

A PROCESS OF FORMING SILICA GLASS

This invention is related to processes of forming silica glass.

Since it is possible to prepare silica glass of high purity, it has many uses, such as for crucibles, boards and quartz tubes of furnaces for the manufacture of semiconductors. Moreover, silica glass is used for equipment such as chemistry beakers and cells for optical measurement. Further, the development of silica glass having fewer hydroxyl groups or having good optical uniformity permits various optical uses. Especially, attention is drawn to the use of silica glass fibres for optical communication. Furthermore, silica glass is used as a substrate of thin film transistors. In this way, silica glass is widely used in various fields and the demand therefor is expected to increase still more in future.

At present, silica glass is mainly obtained by one of the following methods:

Method (1) wherein:

Cleanly refined natural quartz is washed and melted.

Method (2) wherein:

SiO_2 is formed from SiCl_4 or SiH_4 of high purity.

Method (3) wherein:

Natural silica sand is melted.

Whichever method is used, however, the resulting silica glass is expensive due to the high temperature treatment which is inevitably included in the manufacturing process.

Accordingly, a more economical process for preparing silica glass is desirable. In order to prepare silica glass cheaply, two approaches are practiced; one is a sol-gel process where metal alkoxide is used as raw material, the other is a sol-gel process wherein fumed silica is used as raw material.

The sol-gel process for economically preparing silica glass from metal alkoxides was studied by Nogami and Moriya, in Journal of Non-Crystalline Solids, 37, (1980) pp 191-201.

The steps of this process are as follows: silicon alkoxide, water, alcohol and proper catalyst such as hydrochloric acid or ammonia are mixed together and hydrolysed. After gelling the hydrolysed solution, the gel is dried. The resulting dry gel is sintered by increasing the temperature to form silica glass. This sol-gel process results in silica glass of high purity since the alkoxide used as raw material is easily purified. Moreover, manufacturing cost is less than the conventional methods because heat treatment is carried out at relatively low temperature.

On the other hand, this sol-gel process suffers the disadvantage that large articles of dry gel tend to crack during drying and similarly during heating to convert the dry gel to silica glass. Consequently silica glass of sufficient size for practical purposes cannot be obtained. So far is known, a disc of silica glass of 28mm diameter obtained by Nogami and Moriya is the largest possible at present.

A sol-gel process in which fumed silica is used as raw material is disclosed in Journal of Non-Crystalline Solids, 47, (1982) pp 435-439 by E.M. Rabinovich et al. Fumed silica (Trade Mark:

Cab-o-sil supplied by Cabot Corp.) is mixed with water to form a hydrosol. After the hydrosol has gelled, the gel is dried to form a dry gel, which is converted to silica glass by sintering. As this sol-gel process uses fumed silica there is the advantage
5 that the dry gel is less liable to breaking or cracking during drying and sintering, which permits the formation of fairly large silica glass. Nevertheless, the maximum size of silica glass obtained in the aforesaid reference is at most 95 x 15 x 5 mm (including a 4% B₂O₃). Moreover, this sol-gel process is
10 disadvantageous in that bubbles are so easily generated that many bubbles occur in the resulting silica glass. Therefore, this sol-gel process is unsuitable for applications requiring optical uniformity.

As mentioned above, the conventional sol-gel processes are
15 such that they cannot be used in various fields, since the resulting silica glass is not sufficiently large nor of good enough quality.

The present invention seeks to provide a process for forming a silica glass plate of large size or a silica glass mass of large volume at low cost compared to conventional processes.

20 According to the present invention there is provided a process of forming silica glass comprising dispersing, in a sol solution prepared by hydrolysing a metal alkoxide, 0.2 - 5 mol, per mol of the metal alkoxide, fumed silica to gel, drying the gel obtained and sintering the dry gel and during sintering said dry gel,
25 (a) removing absorbed water, (b) removing carbon, and (c) making the dry gel non-porous.

Water and hydrochloric acid may be added into the metal alkoxide and hydrolysed to a sol. Fumed silica (white carbon such as Trade

Mark: Aerosil supplied by Deutsche Gold & Silber Scheideanstalt
Vormals Roessler Co., Trade Mark: Cab-o-Sil supplied by Cabot Co.,
Trade Mark: D.C. Silica supplied by Dow Corning Co., Trade Mark:
Arc Silica supplied by PPG Industries Inc., and so on) are added
5 to the sol and stirred well. The sol may be cast into a container
of hydrophobic material such as polypropylene, polyvinylchloride,
polytetrafluoroethylene or glass. The cast sol is gelled and
dried to be dry gel. The dry gel is slowly heated from room
temperature to a predetermined temperature where the dry gel is
10 kept until the pores therein are completely collapsed, to form
a silica glass. Nogami et al's paper above discloses the way for
preventing the dry gel, using a metal alkoxide as raw material,
from cracking during sintering is to form a porous dry gel including
a great quantity of large pores of about 50 to 100 μ in diameter.
15 E.M. Ravinovich et al's paper above discloses that a dry gel,
obtained using a fumed silica as raw material, is hard to crack
during sintering, and that the dry gel synthesised by hydrolysing
a metal alkoxide with ammonia (which is more porous than a dry
gel obtained by hydrolysing a metal alkoxide with acid) is hard
20 to crack during sintering. Research by the present inventors
proves that the hardness of a dry gel relative to intensive shrinkage
during drying is determined by the pH value of the sol solution.
In one embodiment a sol solution in which a metal alkoxide is
hydrolysed using an acid as a catalyst to 1-2 pH value, results
25 in a dry get that is hard to crack, enabling larger dry gels to
be achieved.

