

[54] FREEZING NUCLEANT

3,127,107	3/1964	Merryweather .....	239/2 R
3,545,677	12/1970	Power .....	239/2 R
3,788,543	1/1974	Amand et al. ....	239/14

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

[58] Field of Search..... **239/2 R, 14**

[56] **References Cited**

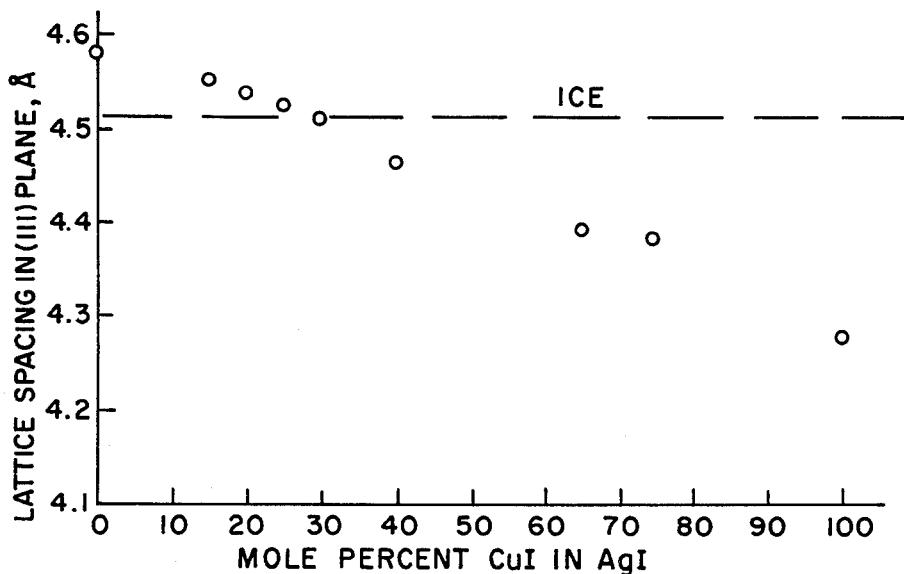
UNITED STATES PATENTS

3,126,155 3/1964 Lohse ..... 239/14

[57] **ABSTRACT**

A solid solution of silver iodide and cuprous iodide for the purpose of more effectively nucleating the formation of ice at higher temperatures than the nuclei in the environment is provided. These compounds may be dispersed into the atmosphere with similar equipment to that used for the dispersal of silver iodide, and the resultant aerosol is equal to or superior to silver iodide for the purpose of nucleating clouds while being less toxic, less expensive and less susceptible to photodeactivation by sunlight than pure silver iodide.

