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Continuation-in-part of application Ser. No. 547,820, May 5, 1966, now abandoned.

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[54] **FREEZING NUCLEATION**
20 Claims, 4 Drawing Figs.

[52] **U.S. Cl.** **239/2,** 210/46, 239/14, 252/1, 252/194

[51] **Int. Cl.** **A01g 15/00**

[50] **Field of Search** ..... 252/194, 302, 1, (Chem. Abstracts); 239/2, 14; 210/62, 46, 51

[56] **References Cited**

UNITED STATES PATENTS

3,272,434 9/1966 Zettlemoyer et al..... 239/2

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ABSTRACT: A process of nucleating crystallization of a hydrogen-bonding crystal from a cloud or vapor medium, or a freezing nucleant consisting of an insoluble oxide substrate of suitable particle sizes burned together with sodium or potassium chloride or iodate.

Fig. 1.

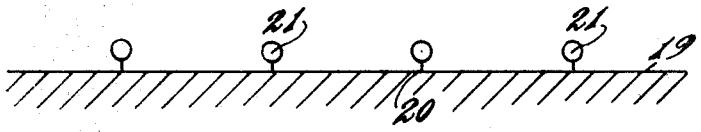


Fig. 2.

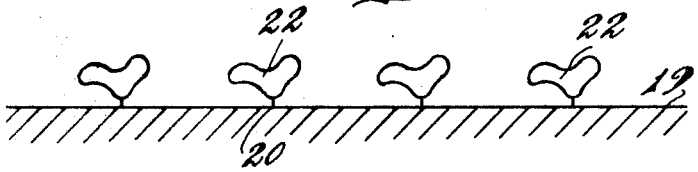


Fig. 3.

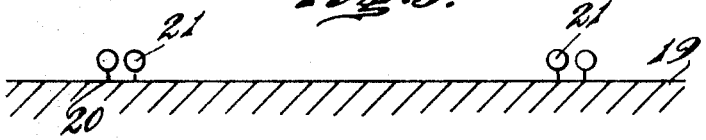
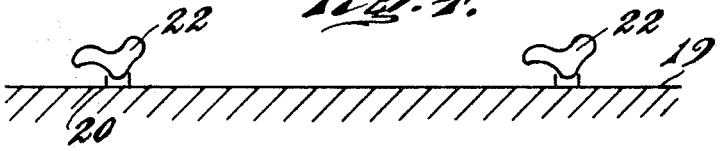


Fig. 4.



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FREEZING NUCLEATION

This application is a continuation-in-part of our copending application Ser. No. 547,820, filed May 5, 1966, for Freezing Nucleation and now abandon.

The present invention relates to depositing ice and other hydrogen-bonding crystals from clouds and to freezing nucleants for causing deposition of ice from clouds.

A process of the invention is to provide more effective freezing nucleants to cause ice to separate from clouds.

A further purpose is to reduce the cost of creating freezing nucleants.

A further purpose is to facilitate the control of the nucleating action of freezing nucleants.

A further purpose is to modify the surface of an insoluble oxide substrate and especially a silica substrate having a particle size between 0.01 and 10 microns and preferably between 0.03 and 1 micron by burning together with the substrate a sodium or potassium halide or iodate, especially a sodium or potassium chloride and particularly sodium chloride or potassium iodate.

A further purpose is to make it possible to modify the surfaces of insoluble oxide substrates which are either substantially completely hydrophobic or substantially completely hydrophilic, by burning together with the substrate sodium or potassium halide or sodium or potassium iodate forming sites thereon, until the monolayer volume for isopropanol divided by the monolayer volume for water is in the range from 0.35 to 0.75, preferably 0.4 to 0.6, and most desirably about 0.5.

The drawings are sectional diagrams showing location of hydrophilic sites on the surface of a substrate, and explaining their significance in terms of monolayer volumes of water and isopropanol.

There is need in the art for development of more easily available freezing nucleants for clouds, and ones which are less toxic. Such nucleants are useful for cloud seeding in connection with artificial creation of rain, and also as controls for measurement of other nucleants in connection with precipitation of ice or freezing nucleation in cloud chambers.

It is important to distinguish freezing nucleation from condensation nucleation, which is a completely different phenomenon, and relates to forming water droplets for clouds and to removal of warm fog.