In the light of the above, the present invention includes the feature that fumed silica is added to a sol solution including a hydrolysed metal alkoxide. The advantages brought about by the addition of a fumed silica is that the resulting dry gel becomes
5 so porous as rarely to crack during sintering, and that the pH value of the sol increases to about 2-3 so that the gelling speed is increased and the gel becomes scarcely crackable during drying. Thus, relative large silica glass which has not been obtainable heretofore, can now be obtained. In addition, silica glass obtained
10 by a process according to the present invention has good optical quality with pores being removed during sintering.

The fumed silica is white carbon obtained by hydrolysing SiCl_4 with an oxyhydrogen flame burner. The fumed silica may be that sold under the Trade Marks Aerosil and Cab-o-sil.

15 Alternatively, said fumed silica may be prepared either by a wet process using a sodium silicate as raw material or by hydrolysing a metal alkoxide in ammonia solution.

A container of hydrophobic material, in which the gel is cast, is suitable for the drying step. This is because the dry
20 gel shrinks to 70% of the original length during drying, so that the gel must be easily slid into the container with weak affinity therebetween. An organic polymer such as polypropylene, polyvinylchloride, polyethylenefluoride, polyethylene and polystyrene is suitable as materials for the container. A container of inorganic
25 material with an organic coating is also suitable.

With reference to conditions of drying, the solvent, e.g. water or alcohol, has to be evaporated. The optimum drying conditions, in the preferred embodiments, must be set up with due consideration of the ratio of the area of the holes in a lid of the container in which the gel is cast to the total area of the lid, the drying temperature and the humidity.

Reduction in the rate of evaporating of the solvent in the gel contributes to make the gel uncrackable. However, it then may take days to manufacture the dry gel, and manufacturing costs increase. Consequently, it is desired to increase yield with short manufacturing time. Drying temperature influences the toughness of the gel. The higher the temperature is, the tougher the gel is. As a result, yield is improved. However, a temperature which exceeds the boiling point of the solvent is so high that the rate of evaporating cannot be controlled. The maximum temperature is preferably about 120°C . It has been found by experiment that it is preferred that the gel is cast into a mould covered by a lid having apertures amounting to less than 50% of the surface area thereof during gelation and formation of dry gel.

Furthermore, it is preferable that the sol cast in the container should be gelled at as low a temperature as possible to prevent generation of bubbles therein. Normally, bubbles are apt to be generated in the sol or in the interface between the sol and the container. The lower the gelation temperature is, the fewer bubbles are generated. When the temperature is greater than 60°C , bubbles generate in almost

all the sols. After sintering, these bubbles remain in the silica glass and optical quality is inferior. On the other hand, when the gelling temperature is too low, rate of gelation of gells and the manufacturing cost increases. The minimum temperature is 5°C for practical purposes. The practical temperature of gelation should be between 5°C and 60°C. After gelation is completed, the rate of increase of temperature from the gelling temperature to the drying temperature should ^{preferably} be relatively low in order to obtain good yield, while it should be high in order to decrease the manufacturing time. A heating rate from the temperature at which the sol solution is gelled to the temperature at which the wet gel is dried may be less than 120°C/h. A maximum dry gel of 10cm is obtained under the above mentioned conditions.

As stated above the pH value of the sol is increased from 1-2 to 2-3 by adding a fumed silica, with the result that a tough gel can be obtained which is uncrackable even with the intensive shrinkage during drying. A large dry gel may be obtained by increasing the pH value with addition of a base such as ammonia. Preferably the pH of said sol solution including the fumed silica is adjusted to 3-6 by adding a basic reagent. Thus, in a process according to the present invention, large silica glass can be obtained by adjustment of the pH of the sol solution. Said basic reagent may be ammonia solution, ammonia gas, triethylamine or solution of triethylamine, pyridine or solution of pyridine, aniline or solution of aniline.

In contrast an inorganic base including a metal alkaline ion e.g. sodium hydride and potassium hydride, ^{may be} ~~is~~ unsuitable for forming a silica glass since cations remain in the silica glass and change the composition. However, such an inorganic base is
5 suitable for multi-component glass such as a soda glass.

Next, conditions of sintering to obtain a silica glass of high quality in a good yield will be discussed. Preferably the process includes, during sintering said dry gel, (a) removing the absorbed water, (b) removing carbon, and (c) making the dry gel
10 non-porous.

Step (a) influences the yield during sintering. Said gel is heated to a predetermined temperature between 20 and 400°C at a rate of less than 400°C/h and maintained at least once at said predetermined temperature for more than one hour to remove absorbed
15 water. Abrupt rise of temperature for removing the absorbed water makes the dry gel crack easily, resulting in poor yield. Therefore, the heating rate should be low in order to give good yield. However, the heating rate should be high considering manufacturing costs. The maximum heating rate is preferably 400°C/h to give a reasonable
20 yield.

