July 23, 1957 — J. C. SHEPHERD — 2,800,456

REFRIGERANT AND PROCESS FOR MAKING SAME

Filed Aug. 10, 1953

Fig. 1.

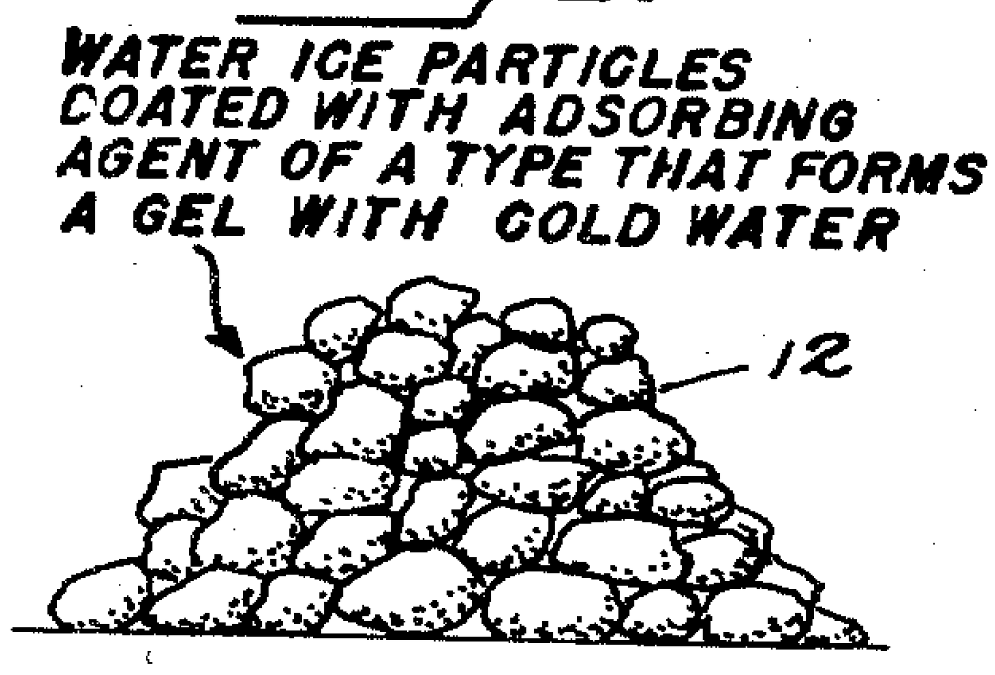


Fig. 2.

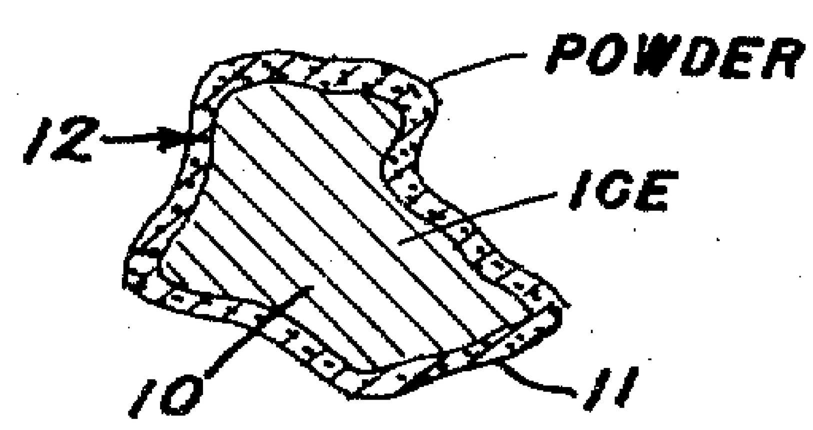


Fig. 3.