The early great success with silver iodide as a freezing nucleant for clouds led to the supposition that because silver iodide has a crystal structure somewhat similar to ice, its success in freezing nucleation was entirely due to this fact. Some fear has recently been expressed about the toxicity of silver iodide. Accordingly, a search has been made for other crystals which would have similar crystalline form, in the hope that they would prove to be freezing nucleants. Limited success has been made in this direction. Zettlemoyer, Tcheurekdjian, and Chessick, 192 Nature 653 (Nov. 18, 1961).

It has been shown by Zettlemoyer, Tcheurekdjian and Chessick, 68 Journal of Physical Chemistry, 773 (1964), that silver iodide has another unusual property which can account for its efficiency as a freezing nucleant. Whereas most materials in nature has surfaces which are either substantially hydrophilic or substantially hydrophobic, silver iodide as usually prepared has 0.07 to 0.37 percent of its surface area covered with hydrophilic sites, and the balance covered with hydrophobic sites.

It has also been shown by Zettlemoyer et al., 14 Journal of Applied Mathematics and Physics (Fasc. 5) 496 (1963), that the surface condition of substrates can be modified artificially to bring them in the range which will have between 5 and 40 percent of the surface area covered with hydrophilic sites and the balance of the surface area covered with hydrophobic sites, and that certain materials thus created are good as freezing nucleants. This is strange because most materials in nature are relatively inert as freezing nucleants.

In U.S. Pat. No. 3,272,434, Zettlemoyer et al., it was stated that alkali metal halides are inoperative for the purposes of modifying the surface condition of substrates to create freezing nucleants.

This statement was based on theoretical consideration which then seemed to be sound. Sodium chloride and the like could not be expected to decompose into an insoluble material. Its high solubility in water would lead one to expect that its presence would depress the freezing point of water and be unfavorable as a freezing nucleant producer. Therefore, such soluble salts were not even tried. A similar statement that sodium chloride is ineffective as a freezing nucleant producer appears in Mason, The Physics of Clouds (Oxford Press 1957) 161.

We have discovered that very surprisingly and for reasons that cannot now be explained, when burned on the surface of an insoluble oxide such as silica, sodium or potassium halides and iodates are unusually effective to modify insoluble oxide substrates which would otherwise be wholly hydrophilic or wholly hydrophobic, to create a relation of areas and spacing of hydrophilic sites and hydrophobic sites which are favorable to freezing nucleation, by providing a ratio of monolayer volume for isopropanol divided by monolayer volume for water of between 0.35 and 0.75, preferably between 0.4 and 0.6 and most desirably about 0.5.

As a starting material, any one of a wide variety of solid insoluble oxides can be employed, of which the best is believed to be relatively dense solid precipitated silica which can readily be obtained in the required particle size of 0.01 to 10 microns and preferably 0.03 to 1 micron. Other solid oxides insoluble in water are magnesia, alumina, hematite and titania.

All of these substrates of course must be capable of reduction to the required fine sizes. Two grades of artificially produced relatively dense solid silica particles have been found to be very effective as substrates in the present invention. These materials are not gels but are dense amorphous precipitated silica.

One of these is a precipitated hydrated silica of very fine ultimate particle size, commonly used in rubber compounding, produced by Pittsburgh Plate Glass Co., Chemical Division, as Hi-Sil 233. The product is produced according to U.S. Pat. No. 2,805,955 and 2,805,956.

It has the following properties:

Silica by weight, percent	89. 2
Lime by weight	0. 6
R_2O_3 by weight	0. 78
NaCl by weight	1. 5
Loss on ignition at 105° C	5. 2
Total loss on ignition at 1,200° C	9. 3
pH of 5% water suspension	6. 5–7. 3
Specific gravity	1. 95
Ultimate particle size, micron	0. 022
Oil adsorption (Gardner-Sward), gms. oil/100 gms	125–165
Surface area, sq. meters/gm	140–160

This material as marketed is completely hydrophilic and disperses completely in water. As supplied on the market, it is relatively inert as a freezing nucleant.

Another dense silica substrate used in these experiments is otherwise similar but has been treated with a silicone oil, for example polydimethyl siloxane.

This material is produced by Philadelphia Quartz Co., as Quso M 51 and has the following properties:

Ultimate particles size, millimicrons	18
Surface area in sq. meters per gram	140
Loss on ignition at 105° C. less than, percent	1. 5
Loss on ignition on 1,000° C., percent	6
pH in mixture of isopropanol and water	5
Viscosity in Gulf oil 560	2, 000
10% loading, Brookfield Spindle #2, at 10 r.p.m. cps. at 25° C. water repellency, percent	100

This material is essentially hydrophobic and floats on water. It is inert as a freezing nucleant unless modified.