Step (b) is carried out at 400°C-1100°C. Said gel may be heated to a predetermined temperature between 400 and 1100°C at a rate of 30-400°C/h and maintained at least once at said predetermined temperature for more than 3 hours to remove carbon. The heating
25 rate during this heat treatment also has an influence on yield, even though not so much as step (a). At the same time when the

pH value is adjusted, basic-acid reaction products remain in the dry gel. To be effective, these basic-acid reaction products are decomposed during removing the carbon. It is desirable to lengthen the time the gel is maintained at the predetermined temperature.

In step (c) preferably said gel is heated to a temperature between 1000 and 1400°C at a heating rate of 30-400°C to make it non-porous. A transparent silica glass having the same near infrared spectrum, Vickers hardness, a bulk density, etc., as silica glass on the market is formed by maintaining a dry gel for a predetermined time at a temperature where any pores collapse. In this case, if the dry gel is maintained for a relatively long time at a temperature exceeding the above after the pores are completely collapsed, bubbles are apt to be generated. Generation of bubbles is due to the water remaining in the silica glass after collapsing of the pores. The less water in the silica glass, the less bubbles are generated. Water content in a silica glass is a function of the amount of fumed silica added. With increased addition of fumed silica, the water content is decreased so that bubbles are hardly generated. Therefore, a large amount of added fumed silica is favourable for preventing generation of bubbles. On the other hand, the yield of dry gel is reduced with the addition of large amounts of fumed silica. In order to generate few bubbles and obtain a good yield, fumed silica should be added so that the metal alkoxide and fumed silica may be in the ratio mol of 1:0.2-5.

On the other hand, there is a case where crystalline material such as cristobalite and tridymite are generated in a silica glass after sintering. This is a sort of devitrification. It has been found that a non-homogenous dispersion of fumed silica in the sol and/or a very small amount of impurities cause devitrification. Ultrasonic wave vibration and centrifugal separation is effective for improving dispersion. Small amounts of impurities are removed by the centrifugal separation, preventing occurrence of devitrification.

As described above, the present invention can provide large silica glass of about 15 x 15 cm with more than 90% yield and with much lower cost than conventionally.

Furthermore, a multicomponent glass such as borosilicate glass, soda glass, silica/alumina glass, alkali-proof glass of SiO_2 - B_2O_3 group, and low-expansion coefficient glass of SiO_2 - TiO_2 group may be manufactured with low cost by use of the present invention.

This invention is of great advantage to satisfy the exacting demand for silica glass in existing and new fields.

The drawing illustrates the near-infrared spectra of silica glass obtained by a process according to the present invention and silica glass obtained by a conventional process.

Example 1

280 ml of 0.01 mol/l hydrochloric acid was added to 208g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 72g (1.2 mol) of fumed silica (Trade Mark: Cab-o-sil, whose surface area is 200 m²/g supplied by Cabot Corp.) was added to the solution with stirring. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1 cm in a cubic container of polypropylene having the width of 30cm, the length of 30cm and the height of 10cm and the container was sealed. The casting was permitted to stand at a temperature of 20°C and was gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 2% of its surface area and the casting was heated from 20°C to 60°C at a rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel 19cm x 19cm x 0.6cm which did not crack at room temperature (20°C). In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 2 out of 20 gels so formed cracked and 18 were perfect, giving a yield of 90%.

The 18 samples of dry gel were then heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 1 hour to remove absorbed water. The samples then were heated to 950°C at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating

to 1200°C at a rate of 180°C/h and maintaining at 1200°C for 1.5 hours, the samples became non-porous and transparent silica glass samples 15cm x 15cm x 0.5cm were obtained. The above sintering process did not cause cracking of any of 18 gels.

5 The near-infrared spectra of the silica glass prepared in accordance with the above process (indicated by reference numeral 1) and silica glass marketed by Sinetsu Sekiei Co., Ltd. and prepared by a melting process (indicated by reference numeral 2) are shown in the drawing. As obvious from the drawing, both have almost
10 the same near infrared spectrum. Moreover, the silica glass of this Example has the same properties as the silica glass already on the market, such as a bulk density of 2.2, a Vickers hardness of 792 and thermal expansion coefficient of 5.4×10^{-7} . Therefore, the silica glass of this Example is regarded to be the same material
15 as the fused silica glass on the market.

Example 2

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 25.8 g (0.43 mol)
20 of fumed silica (Trade Mark: Nipsil E220A which is obtained by wet process using sodium silicate as the raw material supplied by Japan Sekiei Industry Corp., diameter of particle is 1.5µm) was added to the solution with stirring and ultrasonic vibration was applied. The pH of the resultant sol was adjusted to 4.5 by
25 dropwise addition of 0.1 mol/l ammonia solution. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having the width of 30cm, the length of 30cm and the height of 10cm

and the container was sealed. The casting was permitted to stand at a temperature of 20°C and was gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid
5 with apertures amounting to 0.8% of the surface area and the casting was heated from 20°C to 70°C at a rate of 2°C/h. The gel was dried at 70°C for 12 days to yield a hard dry gel 18cm x 18cm x 0.6cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar
10 containers and dried under the same conditions. 3 out of 20 gels so formed cracked and 17 were perfect, giving a yield of 85%.