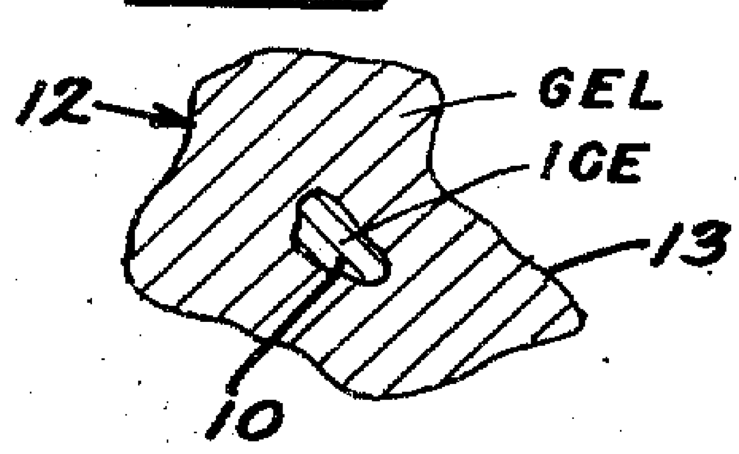
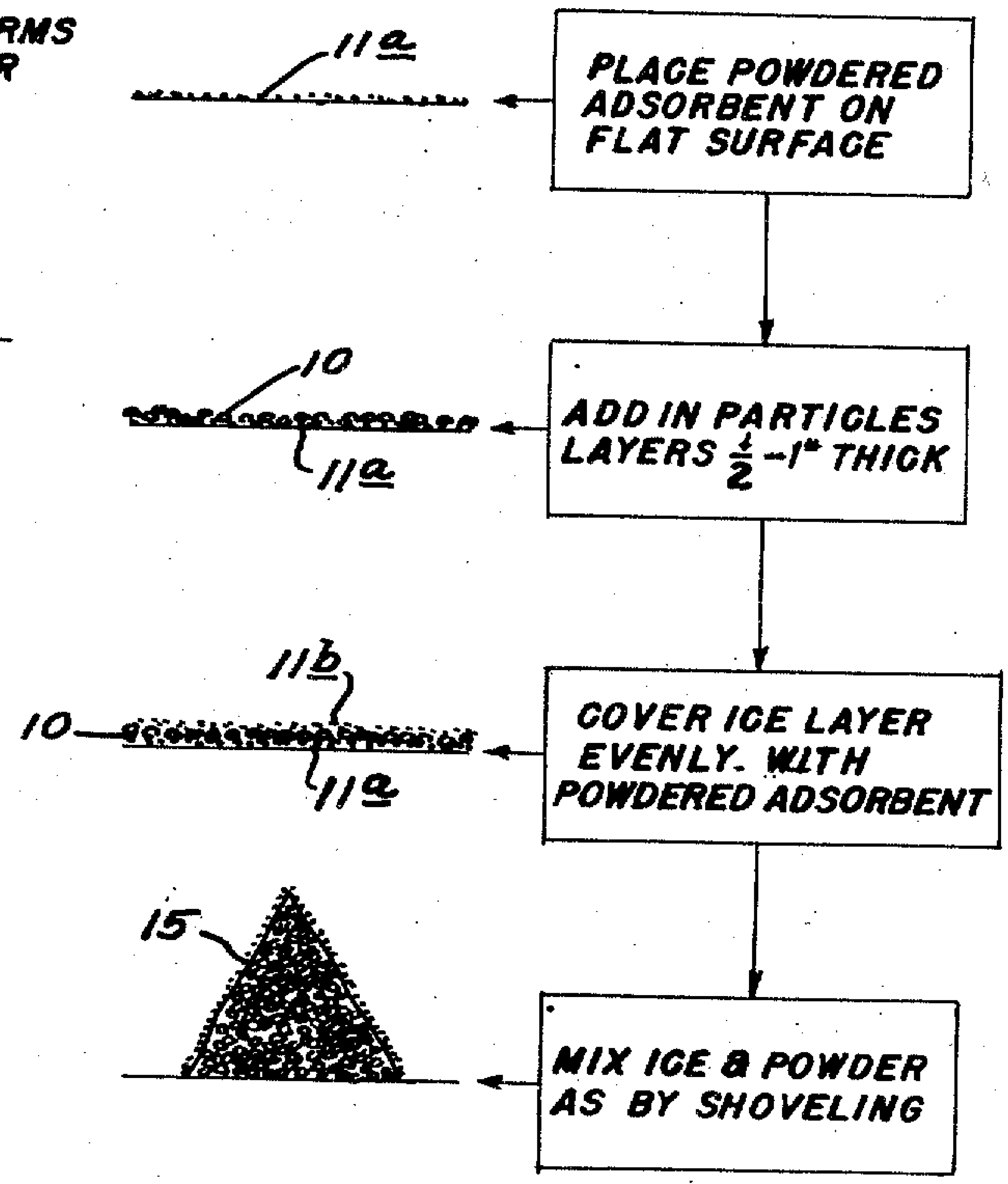


