

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, 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 provides a method for producing a silica gel which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous solution of sodium silicate to provide a silica hydrogel slurry having an SiO_2 concentration of from 5 to 12% by weight of 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 to 8 and at a temperature of from 50° 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) adding an organic liquid which forms an azeotropic mixture with water, (e) distilling said azeotropic mixture so as to separate the water from said gel, and (f) removing the excess organic liquid from the resulting gel.

In one procedure, the organic liquid in step (d) is added in an amount in excess of that required to provide an azeotropic mixture; in another procedure the organic liquid in step (d) is added in an amount substantially less than that required to provide an azeotropic mixture, the liquid being continuously recycled after decantation of the water from the distilled azeotropic mixture.

A preferred method according to the invention involves:

1. Precipitation of a silica gel by reducing the pH of an aqueous sodium silicate solution with an acid e.g. CO_2 or H_2SO_4 , ion exchange resins, or by other suitable procedure, carried out in stoichiometric proportions with

agitation and in accordance with the following conditions:

- (a) The SiO_2 concentration in the final slurry is from 5 to 12 per cent by weight and preferably from 8 to 9 per cent. 50
- (b) The pH-reducing medium is added at the rate of 40 per cent by weight of the needed amount in from 30 minutes to 120 minutes, and preferably about 60 minutes, and the remaining 60 per cent of the amount is added in from 20 to 90 minutes more, and preferably about 45 minutes more. 55
- (c) The temperature during precipitation is maintained between 0 and 10°C . and preferably at about 5°C ., and 60
- (d) The final pH of the slurry is from 3 to 8 and preferably from 5 to 7 and most preferably from 5 to 6. 65

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. 70
- (b) A temperature 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. 75

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 and mixtures thereof. The displacing can also be accomplished by washing with strong acid such as hydrochloric acid or H_2SO_4 . 80

4. Optionally communicating the gel by high shear mixing (homogenising) from step 3 to obtain particles having a mean diameter of less than 200 microns and preferably in the range of from 30 to 150 microns. 85

5. Adding an organic liquid which forms an azeotrope with water when distilled and distilling the azeotrope so as to remove substantially all the water. 90

6. Distilling off the excess organic liquid.
7. Calcining the product from step 6 at a temperature of from 260°C to 650°C, and preferably at about 540°C.

5 The azeotropic distillation may be conducted by admixing organic liquid with the wet gel in an amount in excess of the azeotropic mixture. The admixture is then preferably alternately refluxed for 0.5 to 2
10 hours and distilled for a total cycle time of from 5 to 20 hours and preferably about 8 hours. The temperature of the distillation is dependent upon the particular organic liquid used and the pressure of the system.

15 A preferred method of carrying out this distillation process is shown in Figure 1. In this process, the hydrogel is charged into the jacketed vessel 1 through valve A. An organic liquid which forms an azeotrope with water, is retained in storage tank 3 and is pumped
20 into vessel 1. Vessel 1 is then heated to provide the required distillation.

The distillate is recovered through heat exchanger 2 into storage tank 3 where the azeotrope separates into two phases and water
25 is removed by decantation.

The organic portion is recirculated into the system by being continuously pumped back into vessel 1 and the system is operated for
30 between 2 and 20 hours, preferably about 5 hours, after which pump 4 is stopped and excess organic liquid is distilled until the silica gel is dried.

35 Two high and low capacitance probes 5 and 6 are located at the bottom of tank 3 which activate motor valve 7 draining the water from the tank through line 8.

The dry silica gel is discharged through valve B.

40 Suitable organic liquids for use in the present process include: benzene, toluene, xylene, ethyl - acetate, n - propyl formate, n and iso - butyl formate, n and iso - amyl formate, benzyl formate, n - propyl acetate,
45 n and iso - butyl acetate, n and iso - amyl acetate, benzyl acetate, phenyl acetate, ethyl propionate, n - propyl propionate, iso - butyl propionate, iso - amyl propionate, methyl butyrate, n - propyl butyrate, n and
50 iso - butyl butyrate, iso - amyl butyrate, methyl iso - butyrate, ethyl iso - butyrate, di - iso - butyl ether, di - iso - amyl ether, diphenyl ether, phenetole, anisole, and resorcinol diethyl ether.