The 17 samples of dry gel were heated from room temperature to 300°C at a rate of 60°C/h and maintained at 300°C for 2 hours to remove absorbed water. The samples then were heated to 950°C
15 at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1120°C at a rate of 180°C/h and maintaining at 1120°C for 1.5 hours, the samples became non-porous and transparent silica glasses 15cm x 15cm x 0.5cm were obtained. During the sintering process,
20 2 out of the 17 samples cracked, giving a yield of 88.2%.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the
25 market, e.g. a bulk density of 2.18, Vickers hardness of 790 and thermal expansion coefficient of 5.4×10^{-7} .

Example 3

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. A mixture of 14 ml of 28% ammonia solution, 10 l of ethanol and 200 ml of water was added to the solution of 800 ml of ethylsilicate and 3.4 l of ethanol and stirred at room temperature. The stirred mixture was left overnight and then powdered silica was recovered under reduced pressure. Then, the powdered silica was left to stand at 200°C under nitrogen all night. 60 g (1 mol) of powdered silica obtained in this way was added to the hydrolysed solution with stirring and ultrasonic vibration to obtain a sol with better uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm in a cubic container of polypropylene having the width of 30cm, the length of 30cm and the height of 10cm and the container was sealed. The casting was permitted to stand at 20°C and was gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 1% of the surface area and the casting was heated from 20°C to 60°C at a rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel 21cm x 21cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 3 out of 20 gels cracked

and 17 were perfect, giving a yield of 85%.

The 17 samples of dry gel were heated by sintering from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours and further heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the sample became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process caused cracking of 5 of the 17 samples and 12 perfect gels were obtained giving a yield of 70.6%. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality. The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of silica glass now on the market. Moreover, the silica glass of this Example has the same properties as silica glass on the market, e.g. bulk density of 2.21, Vickers hardness of 811 and thermal expansion coefficient of 5.6×10^{-7} .

Example 4

280 ml of 0.01 mol/l hydrochloric acid was added to 152g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 90 g (1.5 mol) of fumed silica (Trade Mark Aerosil OX50, whose surface area is 50 m²/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Masses were removed

from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ammonia solution. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 20°C and was gelled in 30 minutes. The gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 0.8% of the surface area and the casting was heated from 20°C to 70°C at a rate of 5°C/h. The gel was dried at 70°C for 7 days to yield a hard dry gel 20cm x 20cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. None of the 20 gels cracked, giving a yield of 100%.

The 20 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours. The samples then were heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. These samples were further heated to 950°C at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1230°C at a rate of 180°C/h and maintaining at 1230°C for 1 hour, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process did not cause cracking of any of the 20 samples giving a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the silica glass now on the market. Moreover, the silica glass of this Example has the same properties as silica glass on the market, e.g. a bulk density of 2.19, Vickers hardness of 771 and thermal expansion coefficient of 5.8×10^{-7} .

Example 5

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 73 g (1.22 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50\text{m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ethanol solution of triethylamine. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 40°C and was gelled in 10 minutes. The gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 1% of the surface area and the casting was heated from 40°C to 70°C at a rate of $5^\circ\text{C}/\text{h}$. The gel was dried at 70°C for 7 days to yield a hard dry gel $18.5\text{cm} \times 18.5\text{cm} \times 0.65\text{cm}$ which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers

and dried in the same way. 2 out of 20 gels cracked and 18 were perfect, giving a yield of 90%.

The 18 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours, and further heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 900°C at a rate of 180°C/h and maintained at 900°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process did not cause cracking of any of the 18 samples giving a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 790 and thermal expansion coefficient of 5.6×10^{-7} .

Example 6

280ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 73 g (1.22 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring

and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ethanol solution of pyridine thereto.

- 5 The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 5°C. Then the cover of the container was replaced by a lid with apertures amounting to 1% of the surface
- 10 area and the casting was heated from 5°C to 60°C at a rate of 5°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel 18.8cm x 18.8cm x 0.65cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions.
- 15 3 out of 20 gels cracked and 17 were perfect, giving a yield of 85%.

- The 17 samples of dry gels were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours. The dry gels were further heated from 200°C to 300°C at a rate
- 20 of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 900°C at a rate of 180°C/h and maintained at 900°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-
- 25 porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process as above did not cause cracking of any one of the 17 samples, giving a yield of 100%.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 760 and thermal expansion coefficient of 5.6×10^{-7} .

Example 7

280 ml of 0.01 mol/l hydrochloric acid was added to 208g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 60 g (1 mol) of fumed silica (Trade Mark: Cab-o-sil, whose surface area is $200 \text{ m}^2/\text{g}$ supplied by Cabot Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by bubbling a mixture of ammonia gas and nitrogen thereinto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 30°C and was gelled in 30 minutes. Then the cover of the container was replaced by a lid with apertures amounting to 5% of the surface area and the casting was heated from 30°C to 60°C at a rate of $5^\circ\text{C}/\text{h}$. The gel was dried at 60°C for 7 days to yield a hard dry gel $21\text{cm} \times 21\text{cm} \times 0.7\text{cm}$ which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same condition. 5 out of 20 gels cracked and 15 were perfect, giving a yield of 75%.