Fig. 4.



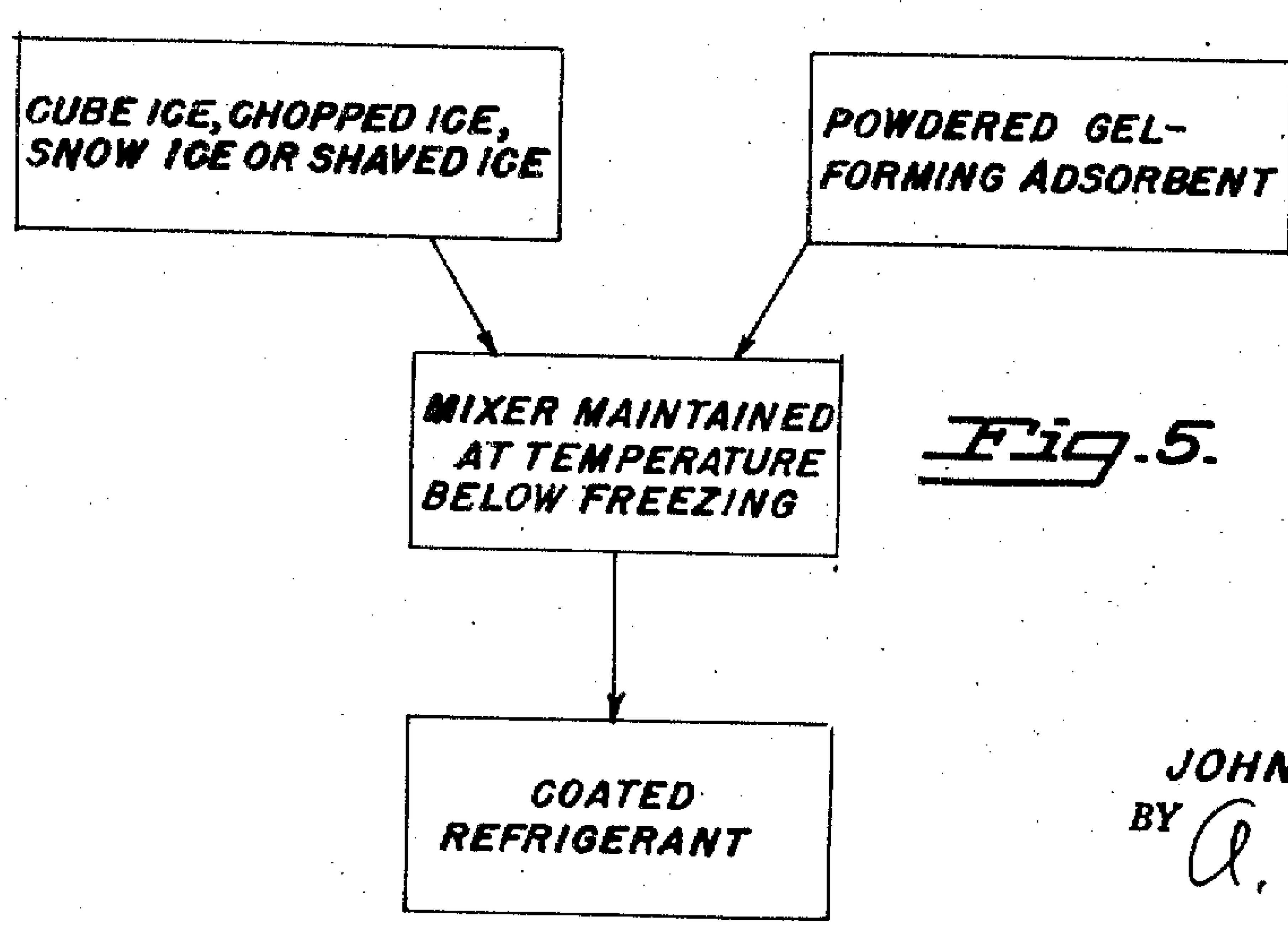


Fig. 5.

INVENTOR.
JOHN C. SHEPHERD
BY A. Denham Owen
ATTORNEY

United States Patent Office

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REFRIGERANT AND PROCESS FOR MAKING SAME

John C. Shepherd, Monrovia, Calif.

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15 Claims. (Cl. 252—70)

This invention relates to an improved refrigerant and to a process for manufacturing the improved refrigerant.

The fact that water ice changes from a solid to a liquid as it absorbs heat, has caused difficulties in many instances. For one thing, unless confined in some manner, water flows off out of contact with the goods being refrigerated. If it could be kept from doing this, the cold water could still be utilized as a cooling agent up to the critical temperature of the goods being refrigerated. But when it flows away, it is no longer present to perform this desirable function, and, without the protection of this cold water, the remaining ice is subjected directly to heat from the outside and melts faster than it would if the cold water were around it.

A second difficulty with water ice is that liquid water damages many types of goods. Heretofore, shippers of such goods have either had to rely on other, more expensive and less efficient refrigerants or have had to separate the goods from the ice by water-proof containers, thereby losing some of the cooling value of the ice and adding to the cost of materials. Accordingly, higher prices were charged for handling refrigerated goods that were likely to be damaged by water.

A third difficulty with water has been that its liquidity made it impossible to use many inexpensive and convenient types of shipping containers. This difficulty has caused carriers to charge higher freight rates for handling those commodities because of the fact that special containers had to be used.

A fourth difficulty with water ice has been that its temperature was not cold enough to preserve some goods (e. g., ice cream) and that when salt was added to lower the temperature, the melted brine increased the likelihood of damage to the goods.