In order to modify a substrate according to the present invention and have the desirable percentage of the area covered with properly spaced hydrophilic sites, the procedure is as follows:

The particular sodium or potassium halide or iodate to be used in the proper concentration is mixed with the substrate particles which have been reduced to a size in the range of 0.01 to 10 microns, and preferably 0.03 to 1 micron, where they will be suitable as freezing nucleants.

The mixture is then heated to a temperature above about 300° C. and preferably about 400° C., and not in excess of 100° C. above the melting point of the sodium or potassium salt for a time of at least 30 minutes. Preferably the heating should not be above the melting point. If the compound decomposes the heating should not go above the temperature of decomposition. For many sodium or potassium halides the temperature of heating will be in the range of about 400° to 800° C. for a time of at least 30 minutes, preferably at least 1 hour and most desirably at least 2 hours.

Some of the sodium chloride or potassium chloride or the iodate does not effectively burn to impregnate on the surface. It may in some cases be desired to eliminate this excess as by washing, but our experiments indicate that the difference in behavior of the particles as freezing nucleants depending on whether or not the particles are washed to remove the excess of sodium chloride or the like is not significantly beyond the range of experimental error. The sodium or potassium halide or iodate which has reacted with the surface by burning does not readily dissolve.

The size of the particles of sodium or potassium halide or iodate prior to burning is not particularly important but they should be, of course, fine enough to mix with the substrate particles in a uniform manner.

EXAMPLE 1

Hydrophilic solid silica particles in the size range between 0.01 and 10 microns (actual size about 0.022 micron) (Hi-Sil 233) is mixed in separate batches with various percentages of powdered sodium chloride, 1 percent, 5 percent, 10 percent, 15 percent, 20 percent, 50 percent and 75 percent on the weight of the mixture.

Each mixture of sodium chloride and silica was heated in a furnace exposed to air to 650° C. and held at that temperature for 2 hours. The sodium chloride burned together with the surface of the silica, and the resultant particles from an appearance standpoint were the same as the silica particles before treatment. Adsorption tests to determine monolayer volume were run with argon, water and isopropanol in several cases. Each of the resultant batches of particles was separately evaluated in a cloud chamber, as later explained. The testing was done with samples which were not washed with water after burning, and with those which were washed with water.

EXAMPLE 2

Hydrophilic silica particles of a particle size of about 0.022 micron (Hi-Sil 233) were mixed in various batches with 1 percent, 5 percent, 10 percent, 15 percent, 20 percent, 50 percent and 75 percent of powdered sodium chloride by weight. Each of the batches was heated in air in a furnace at 800° C. and held at this temperature for 2 hours. The sodium chloride was approximately at its fusion point. It burned together with the surface of the silica particles, making no visible change. These were tested for monolayer volume in several cases, washed and unwashed batches were tested for behavior in the cloud chamber.

EXAMPLE 3

Examples 1 and 2 were repeated, heating to 450° C. Cloud chamber behavior in this case was good, but not so good as in example 1.

EXAMPLE 4

Hydrophobic silica particles of a particle size of about 0.018 micron (Quso M 51) which was initially hydrophobic, was heat treated to 800° C. for 2 hours in air in a furnace. The silica, after cooling to ambient temperature, was found to be hydrophilic and dispersed readily in water.

Batches of the thus heat treated silica were mixed respectively with 1 percent, 5 percent, 10 percent, 15 percent and 20 percent of sodium chloride particles and each of the batches was heated separately in a furnace in air to 650° C. and held for 2 hours.

The batches were then cooled to ambient temperature and washed and unwashed samples were tested in the cloud chamber as referred to below, where the 5 percent burned silica sample (washed) gave a value of 3, and the 10 percent, 15 percent and 20 percent burned silica washed samples gave values of 5. The values for the unwashed samples are not significantly different.

EXAMPLE 5

The procedure of example 1 was carried out, using anhydrous sodium bromide instead of sodium chloride, and the samples were later evaluated. The cloud chamber rating of the 20 percent product heated to 650° C. and also when heated to 800° C. was 4 (washed). The values for the unwashed samples are practically the same.

EXAMPLE 6

The procedure of example 1 was repeated using potassium bromide and the results were the same as in example 5.