The 15 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours. The samples were further heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove absorbed water. The samples then were heated to 950°C at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5 cm were obtained. The sintering process as above did not cause cracking of any of the 15 samples giving a yield of 100%. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the market, e.g. bulk density of 2.19, Vickers hardness of 790 and thermal expansion coefficient of 5.4×10^{-7} .

Example 8

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 100 g of water and 60 g (1 mol) of fumed silica (Trade Mark Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied to obtain a sol of better uniformity. The pH of this sol was 2.15.

The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 16cm, a length of 16cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 20°C and maintained overnight.

- 5 Then the cover of the container was replaced by a lid with apertures amounting to 0.1% of the surface area thereof and the casting was heated from 20°C to 60°C at a rate of 2°C/h. The gel was dried at 60°C for 15 days to yield a hard dry gel 11.5cm x 11.5cm x 0.7cm which did not crack at room temperature. In an
10 experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 8 out of 20 gels cracked and 12 were perfect, giving a yield of 60%.

- The 12 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours.
15 The gels were further heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a rate of 180°C/h and maintained at 950°C for 3 hours to remove carbon and ammonium chloride. After
further heating to 1200°C at a rate of 180°C/h and maintaining
20 at 1200°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 8cm x 8cm x 0.5cm were obtained. The above sintering process did not cause cracking of any of the 12 samples giving a yield of 100%. Moreover, all of the silica glasses were free of either devitrification or bubbles and proved
25 to be of high quality.

 The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the

silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.21, Vickers hardness of 790 and thermal expansion coefficient of 5.6×10^{-7} .

5 Example 9

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolyzed. 100 ml of water and 73 g (1.22 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of more perfect uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 20°C and was gelled in 30 minutes. The gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 1% of the surface area thereof and the casting was heated from 20°C to 60°C at a rate of $2^\circ\text{C}/\text{h}$. The gel was dried at 60°C for 7 days to yield a hard dry gel 21cm x 21cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same condition. 1 out of 20 gels cracked and 19 were perfect, giving a yield of 95%.

The 19 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours. The dry gels were further heated to 300°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water.

5 The samples then were heated to 950°C at a rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became

10 non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process as above did not cause cracking of any of the 19 samples, giving a yield of 100%. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared

15 in accordance with this Example was almost identical to that of the silica glass now on the market. Moreover, the silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of 5.5×10^{-7} .

20 Example 10

280 ml of 0.01 mol/l hydrochloric acid was added to 208g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 300 g (5 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface

25 area is 50 m²/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation

to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.0 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 25°C and was gelled in 50 minutes. The gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 2% of the surface area thereof and the casting was heated from room temperature to 60°C at a rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel 21cm x 21cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. 5 out of 20 gels cracked and 15 were perfect, giving a yield of 75%.

The 15 samples of dry gel were heated from room temperature to 300°C at a rate of 10°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 600°C at a rate of 320°C/h and maintained at 600°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1400°C at a rate of 320°C/h and maintaining at 1400°C for 0.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. The sintering process as above did not cause cracking of any of the 15 samples giving a yield of 100%. Moreover, all of the obtained silica glasses were free from bubbles in spite of high temperature treatment at 1400°C

40

The near-infrared spectrum of the silica glass prepared in accordance with this Example was almost identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.18, Vickers hardness of 760 and thermal expansion coefficient of 5.8×10^{-7} .

Example 11

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 100 ml of water and 12 g (0.2 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied to yield a sol of better uniformity. The pH of the resultant sol was adjusted to 3.0 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 5°C overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 0.8% of the surface area thereof and the casting was heated from 5°C to 60°C at a rate of $2^\circ\text{C}/\text{h}$. The casting was dried at 60°C for 10 days to yield a hard dry gel $18.0\text{cm} \times 18.0\text{cm} \times 0.6\text{cm}$ which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 10 out of 20 gels cracked and 10 were perfect, giving a yield of 50%.

The 10 samples of dry gel were heated from room temperature to 200°C at a rate of 10°C/h and maintained at 200°C for 3 hours.

Next, the samples were heated to 300°C at a rate of 10°C/h and maintained at 300°C for 5 hours to remove the absorbed water.

5 The samples then were heated to 600°C at a rate of 20°C/h and maintained at 600°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1000°C at a rate of 30°C/h and maintaining at 1000°C for 1.5 hours, the samples became non-porous and transparent silica glasses 14.0cm x 14.0cm x

10 0.45cm were obtained. During the sintering process as above, 3 out of the 10 samples cracked, giving a yield of 70%. Moreover, the obtained silica glasses were free from bubbles even if maintained for 30 minutes at 1200°C, while bubbles generated at 1300°C.

The near-infrared spectrum of the silica glass prepared
15 in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.19, Vickers hardness of 780 and thermal expansion coefficient of 5.6×10^{-7} .

20 Example 12

280 ml of 0.01 mol/l hydrochloric acid was added to 152 g (1 mol) of purified commercially available methoxidesilicate with violent stirring and the material was hydrolysed. 90 g (1.5 mol) of fumed silica (Trade Mark; Aerosil OX50, whose surface
25 area is 50 m²/g, supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied to yield a sol of better uniformity. The pH of the resultant sol

was adjusted to 6.0 by dropwise addition of 0.1 normal ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed.