Many attempts have been made to provide a satisfactory solution to these long-standing problems. Refrigerants such as Dry Ice were sometimes employed, but they have proved unsatisfactory for most uses, because they are too cold for the majority of goods. Other refrigerants have been found too expensive, and their low specific heat, relative to water, has meant that their bulk and weight had to be unreasonably large.

Attempts have also been made to prevent the water from flowing away when the water-ice melted, by using absorbent materials. For example, water has been mixed with or absorbed into sawdust or rubber sponges and some other absorbent material before being frozen. When the ice melted, the absorbent materials tended to hold the water somewhat and to restrict its running out. But they failed to solve the problem because they did not prevent all the water from flowing out, and could not prevent the goods or fibre-board or paste-board containers from being damaged. Moreover, when these products were subjected to pressure, the water was readily squeezed out as the ice melted, and little of it remained. Absorbent materials have their proper uses, but they failed to solve the main problem.

The present invention has solved this problem by producing a novel product and a novel process for making this product. The product is a refrigerant comprising a plurality of pieces of water ice coated with an adsorbing colloid that forms a gel or gel-like coating when it reacts with water. The process for making the product comprises mixing the said absorbing agent, in powder form, with crushed or chunk ice so that the powder attaches itself to the surface of the ice particles. As the ice melts, the powder adsorbs liquid and forms an impermeable gelatinous coating which contains the remainder of the ice and continues to act on the melting ice until all the water therein has become a gel.

