diameters d_{50} of at most 10 μm, preferably < 5 μm, in particular ≤ 3 μm are required since the mechanical properties, such as polishability and abrasion resistance, are improved with increasing fineness (decreasing particle diameter). Excessively large glass particles (< 10 μm) produce a rough surface in the cured plastic or break out and leave holes and sharp edges. The refractive index of the glass powder must agree very closely with that of the plastic in order to achieve high transparency and translucency of the filled plastic. If the glass powder contains, for example, colouring particles or particles having different refractive indices, the translucency and transparency and possibly also the colour of the filled plastic are impaired, so that the plastic can frequently only be used with considerable restrictions, if at all.

Glass powders are prepared by grinding. The grinding processes hitherto have the disadvantages of in some cases high energy consumption for the grinding, long grinding times for fine particle sizes and high abrasion of grinding pebbles and the mill wall. The abrasion particles impair the transparency and translucency of the filled plastic and make the production of very pale tooth colours difficult.

The conventional dry-grinding processes are at the limit of their performance for these small particle sizes, require long grinding times and generally require an additional air separator for classifying the grinding material. Abrasion of the grinding elements, wear of the grinding container or of the air separator and the energy

consumption are so high that these grinding processes are unsuitable for the preparation of very fine glass powders.

Although wet-grinding processes using water give fine particle sizes in a shorter time than do dry-grinding processes, the grinding elements are still subject to considerable abrasion, and a particular disadvantage is that numerous agglomerates, i.e. very solid clusters of powder particles, which act in a similar way to large individual particles and dramatically impair the properties of the filled plastic, form from the grinding slurry on drying. If, by contrast, the grinding is carried out in the presence of organic liquids in which agglomeration is substantially suppressed on drying (for example low-boiling hydrocarbons), the grinding times are considerably extended, the amount of grinding abrasion increases correspondingly and additional safety precautions, for example explosion protection, become necessary.

The object of the invention is to find a process for the preparation of very fine glass powder of high purity in which the grinding operation can be carried out in a relatively short time and with a low consumption of energy and in which mean particle sizes d_{50} of from 0.2 to 10 µm, preferably from 0.5 to 5 µm, in particular from 0.5 to 2 µm, can be produced and in which a glass powder having a purity which allows even the preparation of filled plastics which give very pale tooth colours in the dental sector is obtained.

~~This object is achieved by the process described~~ in Patent Claim 1.

The process is carried out using a stirred mill (Attritor mill) since a mill of this type allows glass powders having the desired fineness to be prepared particularly simply. In order to achieve short grinding times, it is furthermore necessary to carry out the grinding in the presence of a grinding liquid comprising water or mixtures of at least 50% by weight of water and ~~at least one water-soluble, oxygen-containing organic~~

Accordingly, the present invention provides a process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of $\leq$ 10µm by wet-grinding in the presence of grinding elements, characterised in that glass powder having a maximum particle size of $\leq$ 300µm is ground to the desired particle size in a stirred mill by means of grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder, in the presence of a grinding liquid comprising water or mixtures of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule, the grinding slurry is then frozen, and the grinding liquid is subsequently removed from the grinding slurry by freeze-drying.

The process is carried out using a stirred mill (Attritor mill) since a mill of this type allows glass powders having the desired fineness to be prepared particularly simply. In order to achieve short grinding times, it is furthermore necessary to carry out the grinding in the presence of a grinding liquid comprising water or mixtures of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic

compound having 1 to 5 carbon atoms in the molecule. Suitable organic compounds are aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and petanal, ketones, such as acetone, methyl ethyl ketone and diethyl ketone, esters, for example ethyl acetate, methyl acetate, propyl acetate, methyl formate, ethyl formate and propyl formate, or acids, such as acetic acid and propionic acid. Monohydric, dihydric and trihydric alcohols are also suitable. An example of a suitable trihydric alcohol is glycerol, but this requires long evaporation times; examples of suitable dihydric alcohols are ethylene glycol and the propanediols. Monohydric alcohols, in particular those having up to five carbon atoms in the molecule, are particularly suitable. Mixtures of water with organic compounds are preferred since attack of water on the glass powder is less pronounced. Of the eight isomeric pentanols, most can only be used mixed with lower alcohols since their water solubility is inadequate up to 2-pentanol. Their use is also associated with disadvantages due to the in some cases unpleasant odour. Of the 4 isomers of butanol, some are likewise only moderately soluble in water, so that they can again only be used mixed with other alcohols. However, tert.-butyl alcohol is highly suitable, both due to its good water solubility and also due to its high melting point.