**8 Claims, 3 Drawing Figures**



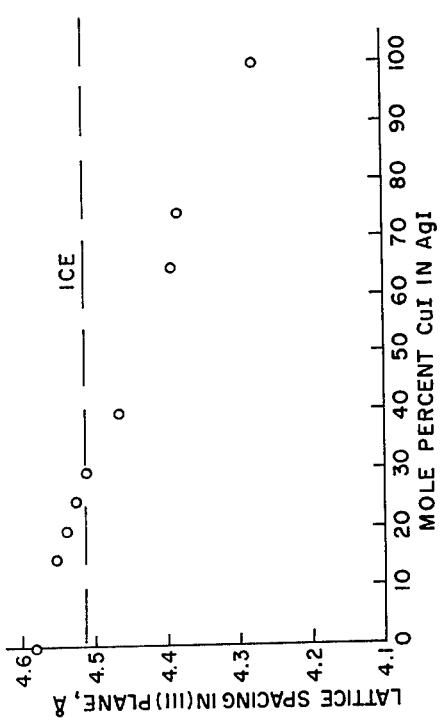


Fig. 1

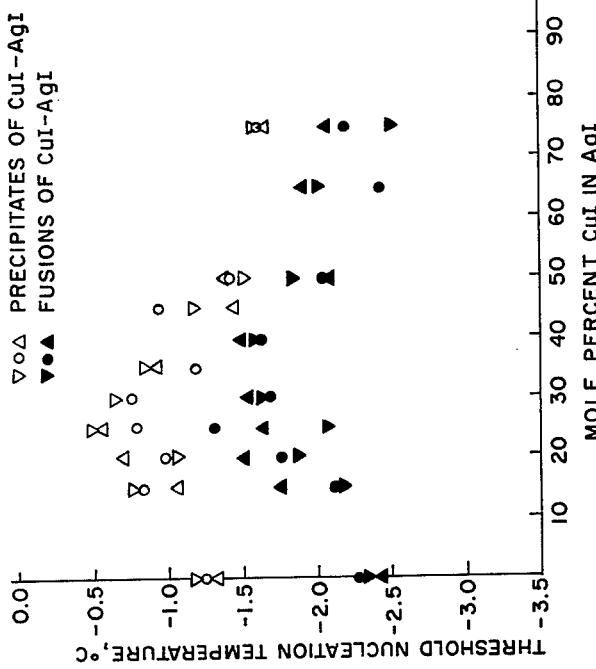


Fig. 2

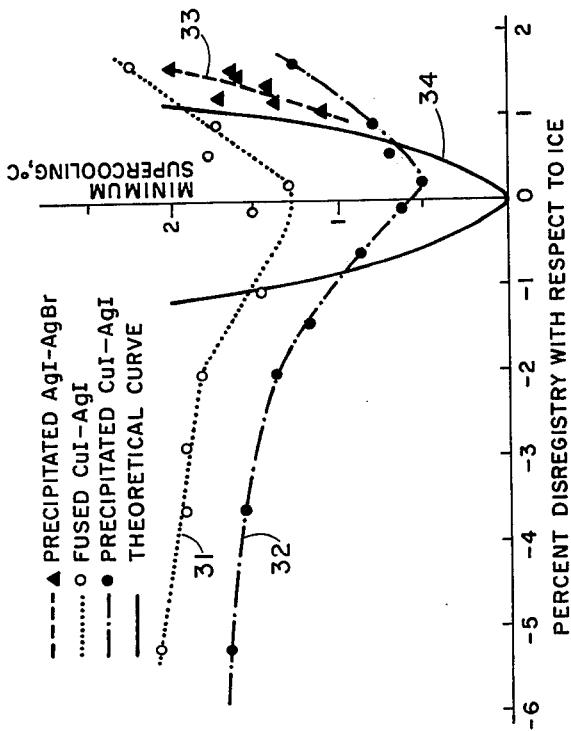


Fig. 3

## FREEZING NUCLEANT

This invention concerns nucleation catalysts and, more particularly, an improved control means which reduces the lattice misfit between ice and silver iodide.

One of the several explanations offered for the effectiveness of silver iodide in initiating the freezing of supercooled water is that its crystal structure is similar to that of ice. Another explanation is that 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 discovered that when burned on the surface of an insoluble oxide such as silica, sodium or potassium halides and iodates are unusually effective in modifying insoluble substrates which would be wholly hydrophilic or wholly hydrophobic, to create a relation of areas and spacing of hydrophilic and hydrophobic sites which are favorable to freezing nucleation by providing a ratio of monolayer volume by isopropanol divided by a monolayer volume for water between 0.35 and 0.75, preferably between 0.4 and 0.6 and most desirably about 0.5. Any one of a wide variety of solid insoluble oxides may be employed such as relatively dense solid precipitated silica and other solid oxides insoluble in water such as magnesia, alumina, hematite and titania.

It has further been found that within the same temperature interval as silver iodide and lead iodide the following substances in dispersed form act as ice-forming nuclei — copper iodide (CuI), cupro-oxide (Cu<sub>2</sub>O), copper sulphide (CuS), copper selenide (CuSe), mercury telluride (HgTe), vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), silver sulphide (AgS), silver nitrate (AgNO<sub>3</sub>), silver oxide (Ag<sub>2</sub>O) and cadmium telluride (CdTe). Of these compounds, only copper sulphide and cupro oxide were found practical for influencing weather because of the toxicity or excessive cost of the remaining compounds, among other deficiencies. Applicants have diverged from the direction taken in prior searches for more efficacious nucleants and have discovered a less toxic, less expensive and more effective seeding material by achieving a better crystal match for the lattice misfit between ice and silver iodide.

Accordingly, it is an object of the present invention to provide an improved nucleation catalyst for cloud seeding.

Another object of the invention is to provide for improved cloud seeding by reducing the lattice misfit between ice and silver iodide.

A further object of the invention is to provide for improved cloud seeding by an improved crystal match in a composition which includes silver iodide and reduces some of the undesirable aspects of that substance.

Other objects, advantages and novel features of the invention will become apparent from the following detailed description thereof when considered in conjunction with the accompanying drawings in which like numerals represent like parts throughout and wherein:

FIG. 1 is a graph showing changes in lattice spacing due to changes in the mole percent of CuI and AgI;

FIG. 2 is a graph showing the observed threshold nucleation temperature as a function of composition of both fusions and precipitates; and

FIG. 3 is a graph illustrating the symmetry of data of catalysts of varying disregistry.