EXAMPLE 7

The procedure of example 1 was carried out using anhydrous potassium chloride instead of sodium chloride. The cloud chamber results of potassium chloride 20 percent when heated at 650° C. and washed and also when heated at 800° C. and washed was 4 (3—4 at 800° C.) The unwashed samples give cloud chamber values which are practically the same.

EXAMPLE 8

In order to evaluate the possible presence of an excess of sodium chloride on the surface beyond that which burns together with the surface to produce sodium halide sites, a sample of silica having 20 percent by weight of sodium chloride burned together with the surface by heating for 2 hours at 650° C. (example 1) was removed from the bulk after cooling to ambient temperature and washed with water at ambient temperature until the washings showed freedom from chloride. The silica particles on the suction filter agglomerated together and were no longer separate particles which were capable of nucleating.

The experiment was repeated, washing with water but before the particles on the suction filter reached dryness, the remaining water in contact with the particles was removed by washing with anhydrous acetone. The particles were then obtained in dry form on the suction filter in their original particle size, without agglomeration.

From the washings it was found that the residual sodium chloride remaining on the particles and not removable by washing with water under the conditions of the test amounted to 1 percent of the weight of the particles.

The silica particles with the sodium chloride burned together with the surface were compared (washed and unwashed) as freezing nucleants in the cloud chamber and both were found to be highly effective and equally effective.

EXAMPLE 9

The procedure of example 1 was carried out except that potassium iodate was used instead of sodium chloride, heating for 2 hours at 650° C. and washing. The cloud chamber values were (5 percent) 4—5 and (10 percent) 5. The unwashed samples give cloud chamber values which were roughly the same. 8

EXAMPLE 10

The procedure of example 1 was carried out except that potassium iodate was used instead of sodium chloride and heating was carried out at 450° C. for 2 hours and washed. The cloud chamber values were:

5 percent 4

10 percent 5

The unwashed samples give cloud chamber values which are practically the same.

EXAMPLE 11

The established procedure in the art for determining the hydrophilic area is to determine the water monolayer volume at standard conditions of temperature and pressure. This indicates the number of water molecules adsorbed per gram by well-known techniques. This result also indicates the area having hydrophilic sites.

The total area is obtained by determining the adsorption of nitrogen or argon as is well known. Knowing these figures, dividing the water monolayer volume by the total monolayer volume, the percentage of the sites having hydrophobic properties is then determined by difference from 100.

The present inventors have considered the possibility that water adsorption may give an improper value for the area having hydrophilic sites because the water molecule is so small. For example, it might be possible that 35 percent of the surface would be accepting adsorbed water molecules, at sites, but the sites might be so widely spaced that they would not be efficient as a freezing nucleant. At the other extreme, it might be possible that more than 40 percent of the area would have hydrophilic sites and yet these sites might be grouped in such a way as to be favorable for freezing nucleation.

Accordingly, we conceived the idea of using steric hindrance to discover the nature of the spacing of the hydrophilic sites and thus to give a check on the utility of monolayer water volumes per gram at standard conditions of temperature and pressure.

It is also possible that in some particles there may be micropores as in silica gel which induce error into the computation by suggesting that the water monolayer volume is much greater than the nitrogen or argon monolayer volume because water disappears into the fine pores, and the other molecules may not.

As a means of introducing steric hindrance for the two purposes mentioned, we have selected isopropanol as the most suitable existing compound, since it has an hydroxyl group, but this group is placed in the middle and the methyl groups at both ends are available to produce steric hindrance. It is applied by the same technique that water has been used to determine monolayer volumes.

We have determined that ratios of monolayer volume of water as compared to isopropanol at standard conditions of temperature and pressure are more meaningful than ratios of areas since these are proportional to the number of molecules and therefore to the number of sites.

Several conditions may be visualized.

If the ratio of the monolayer volume for isopropanol to the monolayer volume for water is close to or in excess of unity, the sites **20** on the surface **19** which receive water molecules **21** (FIG. 1) and isopropanol molecules **22** (FIG. 2) are distributed so widely that no steric hindrance takes place, and nucleation is not of maximum effectiveness.

For a ratio of monolayer volumes so low that steric hindrance is at a maximum (FIG. 3), it is not possible for one isopropanol (FIG. 4) to be adsorbed at each site so that only one of every two sites is active in bonding in forming the apparent first layer.

When the sites are distributed so that about one in every two can adsorb isopropanol, and every other site is excluded from isopropanol adsorption, this is apparently an optimum from the standpoint of cloud nucleation.

Tables 1 and 2 show values for monolayer volumes V_m, monolayer volume ratios, and cloud nucleation values for various test samples.