- 5 The casting was permitted to stand at 5°C and was gelled in 10 minutes. The gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with apertures amounting to 2% of the surface area thereof and the casting was heated from 5°C to 65°C at a rate of 5°C/h.

- 10 The casting was dried at 65°C for 7 days to yield a hard dry gel 18.5cm x 18.5cm x 0.63cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same condition. 20 samples of dry gel were obtained, giving a yield of 100%.

- 15 The 20 samples of dry gel were heated from room temperature to 200°C at a rate of 60°C/h and maintained at 200°C for 3 hours. Next, the samples were heated to 300°C at a rate of 400°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 1000°C at a rate of 400°C/h
- 20 and maintained at 1000°C for 8 hours to remove carbon and ammonium chloride. After further heating to 1150°C at a rate of 400°C/h and maintaining at 1150°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 14.5cm x 14.5cm x 0.5cm were obtained. During the sintering process as above, 2 out
- 25 of the 20 samples cracked and 18 were perfect giving a yield of 90%. Moreover, all of the obtained silica glasses were free

from bubbles even if maintained for 30 minutes at 1200°C, while bubbles generated at 1300°C.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.19, Vickers hardness of 780 and thermal expansion coefficient of 5.6×10^{-7} .

Example 13

10 280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 75 g (1.22 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is 50 m²/g supplied by Aerosil Corp.) was added
15 to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into
20 a cubic container of polytetrafluoroethylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at room temperature and was gelled in 50 minutes. Further the gelled casting was maintained overnight.

25 Then the cover of the container was replaced by a lid with apertures amounting to 2% of the surface area thereof and the casting was heated from room temperature to 60°C at a rate

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of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel 21cm x 21cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 20 perfect dry gels were obtained, giving a yield of 100%.

The 20 samples of dry gel were heated from room temperature to 300°C at a rate of 180°C/h and maintained at 300°C for 1 hour to remove the absorbed water. The samples then were heated to 950°C at a rate of 320°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 320°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. During the sintering process as above, 1 out of the 20 samples cracked giving a yield of 95%. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of 5.4×10^{-7} .

Example 14

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate

with violent stirring and the material was hydrolysed. 120 g (2 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied.

- 5 Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.3 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of glass whose surface was coated with polyvinyl chloride having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 20°C and was gelled in 30 minutes. The gelled casting was maintained overnight.

- Then the cover of the container was replaced by a lid with apertures amounting to 2% of the surface area thereof and the casting was heated from 20°C to 60°C at a rate of $2^\circ\text{C}/\text{h}$. The gel was dried at 60°C for 7 days to yield a hard dry gel $21\text{cm} \times 21\text{cm} \times 0.7\text{cm}$ which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same conditions. 1 out of 20 gels cracked and 19 were perfect, giving a yield of 95%.

- The 19 samples of dry gel were heated from room temperature to 200°C at a rate of $60^\circ\text{C}/\text{h}$ and maintained at 200°C for 1 hour to removed the absorbed water. The samples then were heated to 950°C at a rate of $180^\circ\text{C}/\text{h}$ and maintained at 950°C for 9 hours to removed carbon and ammonium chloride. After further heating to 1280°C at a rate of $180^\circ\text{C}/\text{h}$ and maintaining at

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1280°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. During the sintering process as above, 1 out of the 18 samples cracked, giving a yield of 94.7%. Moreover, all of the obtained
5 silica glasses were free of either devitrification or bubbles and proved to be of high quality.

The near-infrared spectrum of the silica glass prepared in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass
10 of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 805 and thermal expansion coefficient of 5.5×10^{-7} .

Example 15

280 ml of 0.01 mol/l hydrochloric acid was added to
15 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 73 g (1.22 mol) of fumed silica (Trade Mark Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied.
20 Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.1 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of glass whose surface was coated with polyvinyl
25 chloride having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 60°C and was gelled in 10 minutes. Then the cover

of the container was replaced by a lid with apertures whose area was 0.5% of the total area of the lid and the casting was heated from 60°C to 120°C at a rate of 2°C/h. The gel was dried at 120°C for 4 days to yield a hard dry gel 21cm x 21cm x 0.7cm which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same condition. 6 out of the 20 gels cracked and 14 were perfect, giving a yield of 70%.

The 14 samples of dry gel were heated from room temperature to 400°C at a rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 1100°C at a rate of 180°C/h and maintained at 1100°C for 3 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses 15cm x 15cm x 0.5cm were obtained. During the sintering process as above, 3 out of the 14 samples cracked, giving a yield of 78.6%. The near-infrared spectrum of the silica glass prepared in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of 5.5×10^{-7} .

25 Example 16

280 ml of 0.05 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 73 g

(1.22 mol) of fumed silica (Trade Mark: Aerosil OX50, whose surface area is $50 \text{ m}^2/\text{g}$ supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 5.0 by dropwise addition of 0.1 mol/l ammonia solution thereto. The sol was cast to a thickness of 1cm into a cubic container of polypropylene having a width of 30cm, a length of 30cm and a height of 10cm and the container was sealed. The casting was permitted to stand at 5°C overnight. Then the cover of the container was replaced by a lid with apertures amounting to 50% of the surface area thereof, and the casting was heated from 5°C to 20°C at a rate of $120^\circ\text{C}/\text{h}$. The gel was dried at 20°C for 22 days to yield a hard dry gel $21\text{cm} \times 21\text{cm} \times 0.7\text{cm}$ which did not crack at room temperature. In an experiment, the sol prepared as described above was cast into 20 similar containers and dried under the same condition. 16 out of the 20 gels cracked and 4 were perfect, giving a yield of 20%.