Of the organic compounds, those are preferred whose boiling point is not above 100°C, since otherwise removal from the grinding slurry during drying takes too long. Particular preference is given to acetone, tert.-butyl alcohol, methanol, ethanol and n- and i-propanol. Particularly good grinding results are achieved using mixtures of these alcohols and acetone with from 80 to 99% by weight of water. The proportion of water in the mixture should preferably be selected so that the mixture has a freezing point of above -40°C since the operating costs for freezing equipment which operates at lower temperatures is disproportionately high.

It has furthermore proved advantageous for the

grinding operation to be carried out within a pH range of from 1 to 12. Acid or alkaline attack on the glass can take place outside these limits. It is particularly advantageous to work either in the acidic range, i.e. at a pH of from 1 to 6, in particular from 3 to 6, or in the alkaline range, i.e. at a pH of from 8 to 12, in particular 8 to 11. At these pH values, the viscosity of the grinding slurry drops to lower values. The lower viscosity of the slurry means that the amount of energy used to comminute the glass becomes greater as a proportion of the grinding energy expended, and the amount used for "stirring" the slurry becomes lower, so that the grinding performance increases. The pH can be adjusted using any desired acids and bases so long as they react with the glass only to a slight extent, or not at all. However, preference is given to acid and bases which can also easily be removed again from the grinding slurry, i.e. readily volatile acids and bases, such as acetic acid, HCl, HNO_3, NH_3, methylamine, dimethylamine, ethylamine, diethylamine etc. Preference is given to HCl, HNO_3, NH_3 and ethylamine.

In order to avoid impairing the properties of the resultant glass powder with respect to colour, transparency and translucency in the processed state, grinding elements made of a glass whose abrasion impairs the properties of the resultant glass powder only insignificantly, or not at all, are employed. Optical and mechanical properties, such as refractive index, colour, hardness, resistance to hydrolysis, polishability, etc., of the glass employed for the grinding elements should be similar or preferably identical to the corresponding properties of the glass to be ground. It is preferred for the grinding elements and the glass to be ground to have the same composition.

For grinding in the stirred mill (Attritor mill), the material to be ground must be precomminuted to a maximum particle size of $\leq$ 300 µm, preferably $\leq$ 200 µm. This precommuniution can expediently be effected by dry-grinding of the glass in a ball mill, in which these

particle sizes can be produced rapidly and without measurable abrasion of the grinding container and the grinding balls.

The fine grinding of the precomminuted glass powder to the desired size in the stirred mill is effected using grinding elements having a size of from 0.3 to 10 mm. If the grinding elements are larger than 10 mm, the resultant grinding times are very long and the wear of the grinding elements and of the mill furthermore increases considerably. During grinding in the stirred mill, the glass to be ground is pumped through the mill as a slurry (suspension), and the grinding elements are retained by various measures, for example a filter cartridge or a friction gap of appropriate dimensions. If the grinding elements are smaller than 0.3 mm, there is a danger of them no longer being adequately retained and damaging the retention systems.

The number of grinding elements affects the grinding action and thus the grinding time necessary in order to prepare a powder having a certain particle size. At a constant grinding element:grinding material weight ratio, the number of grinding elements, and thus the number of contact points between which the glass particles are ground, increases with decreasing size, and the grinding time drops. Grinding elements having a size of from 0.5 to 2 mm are therefore preferred. The grinding elements may be in the form of balls, cylindrical elements or glass fragments. The cylindrical shape of the grinding elements is preferred since this shape allows an optimum grinding result to be achieved. These grinding elements can be obtained from sections of a suitable glass rod or by sintering preforms dry-pressed or extruded from glass powders. The size is taken to mean the diameter in the case of spherical grinding elements and the particle size in the case of glass fragments. The length, width and height of cubic and similar elements and the diameter and length of cylindrical elements should be within said sizes. In the case of these elements, it is preferred for the elements to be as

compact as possible, i.e. for the individual dimensions to be substantially identical.

In stirred mills, the grinding container, the stirrer and other abrasion-endangered parts are generally lined with or comprise metal, in particular hard metal, or abrasionproof ceramic, for example Al_2O_3, or porcelain. However, the abrasion of the ceramic impairs the translucency and transparency of the filled resin compositions prepared using these powders, while metal abrasion can even result in a grey coloration; it is therefore preferred to produce these mill parts from the glass to be ground or from a glass which has similar properties or to coat them with a glass of this type or with an abrasion-resistant, solvent-resistant plastic. The mechanical durability of the plastic coating can be improved by reinforcement with glass powders or glass fibres, which preferably comprise the glass to be ground or a similar glass. Suitable plastics from the group comprising the polyurethanes, aramids or chlorofluorocarbon resins are known per se for lining mills.

When the glass powder has been ground to the desired fineness, the glass slurry is frozen and freeze-dried. During the freeze-drying, the frozen solvent is evaporated in a high vacuum by sublimation. The freeze-drying is well known per se, and freeze-drying units are commercially available from numerous manufacturers. Since the cost of freeze-drying units increase considerably with operating temperatures of below -40°C, solvents or solvent mixtures which are already frozen at temperatures down to -40°C are preferred. After the freeze-drying, the glass powder is in finely divided form without agglomeration and is ready to use per se.