It will be noted that although cuprous iodide (CuI) has been listed in the prior art as one of several substances which in dispersed form act as ice-forming nuclei, this and many other listed substances have been discounted as impractical or unsuitable because of their poisonous character or for economic reasons.

In contrast to the findings in the prior art we have found that although by itself cuprous iodide has undesirable features such as having been determined to be somewhat toxic, the combination of cuprous iodide and silver iodide in a solid solution is appreciably less toxic than silver iodide alone. This is believed due to the fact that copper is less toxic than silver. Additionally, the CuI-AgI compound is less expensive than silver iodide and, therefore, the cost of seeding with the compound would be appreciably less than that of seeding with pure silver iodide. It is also believed that the CuI-AgI compound is less susceptible to photodeactivation than pure silver iodide and, therefore, an increase in the efficiency of a seeding operation should be achieved due to a longer residence time in the atmosphere.

In accordance with our invention, we have found that as the proportion of cuprous iodide in a CuI-AgI nuclei is increased to approximately 25 mole percent, the supercooling required to initiate ice formation decreases from 2°C for pure silver iodide to a minimum value of approximately 0.5°C. The cuprous iodide is formed in crystals of a solid solution of silver iodide and cuprous iodide and nucleates the formation of ice in supercooled water. Upon further increase of the percentage of CuI, the supercooling again increases until it reaches a value on the order of 2.5°C for pure CuI, indicating a superiority of the CuI-AgI crystals over the AgI crystals alone used commonly for seeding supercooled clouds. Compounds of the solid solution of silver iodide and cuprous iodide can be dispersed into the atmosphere with similar equipment to that used for the dispersion of silver iodide, and the resultant aerosol is equal to or superior to silver iodide for the purpose of nucleating clouds.

CuI-AgI solid solutions have been prepared each having a lattice parameter smaller than that of pure AgI using two separate methods. The first method was direct fusion at a pressure of 10<sup>-2</sup> torr and a temperature of 20°C above the melting point of the solid solution, about 600°C. The second involved dissolving the proper proportions of reagent grade CuI and AgI in hydroiodic acid and then boiling off the solvent. The crystal class of the resulting solid solutions is face centered cubic, but in the (111) plane the crystal structure is similar to that of ice in the (0001) plane. The lattice spacing in the (111) plane is given by  $\alpha \sqrt{2}/2$ , where  $\alpha$  is the edge of a unit cell in the cubic system. The graph in FIG. 1 illustrates that by varying the mole percent of CuI in AgI, a solid solution can be made to have any lattice spacing from 4.58 to 4.28 Å measured in the (111) plane. This range in lattice spacings corresponds to lattice disregistry with respect to ice ranging from 1.5 percent to -5.2 percent. Since CuI and AgI are not appreciably soluble in water, 10<sup>-5</sup> and 10<sup>-8</sup> mole/liter, respectively, they have a negligible effect in depressing the freezing point of the water.

To determine their relative effectiveness as nucleation catalysts, powdered samples of about 0.5 of CuI-AgI were sealed in dilatometers containing approximately 1 g of distilled water, and the freezing temperature was observed when they were cooled in a vigor-

ously stirred bath. The temperature was measured with a thermometer with an accuracy of  $0.01^{\circ}\text{C}$  and was lowered at a rate of  $0.5^{\circ}\text{C min}^{-1}$ . The water was slightly distilled and had a conductivity of  $3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

The graph of FIG. 2 shows the observed threshold nucleation temperature as a function of composition for 10 samples of both the fusions and the precipitates. The fusions were tested immediately after having been immersed in water. Reduction of the cooling rate from  $0.05^{\circ}\text{C}$  to  $0.01^{\circ}\text{C min}^{-1}$  produced no observable differences in threshold nucleation temperatures.

FIG. 3 presents curves for the smallest observed supercooling for the CuI-AgI fusions and precipitates at 31 and 32, respectively, as a function of lattice disregistry with respect to ice. The disregistry is computed for the (111) plane of the CuI-AgI solid solution and the (0001) plane of ice. A curve for precipitated AgI-AgBr solid solutions is shown at 33 along with a theoretical curve for coherent nucleation at 34.

It is believed that the interfacial energy between ice and a nucleation catalyst is a minimum when nucleation is coherent. Coherent nucleation occurs when the lattice of the forming crystal matches the lattice of the catalyst and can be likened to crystal growth. If the lattices are slightly mismatched, nucleation may still be coherent, but the resulting elastic distortion will increase the bulk free energy of the forming embryo. Consequently, the supercooling necessary for nucleation increases by an amount proportional to the square of the disregistry.