55 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 a surface area of from
60 200 to 500 m²/g the majority of which is provided by pores of a pore diameter of from 300 to 600Å and which is stable up to 1100°C in a fluidized bed.

65 The properties of 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

$$Pd = \frac{4PV}{SA}, \quad 70$$

and pore size distribution. The determination of the values for the various properties were made by a nitrogen absorption-desorption technique which is well known in the art and which is described in greater detail in the
75 literature.

In the following examples, Example I and Example II describe a preferred method for carrying out the process of the invention so as to obtain a silica xerogel of the stated characteristics. The remaining examples illustrate the criticality of various process conditions and describe suitable alternative procedures for obtaining the silica xerogels.

EXAMPLE I

85 20,160 g of sodium silicate solution containing 28.7% SiO₂ and 8.9% Na₂O was added to 25,440 g of H₂O and the mixture cooled to 5°C with agitation.

21,305 g of H₂SO₄ (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 precipitate was 5.0.

95 The slurry was then heated to 95°C. within 2 hours and maintained at 95°C. for 2 hours, washed with a solution of 2225 g of NH₄NO₃ in 45-gallons of water, then with deionized water until the filtrate titrated less than 20 ppm Na₂SO₄.
100

The product was then homogenized for 30 minutes after which a 300 g sample was drawn, allowed to settle and the excess water decanted.

60 g of slurry, containing 11% by weight
105 of solids was recovered and added to 1500 g of ethyl acetate in a distillation flask. The azeotrope was then distilled at atmospheric pressures by using the following procedure: alternatively distilling for 1/2 hour and refluxing for 1-1/2 hours for a total process
110 time of 8 hours. For precaution, the ethyl acetate was continuously added to maintain the same level of liquid in the flask. Temperature fluctuations during the azeotropic distillation were between 70.5°C and 71°C.
115 After 8 hours, the gel was dried by distilling the remaining ethyl acetate.

The silica xerogel recovered was calcined in an oven at 540°C. for 4 hours before
120 evaluating.

Analysis of the physical properties were: S.A.=307 m²/g, P.V.=2.35 cm³/g, Pd=317 Å.

EXAMPLE II

A 1000 g sample obtained in Example I after homogenization was drawn, allowed to settle and the excess water decanted.

5 A 200 g sample of the slurry containing 11% by weight solids was then added to a 2000 ml distillation flask installed in a laboratory set-up equivalent to the one represented in Figure 1. 1000 g of ethyl acetate was pumped into the distillation flask before starting the distillation, and the distillation was run for 5 hours. The ethyl acetate continuously recovered was pumped back into the distillation flask after the water had been separated by decantation, at a rate equal to its distillation rate.

After 5 hours, the pump was stopped and the excess ethyl acetate distilled off to obtain a dried silica gel.

20 The xerogel recovered was calcined in an oven at 537.7°C. for 4 hours and evaluated for its physical properties. S.A.=323 m²/g, P.V.=2.53 cm³/g, Pd=313 Å.

25 Figure 2 is a distribution curve of the pore sizes. It can be seen that the major portion of the pore volume (and hence surface area) of the silica xerogel product is accounted for by pores having pore diameters in the range of from 300 Å to 600 Å.

30 Calcination in a fluidized bed for 3 hours at 982°C did not alter the physical properties which were: S.A.=329 m²/g, P.V.=2.47 cm³/g, Pd=301 Å.

EXAMPLE III

35 In this Example, a 300 g sample obtained after homogenization in Example I was drawn and the excess water decanted.

40 A 60 g sample containing 11% by weight solids was then added to 1500 g of ethyl acetate. The azeotrope followed by the excess ethylacetate were distilled off in a continuous manner.

45 The silica xerogel obtained was calcined in the oven for 4 hours at 540°C. and evaluated for its physical properties: S.A.=342 m²/g, P.V.=1.91 cm³/g, Pd=223 Å.

