

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PREPARATION OF SILICA GELS

- (71) We, NATIONAL DISTILLERS AND CHEMICAL CORPORATION of 99 Park Avenue, New York, State of New York, New York, United States of America, a corporation organised and existing under the laws of the State of Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to silica gels and to their preparation.
- The present invention provides a silica xerogel which is stable at temperatures up to 1100°C in a fluidized bed and which has a surface area of from 200 to 500 m²/g the majority of which is provided by pores of a diameter of from 300 to 600 Å. It also provides a method for producing a silica xerogel according to claim 1 which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous silicate solution to provide a silica hydrogel slurry having an SiO₂ concentration of from 5 to 12% by weight and a pH of from 3 to 8, the temperature during precipitation being maintained between 0° and 10°C., (b) heating the product of step (a) at a pH of from 3—8 and at a temperature of from 50°C to 100°C for from 1 to 6 hours, (c) washing the product of step (b) to remove sodium until the filtrate contains less than 20 ppm by weight of sodium salt, (d) cooling said hydrogel particles to a temperature sufficient to maintain the water in the pores in the frozen state, and (e) vacuum subliming the frozen water from the said gel.
- A preferred method according to the invention involves:
1. Precipitation of a silica gel by reducing the pH of an aqueous solution of a soluble silicate, such as xNa₂O.ySiO₂, with an acid such as CO₂ or H₂SO₄, ion exchange resins or by other suitable procedure, preferably carried out in stoichiometric proportions with agitation and in accordance with the following conditions:
 - (a) The SiO₂ concentration in the final slurry is from 5 to 12 per cent by weight and preferably from 8 to 9 per cent,
 - (b) the pH-reducing medium is most advantageously added at the rate of 40 per cent of the needed amount in from 30 minutes to 120 minutes, and preferably about 60 minutes, and the remaining 60 per cent on the amount is added in from 20 to 90 minutes more, and preferably about 45 minutes more.
 - (c) the temperature during precipitation is maintained between 0 and 10°C. and preferably at about 5°C., and
 - (d) the final pH of the slurry is from 3 to 8 and preferably from 5 to 6.
 2. Heating the precipitated silica hydrogel slurry under the following conditions:
 - (a) A pH of from 3 to 8, and preferably from 5 to 6,
 - (b) a temperature of from 50°C to 100°C., and preferably about 90°C., and
 - (c) for a period of from 1 to 6 hours and preferably about 4 hours.
 3. Washing the product with one or more salts having a displacing effect on sodium until the filtrate titrates less than 20 ppm by weight of sodium salt. Suitable salts include aluminum chloride or sulfate and ammonium chloride or nitrate. The displacing can also be accomplished by washing with strong acid such as hydrochloric acid or H₂SO₄.
 4. Reducing the gel particle size by high shear mixing (homogenising) from step 3 to obtain particles having a mean diameter of less than 200 microns and preferably of from 30 to 150 microns.
 5. Vacuum freeze drying the product, preferably at -110°C to 10°C. Comminution of the gel, if this is necessary, may be effected before or after the gel is frozen.
- The invention will now be described in greater detail with reference to specific examples which illustrate the criticality of process conditions in order to obtain a silica xerogel product having the required properties.

The properties on the silica xerogel obtained in accordance with the invention and particularly the porosity characteristics are discussed in terms of pore volume (PV), surface area (SA), average pore diameter (Pd), where $Pd = \frac{4PV}{SV}$, and pore size distribution.

Determinations of the values for the various properties are made by a nitrogen absorption-desorption technique well known in the art and described in detail in the literature.

In the following examples, Example I is a description of a preferred method for carrying out the process of the invention to obtain a silica gel of the stated characteristics. The remainder of the examples illustrate the criticality of various process conditions or describe suitable alternative procedures for obtaining the silica gels.

EXAMPLE I

20,160 g of sodium silicate solution containing 28.7% SiO_2 and 8.9% Na_2O was added to 25,440 g of H_2O and the mixture cooled to $5^\circ C$ under agitation.