In determining monolayer volumes, the specimen was pumped for 12 hours at 110° C. under high vacuum before test, using a liquid nitrogen trap in the line.

Heating of silica above a temperature of about 900° C. was found not to be desirable because of the tendency to agglomerate the particles at the higher temperature.

Flame hydrolized silica is counterindicated for present purposes.

The same products having 10 percent and 15 percent of sodium chloride (washed and unwashed) burned together with the surface proved to be superior to the 5 percent product in a linear relation, and recognizing that the 20 percent product was given a rating of 6, they were given corresponding intermediate ratings between 4 and 6. The same material having a concentration between 1 and 5 percent burned together with the surface was effective but at a linearly proportional lower level. All the percentages given are the percentages of sodium or potassium halide or iodate which was added prior to burning on, and not the residual sodium or potassium halide or iodate after washing.

These products having between 1 and 50 percent sodium chloride ion impregnated according to example 1 (washed and unwashed), gave massive ice at temperatures of about minus 10° C. in an isothermal cloud chamber.

Hydrophilic dense solid silica (Hi-Sil 233) and containing 20 percent sodium chloride and heat treated at 800° C. for 2 hours (washed and unwashed) was only slightly less active than the product of example 1 containing 20 percent sodium chloride, and was given a rating between 5 and 6.

Hydrophobic dense solid silica (Quso M 51) which was preliminarily heat treated and then had sodium chloride burned on according to example 2 (washed and unwashed), was slightly less active than the corresponding product of example 1. The 20 percent sodium chloride product was given a rating of 5.

The potassium iodate burned together with silica particles of example 8 and washed was slightly less effective than the sodium chloride washed product in the cloud chamber. The product obtained according to example 9 with 10 percent of potassium iodate heated for 2 hours at 650° C. and washed was given a rating of 4 in the cloud chamber. The corresponding unwashed potassium iodate products gave cloud chamber values which were practically the same.

TABLE 1

Silica (Hi-Sil 233)

Sample	V_m(ml. STP/g.)			Ratio V_m i-PrOH	Cloud chamber Value
	Argon	Water	i-PrOH	Water	
Untreated unwashed	27.0	49.3	12.1	0.24	2
10% NaCl 650° C. washed	24.8	16.7	9.1	0.53	5
20% NaCl 650° C. washed	25.4	20.5	10.5	0.50	5+

TABLE 2

Silica (Quso M 51)

Sample	V_m(ml. STP/g.)			Ratio V_m i-PrOH	Cloud chamber Value
	Argon	Water	i-PrOH	Water	
Untreated unwashed	28.4	28.7	3.14	0.11	0
10% NaCl 650° C. washed	25.7	14.6	10.7	0.73	5
20% NaCl 650° C. washed	29.2	24.0	11.1	0.46	4+

Other results are graded by the skilled operator on a judgment basis from 1 to 10, reserving the value of 10 for the best nucleant ever tested, ammoniated silver iodide, recognizing that a superior nucleant will form in a shorter time larger numbers of ice crystals in the viewing volume and also will form ice at a higher onset temperature than a poor nucleant.

Hydrophilic silica (Hi-Sil 233) as sold on the market was poor and was given a rating of 3. Hydrophobic silica (Quso M 51), as originally received, was inactive and was given a rating of zero and this material when heat treated at 800° C. for 3 hours was also inactive and was given a rating of zero.

All of the specimens of hydrophilic dense solid silica (Hi-Sil 233) with sodium or potassium halide or iodate burned together with the substrate in concentrations of from 5 to 75 percent (washed or unwashed) are effective as freezing nucleants, but similar samples having 10 to 50 percent of sodium or potassium halide or iodate (washed or unwashed) were better and those having 20 to 50 percent of the same (washed or unwashed) were best. The product of example 1, with a concentration of 20 percent sodium chloride (unwashed) formed massive ice at minus 8° to minus 10° C. and was given a rating of 6, this being one of the best material obtained by the techniques above set forth. This same material, after washing with water, followed by anhydrous acetone, was equally effective and was given a rating of 6.

The product of example 1, heat treated at 650° C. with 5 percent weight of sodium chloride (washed or unwashed), was given a rating of 4.