However, residues from plastic abrasion of the mill lining or from the solvents used may be present in the glass powder, in some case adsorbed very strongly by the glass surface and in some cases resulting in the resultant glass powder being unusable for very pale tooth colours. In such cases, and also very generally, if very particularly pure glass powders are to be produced, the

glass powder is heated, after the freeze-drying, for from 1 hour to 10 days in an oxidising atmosphere, i.e. normally in air, at temperatures between 250°C and the glass transition temperature T_g of the glass powder, during which the organic constituents are oxidised. The heating time depends on the temperature to which the glass powder is heated and on the strength with which the organic constituents are adsorbed by the glass powder, and should expediently be matched to the particular grinding conditions. Good results are generally obtained using treatment times of from 12 to 48 hours at from 400 to 600°C.

The process which has been found allows very pure glass powders having mean particle sizes d_{50} of from 0.2 to 10 µm to be produced without difficulty, the particle sizes being determined, for example, using laser diffraction or sedimentation methods (DIN 66 111). Glass powders of this type are suitable for the production of sintered glass ceramics, but in particular in dental technology for the production of filled synthetic resins; for this application, the surface of the glass powder particles is very often treated in a manner known per se with suitable silanes, for example chlorosilanes, in order to obtain better mechanical and chemical binding of the glass powder into the resin composition. Synthetic resins in dental technology are preferably filled with glass powders having mean particle sizes of from 0.5 to 3 µm, in particular from 0.5 to 1.5 µm. Although the process also allows mean particle sizes of less than 0.2 µm to be produced, the grinding advance in this range is, however, only small, so that the grinding operation is very lengthy and in general is no longer economically worthwhile.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Process for the preparation of very fine glass powder of high purity having a mean particle size d_{50} of $\leq$ 10µm by wet-grinding in the presence of grinding elements, characterised in that glass powder having a maximum particle size of $\leq$ 300µm is ground to the desired particle size in a stirred mill by means of grinding elements made of glass whose abrasion does not impair the properties of the resultant glass powder, in the presence of a grinding liquid comprising water or mixtures of at least 50% by weight of water and at least one water-soluble, oxygen-containing organic compound having 1 to 5 carbon atoms in the molecule, the grinding slurry is then frozen, and the grinding liquid is subsequently removed from the grinding slurry by freeze-drying.

2. Process according to claim 1, characterised in that grinding elements having the same composition as the glass to be ground are used.

3. Process according to claim 1 or 2, characterised in that grinding elements having a size of from 0.3 to 10 mm are used.

4. Process according to any one of claims 1 to 3, characterised in that grinding elements having a size of from 0.5 to 2 mm are used.

5. Process according to any one of claims 1 to 4, characterised in that cylindrical grinding elements are used.

6. Process according to any one of claims 1 to 5, characterised in that a grinding liquid is used which has a pH of from 1 to 12.

7. Process according to claim 6, characterised in that a grinding liquid is used which has a pH of from 2 to 6.

8. Process according to claim 6, characterised in that a grinding liquid is used which has a pH of from 8 to 12.

9. Process according to claim 6 or 7, characterised in that the pH is set by means of hydrochloric acid or nitric acid.

10. Process according to claim 6 or 8, characterised in that the pH is set by means of ammonia or ethylamine.

11. Process according to any one of claims 1 to 10, characterised in that the grinding liquid used is methanol, ethanol, n- or i-propanol, acetone or tert.-butyl alcohol having a water content of from 80 to 99% by weight.

12. Process according to any one of claims 1 to 11, characterised in that a mill is used in which the parts which come into contact with the material to be ground comprise or are coated with an abrasion-resistant plastic, or glass which has the same or similar properties as the glass to be ground.

13. Process according to claim 12, characterised in that a plastic is used which has been reinforced with glass powder and/or glass fibres which have the same or similar properties as the glass to be ground.

14. Process according to any one of claims 1 to 13, characterised in that the glass powder is heated, after the freeze-drying, for from 1 hour to 10 days in an oxidising atmosphere at a temperature of from 250°C to the glass transition temperature T_g.

15. Process according to claim 14, characterised in that the glass powder is heated for from 12 to 48 hours at a temperature of from 400 to 600°C in air.

16. Use of the glass powder prepared by a process of any one of claims 1 to 15 as a filler for plastics, in particular in the dental sector.

17. A process for the preparation of very fine glass powder of high purity having a mean particle size of $\leq 10\mu m$ substantially as hereinbefore described.

DATED this 17th day of March 1993

CARL-ZEISS STIFTUNG (trading as SCHOTT GLASWERKE)
Patent Attorneys for the Applicant:
F.B. RICE & CO.