Other objects and advantages of the invention will appear from the following description. The fact that several examples are given specifically is not intended to limit the invention to the specific products and processes described in the examples, the scope of the invention being indicated by the appended claims.

In the drawings:

Fig. 1 is a diagrammatic view in elevation of a product embodying the principles of this invention.

Fig. 2 is an enlarged diagrammatic view in section of one particle of said refrigerant.

Fig. 3 is a view similar to Fig. 2 showing the particle after most of the ice has melted.

Fig. 4 is a diagram and flow sheet illustrating one process for making the refrigerant.

Fig. 5 is a flow sheet illustrating a modified process for making the refrigerant.

The product of the invention includes water ice, but not in large blocks. The water ice particles used in this invention should be of a size where the surface area is large enough in comparison with the total volume, so that the powder can be spread in a relatively thin layer and will still react with the water as it melts, to produce a gel or gel-like material that holds the water. If the ice particles are too large, the impermeable coating will be fractured when a large percentage of the water melts and will therefore defeat the purpose of the invention. If the particles of ice are too small, too much powder will generally be required to make the invention economically practicable. I prefer that the pieces of ice be about ¼ inch to ½ inch in diameter—the size normally referred to in the trade as "drug store size." Pieces larger and smaller than this may also be used. Satisfactory results have been obtained with ice cubes and with the grades of ice commonly known as snow ice, sized crushed ice, and flake ice.

As Figs. 1 to 3 show, the ice particles **10** are coated by an adsorbing agent **11** to form the refrigerant **12**. The adsorbent agent **11** should be in powdered form and should be of the type which forms a water-insoluble coating **13** around the ice. Moreover, the coating must hang together so that it is impermeable and will not leak out water. For this purpose, agents which form gels with cold water are the preferred materials. For example, powdered pregelatinized starch (including pregelatinized corn starch, wheat starch and potato starch) gives satisfactory results. For some uses satisfaction can be obtained from bentonite clays in powdered form or cellulose gum (a sodium salt of carboxymethylcellulose having a closely controlled number of sodium carboxymethyl group introduced into the cellulose molecules. This is sold under the trade name "CMC" by Hercules Powder Co.).

Ungelatinized starches, gelatine, agar-agar and other similar gel-forming agents cannot be used, because they form gels only with hot water and will not react properly with cold water or with melting ice. On the other hand, bentonite and cellulose gum form gels better when applied to the ice, as herein, than with water, because the cool temperature slows down the reaction and makes it very uniform, preventing the formation of lumps.

The amount of adsorbing agent to be used depends upon the sizes and shapes of the ice particles used, upon the adsorbing capacity of the powder, upon the characteristics of the gel or similar impermeable coating which it forms, upon the method used in mixing the powder and ice (for some methods are less efficient than others) and upon the use to which the product is to be put. In general, the larger sizes of ice particles require more powder than the smaller sizes. For example, extremely large sizes, such as two-inch ice cubes, are used, and must be heavily coated, because the likelihood of the melting water getting to each particle of powder is reduced.

Some examples of proportions that may be used are given below after the following description of the processes of making the coated refrigerant, but it will be understood that these are examples and are not intended to express all the possible mixes which may be useful.

A preferred method of mixing the ice and the powder, is to place the desired quantity of powder in a bag of waterproof paper or waterproof plastic, add the desired quantity of ice, and roll the mixture around and back and forth to achieve a thorough mixture, the bag being oversize to give excess room for mixing. The mixed refrigerant may be left in the bag for use therein or may be removed from it.