The 4 samples of dry gel were heated from room temperature to 200°C at a rate of $10^\circ\text{C}/\text{h}$ and maintained at 200°C for 2 hours. Next, the samples were heated to 300°C at a rate of $10^\circ\text{C}/\text{h}$ and maintained at 300°C for 2 hours to remove the absorbed water. The samples then were heated to 950°C at a rate of $180^\circ\text{C}/\text{h}$ and maintained at 950°C for 6 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a rate of $180^\circ\text{C}/\text{h}$ and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses $15\text{cm} \times 15\text{cm} \times 0.5\text{cm}$

were obtained. The sintering process as above did not cause cracking of any one of the 15 samples giving a yield of 100%. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high quality.

- 5 The near-infrared spectrum of the silica glass prepared in accordance with this Example was substantially identical to that of the silica glass now on the market. The silica glass of this Example has the same properties as the silica glass on the market, e.g. a bulk density of 2.19, Vickers hardness
10 of 810 and thermal expansion coefficient of 5.4×10^{-n} .

Example 17

- 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate. The mixture was stirred for 30 minutes sufficiently
15 to conclude the hydrolysis. Then 40 g of fumed silica (Trade Mark Cab-o-sil) was added to the hydrolysed mixture with stirring. After ultrasonic vibration is applied for homogenising the solution for 30 minutes, large masses of Cab-o-sil (Trade Mark) or other foreign particles were removed by filtration. 0.1 mol/l ammonia
20 solution was added dropwise to the homogenised sol to adjust the pH of the solution to 4.4. The sol was cast to a thickness of 1cm into the container of polypropylene (23cm in inside diameter) and maintained. The casting was gelled in 30 minutes. Further the casting was maintained for 10 days at room temperature,
25 the resulting white dry gel of 15cm was obtained with shrinkage of the gel. Subsequently, the dry gel was heated to 1150°C at a rate of 180°C/h , so that the dry gel becomes transparent. As

a result, a silica glass of 10.2cm ϕ was obtained.

The silica glass obtained in this Example has a bulk density of 2.2, Vickers hardness of 800 and substantially the same near-infrared spectrum as the silica glass on the market.

5 Example 18

Similar to Example 17, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 50 ml of water and 60 g of fumed
10 silica (Trade Mark: Cab-o-sil) were added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same condition as in Example 17. The dry gel was sintered at 1200°C
15 and then the silica glass of 3cm ϕ was obtained.

The silica glass thus obtained has the same properties as the silica glass on the market and similar to that of Example 17.

Example 19

20 Similar to Example 18, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 400 ml of water and 140 g of fumed
silica (Trade Mark: Cab-o-sil) were added to the solution with
25 stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same

conditions as Example 18 and dried. The dry gel was sintered, so that the silica glass of 10.3cm was obtained.

The silica glass thus obtained has the same properties as the silica glass on the market.

5 Example 20

Similar to Example 18, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violent stirring and the material was hydrolysed. 800 ml of water and 240 g of fumed silica (Trade Mark: Cab-o-sil) were added to the solution with stirring and ultrasonic vibration was applied. Masses were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same conditions as Example 18 and dried. The dry gel was sintered, so that the silica glass of 10.3cm ϕ was obtained.

The silica glass thus obtained has the same properties as the silica glass on the market.

Exmaple 21

1800 ml of 0.1 mol/l hydrochloride was added to 2080 g (10 mol) of purified ethylsilicate on the market. The mixture was stirred for 30 minutes sufficiently to conclude hydrolysis, to which 1000 ml of water was added. Then 750 g of fumed silica (Trade Mark: Cab-o-sil) was added to the hydrolysed mixture with stirring. After ultrasonic vibration was applied for 30 minutes to homogenise the solution, masses of Cab-o-sil (Trade Mark) or other foreign particles were removed by filtration. 0.1 mol/l ammonia solution was added dropwise to the homogenised sol to adjust the pH of the solution to 4.4. The sol was cast to a

thickness of 1cm into the container of polypropylene (23cm in inside diameter). Then the sol was tested to examine how long a time was required for forming silica glass and how the yield varied with the aperture rate (area of apertures as a percentage of the surface area) of a lid of the container and the drying temperature as indicated in Table 1.

Table 1 shows that there is the maximum of the aperture rate to obtain 100% yield with proper drying temperature. Namely, the aperture rate must be less than 10% at a drying temperature of 30°C. Transparent silica glass is obtained by sintering any of the thus obtained dry gel.