21,305 g of H_2SO_4 (12.75 wt. %) were then added as follows:

8,520 g were added in one hour and the remaining amount in 45 minutes. The final pH of the slurry was 5.0.

The slurry was then heated to $95^\circ C$. within 2 hours and maintained at $95^\circ C$. for 2 hours.

A 30 g sample was drawn and washed with a solution of 10 g of NH_4NO_3 in 3000 ml of H_2O , then with deionized water until the filtrate titrated less than 20 ppm Na_2SO_4 . The product was homogenized and 10 g of the slurry containing 8.5% solid was vacuum freeze dried. The cold trap was set at $-120^\circ C$. and the sample, pre-frozen, maintained at $-40^\circ C$.

1 gm of sample was recovered and calcined in the oven at $540^\circ C$. for 4 hours before evaluating it. Physical properties of the silica gel obtained were: S.A.=321 m^2/g , P.V.=2.49 cm^3/g , Pd=312 Å.

Calcination in a fluidized bed for 3 hours at $980^\circ C$. did not alter the physical properties: S.A.=329 m^2/g , P.V.=2.47 cm^3/g , Pd=301 Å.

Referring to Figure 1 of the drawings, which is a distribution curve of the pore sizes, it will be seen that the major portion of the cumulative pore volume (and hence surface area) of the silica gel product is accounted for by pores having a pore diameter in the range of from 300 to 600 Å.

EXAMPLE II

To compare the freeze drying technique to the water displacement technique disclosed in our co-pending application No. 39240/69, a

30 g sample was prepared as in Example I and was washed until the filtrate titrated less than 20 ppm Na_2SO_4 . The product was then homogenized, reslurried in acetone and washed with acetone by decantation until the water in the acetone titrated less than 1%.

The acetone was distilled off and the resulting silica gel was calcined in an oven at $540^\circ C$. for 4 hours.

Physical properties of the silica obtained were found to be substantially the same as those obtained by the water displacement technique, S.A.=327 m^2/g , P.V.=2.61 cm^3/g , Pd=319 Å.

EXAMPLE III

All the variables during precipitation, except the concentration of the silica, were maintained the same as in Example I. The final SiO_2 concentration of 7% and 10% were chosen and Figure 2 shows the effect of SiO_2 concentration on the porosity of the gel just after precipitation.

Referring to Figure 2 of the drawing, it will be seen that lower pore volumes are obtained where the final silica concentration in the slurry is 7% and 10% as compared with the pore volume obtained in Example I where an SiO_2 concentration of about 8.5% was obtained. Figure 2 also demonstrates that the surface area increases as the SiO_2 concentration increases. Thus, in order to get maximum pore volume and at the same time to obtain a good surface area level, it is preferable to maintain the SiO_2 concentration at from 8% to 9% and most preferably at about 8.5%.

EXAMPLE IV

All variables during precipitation, except acid addition rate, were maintained as in Example I. Acid addition rate of 0.5 hour and 2.0 hours for the addition of 40% of the stoichiometric amount of SiO_2 were used.

Example IV clearly illustrates, as shown in Figure 3 of the drawings, that both pore volume and surface area of the precipitated hydrogel are dependent upon the rate in which the pH-reducing medium, in this case, sulfuric acid, is added to the aqueous silicate solution. It will be seen that optimum pore volume and surface area values are obtained using an addition rate of about 1 hour for 40% of the stoichiometric amount and that lower values for pore volume and surface area are obtained where more rapid or slower addition rates are employed.

EXAMPLE V

All variables during precipitation, except temperature, were maintained as in Example I. Temperatures of $25^\circ C$ and $50^\circ C$ were used during precipitation.

As will be seen by reference to Figure 4, the pore volume of the precipitated hydrogel

- decreases as the precipitation temperature increases. Surface area also tends to decrease with an increase in the precipitation temperature, but this value flattens out at about 5°C. This is the preferred temperature of precipitation in order to secure optimum values for pore volume and surface area.

EXAMPLE VI

- All variables during precipitation were maintained the same as in Example I, except CO₂ was used to neutralize the sodium silicate instead of sulfuric acid. The physical properties of the silica gel were similar to those obtained under Example I.

EXAMPLE VII

- In this example, a silica gel was produced as in Example I except that the washed gel was tray dried at 80°C instead of being vacuum freeze dried.

- Physical properties of the gel were: S.A.=110 m²/g, P.V.=0.41 cm³/g, and Pd=149 Å.

- The product obtained by tray drying at 80°C is severely adversely affected in terms of surface area, pore volume and average pore diameter in comparison with the results obtained by freeze drying as in Example I.

- Example I and II illustrate the similar effectiveness, in obtaining a xerogel of appropriate properties from the hydrogel, of the acetone treatment and vacuum freeze drying. Reference is directed to Examples VI, VII and VIII of copending application number 39240/69 (Serial No. 1284086) for a demonstration of the effect on final product properties of the process parameters of ageing time and pH, and degree of sodium removal; using the acetone treatment method disclosed and claimed in application No. 39240/69 (Serial No. 1284086).

Variation of these parameters has similar effect in the present freeze drying process.

WHAT WE CLAIM IS:—

1. A silica xerogel which is stable at temperatures up to 1100°C in a fluidized bed and which has a surface area of from 200 to 500 m²/g the majority of which is provided by pores of a diameter of from 300 to 600 Å.
2. A method for producing a silica xerogel which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous silicate solution to provide a silica hydrogel slurry having an SiO₂ concentration of from 5 to 12% by weight and a pH of from 3 to 8, the temperature during precipitation being maintained between 0° and 10°C., (b) heating the product of step (a) at a pH of from 3—8 and at a temp. of from 50°C to

100°C for from 1 to 6 hours, (c) washing the product of step (b) to remove sodium until the filtrate contains less than 20 ppm by weight of sodium salt, (d) cooling said hydrogel particles to a temperature sufficient to maintain the water in the pores in the frozen state, and (e) vacuum subliming the frozen water from said gel.

3. A method according to claim 2 wherein the precipitation of silica hydrogel in step (a) is accomplished by reducing the pH of an aqueous solution of sodium silicate with an agent selected from acids and ion-exchange resins.

4. A method according to claim 3 wherein 40% of the amount of pH-reducing agent necessary for the precipitation is added over a period of from 30 to 120 minutes and the balance is added during a subsequent period of from 20 to 90 minutes.

5. A method according to claim 4 wherein the first 40% of the pH-reducing agent is added over a period of about 1 hour.

6. A method according to claim 4 or 5 wherein the said balance of the pH-reducing agent is added over a period of about 45 minutes.

7. A method according to any of claims 2 to 6 wherein the SiO₂ Concentration in the hydrogel precipitate of step (a) is from 8 to 9% by weight.

8. A method according to any of claims 2 to 7 wherein the temperature during step (a) is about 5°C and the temperature of the slurry during step (b) is about 90°C.

9. A method according to any of claims 2 to 8 wherein the pH in steps (a) and (b) is from 5 to 6.

10. A method according to any of claims 2 to 9 wherein step (b) is conducted for about 4 hours.

11. A method according to any of claims 2 to 10 wherein step (c) is accomplished by washing with a solution of one or more displacing salts selected from aluminum chloride, aluminum sulfate, ammonium chloride, and ammonium nitrate.

12. A method according to any of claims 2 to 10 wherein step (c) is accomplished by washing with a solution of HCL or H₂SO₄.

13. A method according to any of claims 2 to 12 wherein the gel is comminuted to a particle size less than 200 microns before or after step (d).

14. A method according to any of claims 2 to 15 wherein the dried xerogel is calcined at a temperature of from 260 to 650°C.

15. A method according to any of claims 2 to 14 wherein said hydrogel is cooled in step (e) to a temperature of from—100°C. to 10°C.

16. A method of preparing a silica xerogel substance as described in Example I or VI.

increases as the precipitation temperature increases. Surface area also tends to decrease with an increase in the precipitation temperature, but this value flattens out at about 5°C. This is the preferred temperature of precipitation in order to secure optimum values for pore volume and surface area.

EXAMPLE VI

All variables during precipitation were maintained the same as in Example I, except CO₂ was used to neutralize the sodium silicate instead of sulfuric acid. The physical properties of the silica gel were similar to those obtained under Example I.

EXAMPLE VII

In this example, a silica gel was produced as in Example I except that the washed gel was tray dried at 80°C instead of being vacuum freeze dried.

Physical properties of the gel were: S.A.=110 m²/g, P.V.=0.41 cm³/g, and Pd=149 Å.

The product obtained by tray drying at 80°C is severely adversely affected in terms of surface area, pore volume and average pore diameter in comparison with the results obtained by freeze drying as in Example I.

Example I and II illustrate the similar effectiveness, in obtaining a xerogel of appropriate properties from the hydrogel, of the acetone treatment and vacuum freeze drying. Reference is directed to Examples VI, VII and VIII of copending application number 39240/69 (Serial No. 1284086) for a demonstration of the effect on final product properties of the process parameters of ageing time and pH, and degree of sodium removal; using the acetone treatment method disclosed and claimed in application No. 39240/69 (Serial No. 1284086).

Variation of these parameters has similar effect in the present freeze drying process.

WHAT WE CLAIM IS:—

1. A silica xerogel which is stable at temperatures up to 1100°C in a fluidized bed and which has a surface area of from 200 to 500 m²/g the majority of which is provided by pores of a diameter of from 300 to 600 Å.

2. A method for producing a silica xerogel which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous silicate solution to provide a silica hydrogel slurry having an SiO₂ concentration of from 5 to 12% by weight and a pH of from 3 to 8, the temperature during precipitation being maintained between 0° and 10°C., (b) heating the product of step (a) at a pH of from 3—8 and at a temp. of from 50°C to

100°C for from 1 to 6 hours, (c) washing the product of step (b) to remove sodium until the filtrate contains less than 20 ppm by weight of sodium salt, (d) cooling said hydrogel particles to a temperature sufficient to maintain the water in the pores in the frozen state, and (e) vacuum subliming the frozen water from said gel.

3. A method according to claim 2 wherein the precipitation of silica hydrogel in step (a) is accomplished by reducing the pH of an aqueous solution of sodium silicate with an agent selected from acids and ion-exchange resins.

4. A method according to claim 3 wherein 40% of the amount of pH-reducing agent necessary for the precipitation is added over a period of from 30 to 120 minutes and the balance is added during a subsequent period of from 20 to 90 minutes.

5. A method according to claim 4 wherein in the first 40% of the pH-reducing agent is added over a period of about 1 hour.

6. A method according to claim 4 or 5 wherein the said balance of the pH-reducing agent is added over a period of about 45 minutes.

7. A method according to any of claims 2 to 6 wherein the SiO₂ Concentration in the hydrogel precipitate of step (a) is from 8 to 9% by weight.

8. A method according to any of claims 2 to 7 wherein the temperature during step (a) is about 5°C and the temperature of the slurry during step (b) is about 90°C.

9. A method according to any of claims 2 to 8 wherein the pH in steps (a) and (b) is from 5 to 6.

10. A method according to any of claims 2 to 9 wherein step (b) is conducted for about 4 hours.

11. A method according to any of claims 2 to 10 wherein step (c) is accomplished by washing with a solution of one or more displacing salts selected from aluminum chloride, aluminum sulfate, ammonium chloride, and ammonium nitrate.

12. A method according to any of claims 2 to 10 wherein step (c) is accomplished by washing with a solution of HCL or H₂SO₄.

13. A method according to any of claims 2 to 12 wherein the gel is comminuted to a particle size less than 200 microns before or after step (d).

14. A method according to any of claims 2 to 15 wherein the dried xerogel is calcined at a temperature of from 260 to 650°C.

15. A method according to any of claims 2 to 14 wherein said hydrogel is cooled in step (c) to a temperature of from—100°C. to 10°C.

16. A method of preparing a silica xerogel substance as described in Example I or VI.



17. A silica xerogel produced by a method according to any of claims 2 to 15.

18. A silica xerogel substance as described in Example I, II or VI.

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