Another preferred method of practicing the process is shown in Fig. 4, where the coating is done on a level surface, such as a floor **14**. Preferably, a layer **11***a* of the adsorbent powder is first spread even over the floor **14**, although this step may be omitted if desired. Then suitable chunks of ice **10** are spread out over the adsorbent powder **11***a* (or over the floor **14** in case the first step is omitted). The ice **10** is preferably spread in a relatively thin layer about one-half inch to an inch thick. A second layer **11***b* of adsorbent may then be sprinkled evenly over the top of the ice particles **10**. Then the ice **10** and powder layers **11***a* and **11***b* may be mixed with a shovel in a manner somewhat like the way cement is mixed with a shovel. The material may be shoveled up into a pile **15** and then reshoveled back into another pile so as to thoroughly mix the materials together. The result will be that all the particles **10** of ice will be coated with the powder **11**, and when the ice begins to melt, the water will combine with the coating of adsorbent powder **11** to form a gel or similar coating **13** that will fully enclose the remainder of the ice and will not leak water. The method just described may be used either with the ice wet and in a room where the temperature is above the melting temperature of the ice or while the ice is held cold in a room considerablf below its melting point.

Another method of manufacturing the coated refrigerant is to use a mechanical mixer, in the manner shown in the flow sheet of Fig. 5. In such cases the mixer should be kept at a temperature below the freezing temperature of ice, because otherwise the walls of the mixer will become coated with gel formed by water running from the ice and reacting with the powder, and this coating interferes with the efficiency of the mixer and wastes a large amount of the coating powder. Preferably, the powder and ice are added into the mixture simultaneously in a steady stream, in the proper proportions.

The state of the ice particles **10** is important, and may affect the amount of powder **11** needed. When large particles, like two-inch ice cubes, are used, then there is an advantage in having the ice somewhat wet, as it will be if it is just starting to melt, because the wet surface will hold more powder than a dry surface will. On the other hand, when fine snow ice is used, then a dry surface is preferred, because it is difficult to mix small wet ice particles with a dry adsorbing powder; since a homogeneous mixture is necessary, snow ice requires more powder when wet than when dry.

The bag method described above appears to be one of the most efficient methods, and so somewhat less powder can be used for the same amount of ice than where other methods are used.

Regardless of the process used, each particle of ice **10** will have a coating **11** of the adsorbing agent on its surface to form the refrigerant **12**. Even if there is a small amount of loose powder **11** in between the particles of ice, this is not necessarily undesirable, although the more evenly coated the ice particles **10** are, the more efficiently the refrigerant **12** will operate to effectively prevent ice from leaking water.

Fig. 3 shows what happens as the ice **10** melts. The first water that melts around the outside reacts with the powder **11** to form a gel **13** that surrounds the ice. Subsequent melting and the water passes into the powder or gel structure. Eventually, the particle is all gel, though it may be more dilute inside than outside.

The following examples give some formulas which may be used to make the coated refrigerant using either of the methods described or any other suitable method for mixing the powder with the ice. All the parts are by weight.

Example 1

	Parts
Ice ("drug store size"—i. e., ¼" to ½" particles)	800
Pregelatinized starch (e. g., "Amijel 185–40," a product of National Starch Products, Inc.)	100
Fine borax	20

The borax aids in preventing rupture of the gel state and should be mixed thoroughly with the starch before the powder is added to the ice. In all of these examples, the dry ingredients should be mixed thoroughly and added as a mixture to the ice.

Example 2

	Parts
Ice ("drug store size")	300 to 1000
Pregelatinized starch	100
Borax	1 to 100

This example shows a range of values. The borax preferably lies in the range of about 10 to 40 parts. Where the ice is larger than "drug store size," less can be used for this amount of starch.

Example 3

	Parts
Ice ("drug store size")	500
Pregelatinized starch	100

The borax can be omitted where much starch is used, though the gel is not quite so strong.

Example 4

	Parts
Ice ("drug store size")	300 to 700
Pregelatinized starch	100

This example shows the usable range of values, where borax is omitted, to form a somewhat less stable gel coating.

Example 5

	Parts
Ice ("drug store size")	800
Pregelatinized starch	100
Borax	20
Paraformaldehyde	1

Formaldehyde or paraformaldehyde strengthens the gel coating and increases its lasting qualities. It also acts as a preservative, and should be added for that purpose alone in small quantities, as shown, when the refrigerant is not to be disposed of after it has served its purpose or if its time of use is longer than about three days.