The symmetry of the data in FIG. 3 may indicate that catalysts with a positive disregistry have about the same nucleation ability as those with an equal negative disregistry. This result agrees with a prediction that  $\Delta T = k\delta^2$ , where  $\Delta T$  is the supercooling,  $\delta$  is the disregistry, and  $k$  is a constant. However, for our data the supercooling does not approach  $0^{\circ}\text{C}$  as the disregistry tends to zero, but instead reaches a minimum of about  $0.5^{\circ}\text{C}$ . When other nucleation parameters are taken into account, the equation for coherent nucleation can be written as  $\Delta T = k\delta^2 + \Delta T_1$ , where  $\Delta T_1$  is the supercooling due to the combined effect of any nucleation parameters independent of the disregistry. The parallel nature of the data in FIG. 3 tends to confirm this type of relation.

Coherent nucleation theory predicts that nucleation will become incoherent for large disregistries where the bulk free energy of ice formation is less than the free energy required to distort the ice lattice to fit the catalyst lattice. If nucleation is not coherent, a linear relation can be predicted between the disregistry and the supercooling. The data for the CuI-AgI catalysts in FIG. 3 show a sharp dip in supercooling between lattice disregistries of  $\pm 1.5$  percent. This region could correspond to coherent nucleation. The region between  $-1.5$  and  $-5.2$  percent disregistry could correspond to incoherent nucleation, as the supercooling is a fairly linear function of the disregistry.

Since the operation and use of cloud seeding nuclei is based on the ability of cuprous iodide and silver iodide to nucleate ice formation at higher temperatures than the nuclei normally present naturally, the newly developed seeding material consisting of copper iodide and silver iodide makes possible the use of nuclei that are significantly more effective than those which have

been available in the past. Furthermore, since in some cases it may be desirable to control the nucleation temperature to any desired value, the continuous spectrum of nuclei obtainable by varying the composition of the solid solution provides a new tool for use in cloud seeding technology.

What is claimed is:

1. A method of nucleating ice formation by cloud seeding nuclei at higher temperatures than those for nuclei normally present naturally comprising:
  - reducing the lattice misfit between ice and silver iodide by substituting other metallic atoms for a portion of the silver atoms in the silver iodide lattice.
2. The method of claim 1 wherein the amount of lattice misfit is from  $-1.5$  percent to  $+1.5$  percent with respect to ice.
3. The method of claim 2 wherein the other metallic atoms are copper atoms and the proportion of cuprous iodide in a CuI-AgI nuclei is substantially 25 mole percent.
4. The method of inducing crystal formation in a natural atmospheric cloud which is supercooled naturally to between  $-4^{\circ}\text{C}$  and  $-5^{\circ}\text{C}$  which comprises:
  - introducing into said cloud an aerosol comprising crystals of silver and another metallic iodide sufficient to further supercool said cloud substantially  $0.5^{\circ}\text{C}$  thereby initiating ice formation therein.
5. The method defined in claim 4 wherein the other metallic iodide is cuprous iodide and the proportion of cuprous iodide in the CuI-AgI nuclei of said crystals is substantially 25 mole percent.
6. The method of inducing crystal formation in a mass having a temperature of from  $-4^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$  and below which comprises:
  - preparing a solid solution having a lattice parameter smaller than that of pure silver iodide by the direct fusion of another metallic iodide and silver iodide at a pressure of substantially  $10^{-2}$  torr and a temperature substantially  $20^{\circ}\text{C}$  above the melting point of said solution; and
  - adjusting the mole percent of the other iodide in the silver iodide so as to produce a lattice spacing in the (111) plane of from substantially  $4.58 \text{ \AA}$  to substantially  $4.28 \text{ \AA}$ , whereby lattice spacings are produced which correspond to lattice disregistries with respect to ice ranging from 1.5 percent to  $-5.2$  percent.
7. The method defined in claim 6 wherein the other iodide is cuprous iodide and the proportion of cuprous iodide in the solution is substantially 25 mole percent.
8. The method of inducing crystal formation in a mass having a temperature of from  $-4^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$  and below which comprises:
  - preparing a solid solution having a lattice parameter smaller than that of silver iodide by dissolving selected proportions of cuprous iodide and silver iodide in hydriodic acid and thereafter boiling off the solvent, said proportions determining the mole percent of cuprous iodide in silver iodide so as to produce a lattice in the (111) plane of from substantially  $4.58 \text{ \AA}$  to substantially  $4.28 \text{ \AA}$ , whereby lattice spacings are produced which correspond to lattice disregistries with respect to ice ranging from 1.5 percent to  $-5.2$  percent.

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