The following monolayer volumes at standard temperature and pressure were obtained for silica (Hi-Sil 233) particles of the proper size range, plus 50 percent sodium chloride, heated for 2 hours at 650° C., washed, dried and vacuum pumped for 12 hours at 110° C.; with a liquid nitrogen trap in the line and reported in milliliters (STP) per gram:

Argon	23. 4
Water	18. 3
Isopropyl alcohol	8. 10
Ratio water to argon volumes	0. 782
Ratio isopropyl alcohol to argon volumes	0. 346
Ratio isopropyl alcohol to water volumes	0. 443

In addition it is evident from X-ray diffraction studies that burning with the sodium or potassium salts above 600° C. strongly promotes the development of crystallinity in the silicate substrate.

EXAMPLE 12

The test results were evaluated in a constant temperature mixing cloud chamber in which a cloud was artificially created. The chamber is a cylindrical space approximately 9 inches in diameter and 12 inches high, which includes both cooling coils and heating coils so that the temperature can be precisely controlled. The chamber is filled with air. Air free from dust particles is used as a carrier gas for introducing moisture. The air is introduced through wash bottles filled with heated water so that the air becomes a carrier of water vapor. The temperature is adjusted in the cloud chamber until the water vapor forms a cloud in the chamber, and this renders visible through windows at the top and bottom a definite volume of the cloud. A beam of light is projected horizontally through the chamber from one window through the other and this renders the cloud visible.

Prior to making a test, the temperature is carefully adjusted to permit cloud formation as well known in the art, and then air is blown in from the top, carrying water vapor which forms a cloud. There is a slight heating action when the cloud is created and the temperature is stabilized before an experiment can be run. A minute amount of a sample of nucleant particles at room temperature is blown in as by an atomizer at the top of the chamber.

Skill in evaluation is required. The results achieved by ammoniated silver iodide in freezing nucleation are graded as 10. A material which is inert in the cloud chambers is graded as 0. A material which produces incipient ice formation as observed from above, is graded as 1.

In view of our invention and disclosure variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of our invention without copying the process and composition shown, and we therefore claim all such insofar as they fall within the reasonable spirit and scope of our claims.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

We claim:

1. A process of nucleating crystallization of a hydrogen-bonding crystal from a cloud or vapor medium, which comprises seeding the medium until crystals form with particles in a size range between 0.01 and 10 microns consisting of an inorganic insoluble solid oxide substrate and from 5—75 percent by weight of a salt of the class consisting of sodium and potassium halides and iodates burned on the surface thereof, the particles having a ratio of isopropanol monolayer volume to water monolayer volume between 0.35 and 0.75.

2. A process of claim 1, in which the substrate essentially consists of silica.

3. A process of claim 1, in which the salt essentially consists of sodium chloride.

4. A process of claim 3, in which the substrate essentially consists of a silica.

5. A process of claim 1, in which the layer essentially consists of potassium iodate.

6. A process of claim 1, in which the ratio is between 0.4 and 0.6.

7. A process of claim 6, in which the ratio is about 0.5.

8. A process of making a freezing nucleant, which comprises heating together particles of an inorganic insoluble solid oxide substrate, of a size between 0.01 and 10 microns, with 5—75 percent by weight of a salt of the class consisting of sodium and potassium halides and iodates to a temperature between 300° C. and 100° C. and above the melting point of the salt, for a time of at least 30 minutes.

9. A process of claim 8, in which the substrate essentially consists of silica.

10. A process of claim 9, in which the salt essentially consists of sodium chloride.

11. A process of claim 8, in which the salt essentially consists of sodium chloride.

12. A process of claim 8, in which the heating is to a temperature below the melting point of the salt.

13. A process of claim 8, in which the particles are heated to a temperature of 650° C. for a time of at least 2 hours.

14. A process of claim 8, in which the particles are heated to a temperature of 800° C. for a time of at least 2 hours.

15. A freezing nucleant for clouds, essentially consisting of an inorganic insoluble solid oxide substrate and a salt of the class consisting of sodium and potassium halides and iodates burned on the surface thereof, the concentration of said salt being between 5 and 75 percent by weight, the particle size of the nucleant being between 0.01 and 10 microns and the particles having a ratio of monolayer volumes of isopropyl alcohol to water between 0.35 and 0.75.

16. A freezing nucleant of claim 15, in which the substrate essentially consists of silica.

17. A freezing nucleant of claim 15, in which the salt essentially consists of sodium chloride.

18. A freezing nucleant of claim 15, in which the salt essentially consists of potassium iodate.

19. A freezing nucleant of claim 15, in which the ratios are between 0.4 and 0.6.

20. A freezing nucleant of claim 15, in which the ratio is about 0.5.