Example 6

	Parts
Ice ("drug store size")	300 to 1200
Pregelatinized starch	100
Borax	1 to 100
Paraformaldehyde	1 to 100

Where more ice is to be held by the same amount of starch, the quantity of borax and paraformaldehyde should be increased, but not necessarily to the maximum shown. About ten parts of paraformaldehyde and twenty or thirty parts of borax will enable the starch to hold 1200 parts of water-ice.

Example 7

Sodium chloride or other eutectic depressants, including all soluble metallic salts, oxides, and hydroxides, may be added, to lower the eutectic point of the ice. The amount to be added depends on the temperature desired. When sodium chloride in an amount of about 20% of the weight of the ice is added, then the amount of water-ice per starch should be reduced about 100 parts, in the formulas above.

One example of such a solution is:

	Parts
Flake ice	400
Sodium chloride	80
Pregelatinized starch	100

An important feature of this invention is that it retains the salts as well as the water and keeps the brine or solution from harming the goods or their containers.

Example 8

	Parts
Ice ("drug store size")	1200
Cellulose gum (CMC)	100

Sodium chloride, etc., may be added to this formula without reducing the amount of ice.

Example 9

	Parts
Ice ("drug store size")	300 to 1400
Cellulose gum (CMC)	100

This range of values will also hold the water when the ice melts.

Example 10

	Parts
Ice ("drug store size")	500
Fine bentonite clay	100

No salt can be added to bentonite, as it will rupture the gel coating and cause it to leak some water.

Example 11

	Parts
Ice ("drug store size")	300 to 600
Fine bentonite clay	100

This range of values will not leak water.

Example 12

Mixtures of the above may be used, like the following formula.

	Parts
Fine snow ice	600
Ice cubes	200
Crushed ice (½" particles)	200
Pregelatinized potato starch	100
Powdered bentonite	100

The refrigerant which results from the above formulas and from the previously described methods of mixing the adsorbing agent and ice together has many uses. For example, many small shippers of such products as cut flowers, game, fish, dairy products, and packaged produce can mix the powder with the ice just before packing and then use the ice either in direct contact with the goods or in paper bags or in paste-board or in fibre-board containers next to the goods or around ordinary unwaterproofed

bags which contain the goods. The product will not melt away. After the ice has melted, it will have combined with the adsorbing agent to form the gel or gel-like material. All of the cooling quality of the water will still be available for use, because the water will not flow away, nor can any of the goods be damaged by coming into contact with actual water. However, in most forms of the gel it is advisable to use some form of water repellent paper such as wax paper or butcher paper to protect from any absorption of the water out from the gel 13.

Where the refrigerant is to come in contact with an absorbent package or with goods that are absorbent, then it may be advisable to increase the amount of powder relative to the ice, to make a dryer refrigerant, less likely to lose water to the absorbing surface.

The present invention, it will be noted, does not require mixture of anything with the water before freezing. It makes possible the utilization of ice as a non-leaking refrigerant.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the description herein are purely illustrative and are not intended to be in any sense limiting.

I claim:

1. A refrigerant that will not run after thawing, consisting essentially of water ice divided into a plurality of pieces smaller than two-inch cubes, each of which is coated with a dry adsorbent material, chosen from the group consisting of pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose, that acts with cold water to form a jelly-like coating impermeable to liquid flow, the coating weighing between about one-half and one-tenth as much as the ice.

2. A refrigerant that will not flow after thawing, consisting essentially of water-ice in pieces smaller than two-inch cubes coated with a dry adsorbent that forms a gel with cold water, the proportions of ice to adsorbent being between about 2:1 and 10:1 by weight, said adsorbent being chosen from the group consisting of pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose.

3. A refrigerant consisting essentially of between about 300 and 700 parts by weight of water-ice particles having an exterior coating of about 100 parts by weight of dry pregelatinized starch, which as the ice particles thaw capture the water in a gel that prevents leakage of the water.