50 As can be seen when using an azeotropic distillation without using the conditions described in Example I or Example II to dry the product, the pore volume and consequently the average pore diameter were adversely affected.

EXAMPLE IV

55 To compare the azeotropic distillation technique to the water displacement technique described in Copending 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 Na₂SO₄. The product was then homogenized, reslurried in acetone and washed with acetone by decanta-

tion 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°C. for 4 hours.

The physical properties of the silica obtained were found to be substantially the same as those obtained by the azeotropic distillation technique, S.A.=333 m²/g, P.V.=2.50 cm³/g, average Pd=300 Å.

EXAMPLE V

75 All the variables during precipitation, except the concentration of the silica during precipitation were maintained as in Example I. The final SiO₂ concentration was 7% and 10% by weight. Figure 3 shows the effect of SiO₂ concentration on the porosity of the gel just after precipitation.

80 Referring to Figure 3 of the drawing, it will be seen that relatively lower pore volumes are obtained where the final silica concentration in the slurry is between 7% and 10% by weight as compared with the pore volume obtained in Example I where an SiO₂ concentration of about 8.5% by weight was obtained. Figure 3 also demonstrates that surface area increases as the concentration of SiO₂ 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 SiO₂ concentration at between about 8% and 9% by weight and most preferably at about 8.5% by weight.

EXAMPLE VI

100 All variables during precipitation, except the acid addition rate, were maintained as in Example I. An acid addition rate of 0.5 hours and 2.0 hours for the addition of 40% of the stoichiometric amount of pH-reducing medium was used.

105 Example VI clearly illustrated, as shown in Figure 4 of the drawings, that both pore volume and surface area of the precipitated hydrogel are dependent upon the rate 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 VII

120 All variables during precipitation, except temperature, were maintained as in Example I. Temperatures of 25°C. and 50°C. were used during precipitation.

As will be seen by reference to Figure 5, the pore volume of the precipitated hydrogen 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 VIII

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.

Examples I and IV illustrate the similar effectiveness, in obtaining a xerogel of appropriate properties from the hydrogel, of the acetone treatment and azeotropic distillation. 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 parameter of ageing time and pH, and degree of sodium removal; using the acetone treatment method described and claimed in Copending Application No. 39240/69 (Serial No. 1284086). Variation of these parameters has similar effect in the present azeotropic distillation process. Copending Application 39239/69 (Serial No. 1284085) claims *per se* a silica xerogel stable at temperatures up to 1100°C in a fluidised 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 from 300—600 Å.

WHAT WE CLAIM IS:—

1. A method for producing a silica gel which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous solution of sodium silicate 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 to 8 and at a temperature of from 50° 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) adding an organic liquid which forms an azeotropic mixture with water, (e) distilling said azeotropic mixture so as to separate the water from said gel, and (f) removing the residual organic liquid from the resulting gel.

2. A method according to claim 1 wherein the precipitation of silica hydrogel in step (a) is accomplished by reducing the pH of an aqueous solution of sodium silica with an agent selected from acids and ion-exchange resins.

3. A method according to claim 2 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.

4. A method according to claim 3 wherein the first 40% of the pH-reducing agent is added over a period of about 1 hour.

5. A method according to claim 3 or 4 wherein the said balance of the pH-reducing agent is added over a period of about 45 minutes.

6. A method according to any of claims 1 to 5 wherein the SiO₂ concentration in the hydrogel precipitate of step (a) is from 8 to 9% by weight.

7. A method according to any of claims 1 to 6 wherein the temperature during step (a) is about 5°C and the temperature of the slurry during step (b) is about 90°C.

8. A method according to any of claims 1 to 7 wherein the pH in step (a) is from 5 to 7.

9. A method according to any of claims 1 to 8 wherein the pH in step (b) is from 5 to 6.

10. A method according to any of claims 1 to 9 wherein step (b) is conducted for about 4 hours.

11. A method according to any of claims 1 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 1 to 10 wherein step (c) is accomplished by washing with a solution of HCl or H₂SO₄.

13. A method according to any of claims 1 to 12 wherein the gel is comminuted to a particle size less than 200 microns before step (d).

14. A method according to any of claims 1 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 1 to 14 wherein the organic liquid in step (d) is added in an amount in excess of that required to provide an azeotropic mixture.

16. A method according to any of claims 1 to 15 wherein said azeotropic mixture is alternately refluxed for 0.5 to 2 hours and distilled so that the total process time is between 5 and 20 hours.

17. A method according to any of claims 1 to 14 wherein the organic liquid in step (d) is added in amount substantially less than that required to provide an azeotropic mixture, the liquid being continuously recycled after decantation of the water from the distilled azeotropic mixture.

18. A method according to claim 1 for preparing a silica xerogel, substantially as hereinbefore described in any one of Examples I to III and VIII.

19. A silica xerogel which is stable at temperatures up to 1100°C in a fluidized bed and



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 VIII

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.

Examples I and IV illustrate the similar effectiveness, in obtaining a xerogel of appropriate properties from the hydrogel, of the acetone treatment and azeotropic distillation. 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 parameter of ageing time and pH, and degree of sodium removal; using the acetone treatment method described and claimed in Copending Application No. 39240/69 (Serial No. 1284086). Variation of these parameters has similar effect in the present azeotropic distillation process. Copending Application 39239/69 (Serial No. 1284085) claims *per se* a silica xerogel stable at temperatures up to 1100°C in a fluidised 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 from 300—600 Å.

WHAT WE CLAIM IS:—

1. A method for producing a silica gel which comprises (a) precipitating a silica hydrogel by reducing the pH of an aqueous solution of sodium silicate 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 to 8 and at a temperature of from 50° 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) adding an organic liquid which forms an azeotropic mixture with water, (e) distilling said azeotropic mixture so as to separate the water from said gel, and (f) removing the residual organic liquid from the resulting gel.

2. A method according to claim 1 wherein the precipitation of silica hydrogel in step (a) is accomplished by reducing the pH of an aqueous solution of sodium silica with an agent selected from acids and ion-exchange resins.

3. A method according to claim 2 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.

4. A method according to claim 3 wherein the first 40% of the pH-reducing agent is added over a period of about 1 hour.

5. A method according to claim 3 or 4 wherein the said balance of the pH-reducing agent is added over a period of about 45 minutes.

6. A method according to any of claims 1 to 5 wherein the SiO₂ concentration in the hydrogel precipitate of step (a) is from 8 to 9% by weight.

7. A method according to any of claims 1 to 6 wherein the temperature during step (a) is about 5°C and the temperature of the slurry during step (b) is about 90°C.

8. A method according to any of claims 1 to 7 wherein the pH in step (a) is from 5 to 7.

9. A method according to any of claims 1 to 8 wherein the pH in step (b) is from 5 to 6.

10. A method according to any of claims 1 to 9 wherein step (b) is conducted for about 4 hours.

11. A method according to any of claims 1 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 1 to 10 wherein step (c) is accomplished by washing with a solution of HCl or H₂SO₄.

13. A method according to any of claims 1 to 12 wherein the gel is comminuted to a particle size less than 200 microns before step (d).

14. A method according to any of claims 1 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 1 to 14 wherein the organic liquid in step (d) is added in an amount in excess of that required to provide an azeotropic mixture.

16. A method according to any of claims 1 to 15 wherein said azeotropic mixture is alternately refluxed for 0.5 to 2 hours and distilled so that the total process time is between 5 and 20 hours.

17. A method according to any of claims 1 to 14 wherein the organic liquid in step (d) is added in amount substantially less than that required to provide an azeotropic mixture, the liquid being continuously recycled after decantation of the water from the distilled azeotropic mixture.

18. A method according to claim 1 for preparing a silica xerogel, substantially as hereinbefore described in any one of Examples I to III and VIII.

19. A silica xerogel which is stable at temperatures up to 1100°C in a fluidized bed and

- which has a surface area of 200 to 500 m²/g the majority of which is provided by pores having a pore diameter of from 300 to 600 Å, prepared by a method according to any of claims 1 to 17.

5

20. A silica gel substantially as described in any one of Examples I to IV and VIII.

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