TABLE 1

drying temperature (°C)	aperture rate (%)	maintainance day	yield (%)
7 0	2	6	1 0 0
6 0	5	4	2 0
6 0	4	5	8 0
6 0	2	6	1 0 0
6 0	1 /	8	1 0 0
5 0	5	4	4 0
5 0	4	6	9 0
5 0	3	7	1 0 0
5 0	2	7	1 0 0
5 0	1	8	1 0 0
4 0	1 0	6	2 0
4 0	7	8	1 0 0
4 0	5	1 0	1 0 0
3 0	1 2	8	7 0
3 0	1 0	1 0	1 0 0

Example 22

The sol obtained by the same process as Example 21 was cast into the container having a lid of a predetermined aperture rate (first aperture rate) and maintained for a predetermined number of days at room temperature to shrink. Then the casting with the same lid or with an alternative lid of a different aperture rate (second aperture rate) was heated to the predetermined temperature and maintained for the predetermined number of days to produce a dry gel. The yield was examined under the conditions shown in Table 2.

Table 2 teaches that the dry gel can be formed with a 100% yield by being once allowed to shrink at low temperature and subsequently be heated to a high temperature, even if the aperture rate was large. Simultaneously, the time needed for forming the dry gel can be decreased.

TABLE 2

first aperture rate (%)	maintenance days	second aperture rate (%)	drying temperature (°C)	drying days	yield (%)
20	6	20	80	2	80
15	6	15	90	2	90
10	7	10	90	2	90
20	2	2	70	4	90
15	1	2	70	6	100
10	1	2	80	5	100
5	1	3	80	4	90
3	1	3	80	4	100

Example 23

The sol obtained by the same process as Example 21 was dried to make the white dry gel of 15.0cm by the conventional method. As shown in Table 3, the dry gel was heated from room temperature to a first maintenance temperature at a rate of 180°C/h and maintained for a first maintenance time at a first maintenance temperature. Subsequently, the gel was heated to a second maintenance temperature at a rate of 180°C/h and maintained for a second maintenance time at a second maintenance temperature. Similarly the gel was further heated to a third maintenance temperature and maintained for a third maintenance time. Then, the gel was similarly heated to 1150°C and maintained for 3 hours, and the silica glass was prepared by sintering.

It has been shown that the silica glass obtained in this Example is free from bubbles even if heated for 30 minutes at 1300°C. In the case where the sum total of maintenance time is equal, the longer the maintenance time at high temperature, the less bubbles generated.

TABLE 3

first maintenance		second maintenance		third maintenance	
temperature (°C)	time (h)	temperature (°C)	time (h)	temperature (°C)	time (h)
950	18	1000	6	1050	3
950	18	1000	6	1050	6
950	9	1000	6	1050	3
950	6	1000	6	1050	6
950	6	1000	3	1050	3
950	3	1000	2	1050	3
950	3	1000	2	1050	1
950	9	1050	3	1100	2
950	6	1050	3	1100	3
950	3	1050	4	1100	5



CLAIMS

1. A process of forming silica glass comprising dispersing,
in a sol solution prepared by hydrolysing a metal alkoxide,
0.2 - 5 mol, per mol of the metal alkoxide, fumed silica to gel,
drying the gel obtained and sintering the dry gel, and during
5 sintering said dry gel, (a) removing absorbed water, (b) removing
carbon, and (c) making the dry gel non-porous.
2. A process as claimed in claim 1 in which the fumed silica
is white carbon obtained by hydrolysing SiCl_4 with an oxyhydrogen
flame burner.
- 10 3. A process as claimed in claim 1 in which said fumed silica
is prepared either by a wet process using a sodium silicate as
raw material or by hydrolysing a metal alkoxide in ammonia solution.
4. A process as claimed in claim 1 in which said fumed silica
is homogenously dispersed in said sol solution by applying ultrasonic
15 vibration thereto.
5. A process as claimed in claim 4 in which masses of fumed
silica are removed by centrifugal separation.
6. A process as claimed in any preceding claim in which the
pH of said sol solution including the fumed silica is adjusted
20 to 3-6 by adding a basic reagent.
7. A process as claimed in claim 6 in which said basic reagent
is ammonia solution, ammonia gas, triethylamine or solution of
triethylamine, pyridine or solution of pyridine, aniline or solution
of aniline.
- 25 8. A process as claimed in any preceding claim in which said
sol solution is cast into a mould covered by a lid having apertures



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amounting to less than 50% of the surface area thereof during gelation and formation of dry gel.

9. A process as claimed in any preceding claim in which said sol solution is gelled at 5-60°C and then dried at 20-120°C to
5 form the dry gel.

10. A process as claimed in claim 9 in which a heating rate from the temperature at which the sol solution is gelled to the temperature at which the wet gel is dried is less than 120°C/h.

11. A process as claimed in any preceding claim in which said
10 gel is heated to a predetermined temperature between 20 and 400°C at a rate of less than 400°C/h and maintained at least once at said predetermined temperature for more than one hour to remove absorbed water.

12. A process as claimed in any preceding claim in which said
15 gel is heated to a predetermined temperature between 400 and 1100°C at a rate of 30-400°C/h and maintained at least once at said predetermined temperature for more than 3 hours to remove carbon.

13. A process as claimed in any preceding claim in which said
20 gel is heated to a temperature between 1000 and 1400°C at a rate of 30-400°C to make it non-porous.

14. A process as claimed in any preceding claim and substantially as herein described with reference to the Examples.

15. Silica glass when formed by the process as claimed in any
25 preceding claim.