4. A refrigerant consisting essentially of between about 300 and 1000 parts by weight of water-ice particles coated with a dry mixture of about 100 parts by weight of pregelatinized starch and between about 1 and 100 parts by weight of borax, so that the thawing sets up a gel coating that captures the water as it melts and prevents its leakage.

5. A refrigerant consisting essentially of between about 300 and 1200 parts by weight of water-ice particles coated with a dry mixture of about 100 parts by weight of pregelatinized starch, between about 1 and 100 parts by weight of borax, and between about 1 and 100 parts by weight of paraformaldehyde.

6. A non-leaking refrigerant consisting essentially of between about 300 and 1400 parts by weight of ice particles coated with about 100 parts by weight of dry powdered sodium carboxymethylcellulose.

7. A refrigerant consisting essentially of between about 300 and 600 parts by weight of ice particles coated with about 100 parts by weight of dry powdered bentonite clay.

8. A process for making a water-ice refrigerant that does not flow when thawing, comprising coating about 2–10 parts by weight of water-ice in particles smaller than two-inch cubes with about 1 part by weight of a dry adsorbent that reacts with cold water to form a gel coating, said adsorbent being chosen from the group con-

sisting of pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose.

9. A process for making a refrigerant that utilizes water as the heat-exchanging agent but that does not flow on thawing, comprising mixing ice particles smaller than two-inch cubes with a powdered adsorbing agent, chosen from the group consisting of pregelatinized starch, fine bentonite and sodium carboxymethylcellulose, that forms a gel with cold water, in the proportions of about one part by weight of adsorbing agent to about two to ten parts by weight of ice, said mixing being done at a temperature below the melting point of the ice and being carried on until said ice particles are coated with said powdered adsorbing agent.

10. The process of claim 9 in which said mixing is carried on continuously in a zone to which a stream of ice particles and a stream of adsorbing agent are simultaneously introduced.

11. The process of claim 9 wherein the mixing is accomplished by spreading a layer of the powdered adsorbing agent over a substantially flat surface, placing thereon a layer of ice about one-half to one-inch thick, and then shoveling the layers around on said surface until the ice is coated with the adsorbing agent.

12. The process of claim 9 wherein the mixing is accomplished by spreading a layer of the ice particles on a substantially flat surface to a thickness between about one-half and one inch, covering said layer with a layer of said adsorbing agent, and shoveling them around on said surface until the ice is coated with said adsorbing agent.

13. A process for making a refrigerant that employs water but that does not flow when thawed, comprising coating between two and ten parts by weight of water ice in particles smaller than two-inch cubes with about one part by weight of a dry adsorbent that reacts with cold water to form a gel coating, said adsorbent being chosen from the group consisting of pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose.

14. A process for making a refrigerant that utilizes water as the heat-exchanging agent but that does not flow on thawing, comprising mixing between two and ten parts by weight of ice particles smaller than two-inch cubes with one part by weight of a powdered adsorbing agent that forms a gel with cold water, said adsorbent being chosen from the group consisting of pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose, said mixing being done at a temperature below the melting point of the ice, and being carried on until said ice particles are coated with said powdered adsorbing agent.

15. A process for making a refrigerant, comprising spreading a layer of ice particles on a substantially flat surface to a thickness between about one-half inch and about one inch, covering said layer with a layer of a powdered adsorbent of a type that forms a gel-like substance with cold water, said adsorbent being chosen from the group consisting of the pregelatinized starch, fine bentonite, and sodium carboxymethylcellulose, the proportions of adsorbent to ice being between about 1:2 and 1:10, by weight and mixing said ice and adsorbent by shoveling them around on said surface until said ice is coated with said adsorbent.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,800,456

July 23, 1957

John C. Shepherd

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 6, for "absorbing" read -- adsorbing --; column 3, line 53, for "considerablf" read -- considerably --.

Signed and sealed this 3rd day of December 1957.

(SEAL)
Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents