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[54] **SPRAY-FREEZING APPARATUS AND METHOD**

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[52] **U.S. Cl.** **62/347**, 62/74, 264/14

[51] **Int. Cl.** **F25c 1/00**

[58] **Field of Search**.. 62/123, 74, 347; 34/5; 264/14

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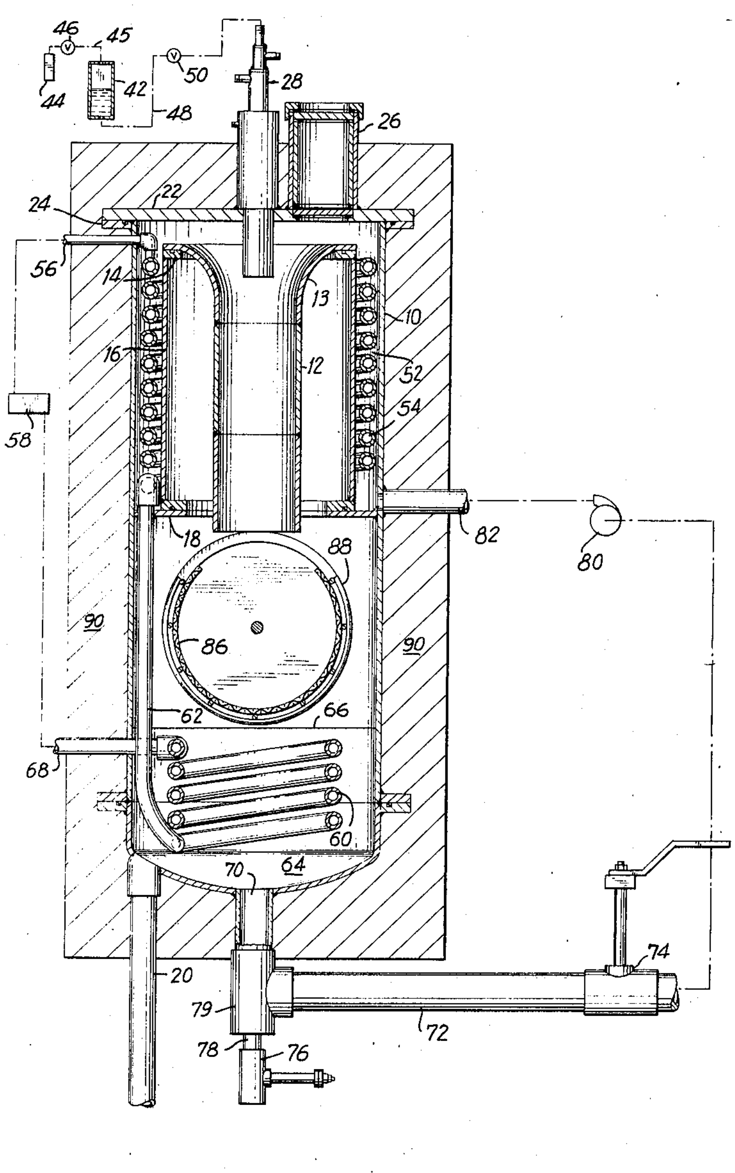
Primary Examiner—William E. Wayner

[57] **ABSTRACT**

An apparatus and method are disclosed for forming fine frozen particles of a solution by using a refrigerated liquid coolant in which the solution is insoluble and the coolant is continuously supplied to a downwardly sloping plate to form a thin film of coolant on a surface of the plate and a nozzle is positioned to spray droplets of the solution against the thin film of coolant whereby the spray droplets of said solution are frozen by the coolant.

10 Claims, 5 Drawing Figures



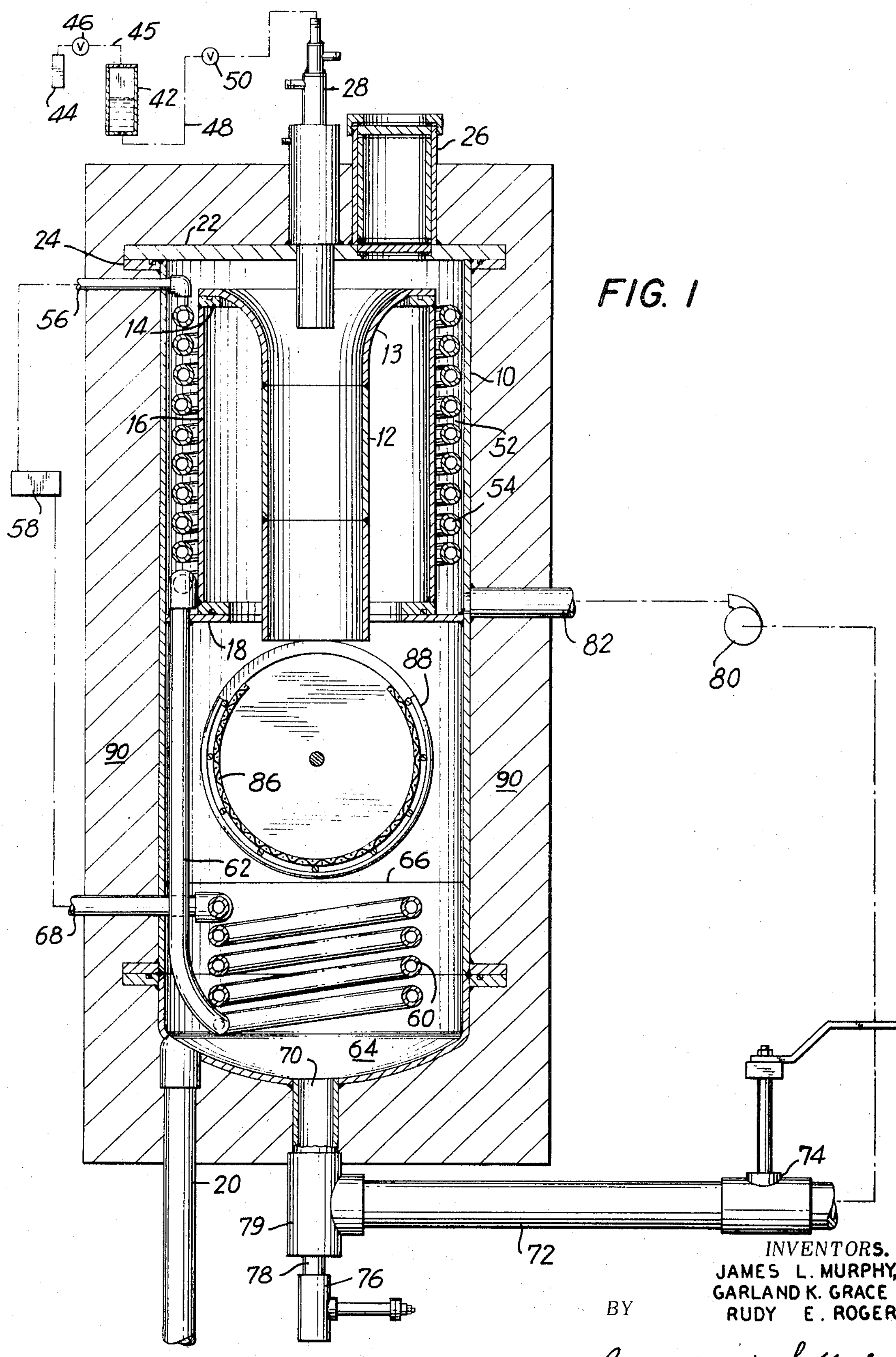


FIG. 1

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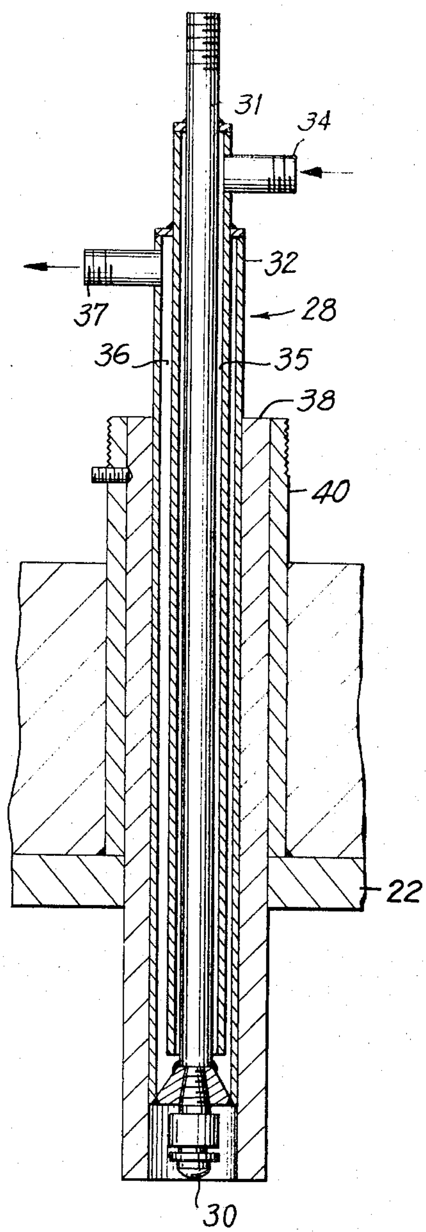
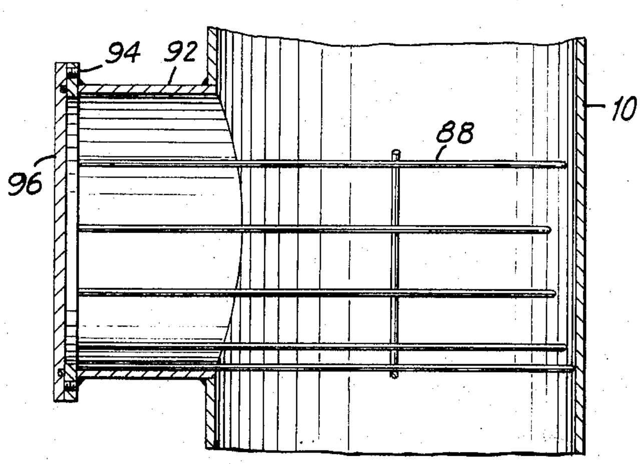


FIG. 2

FIG. 3



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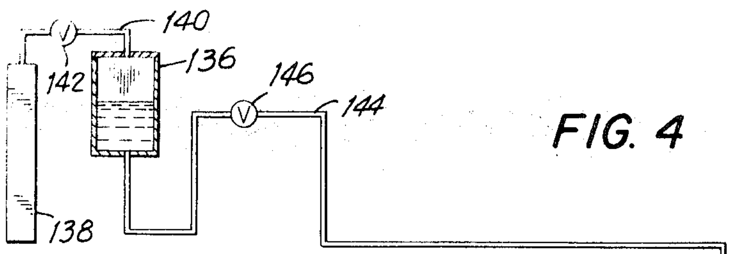

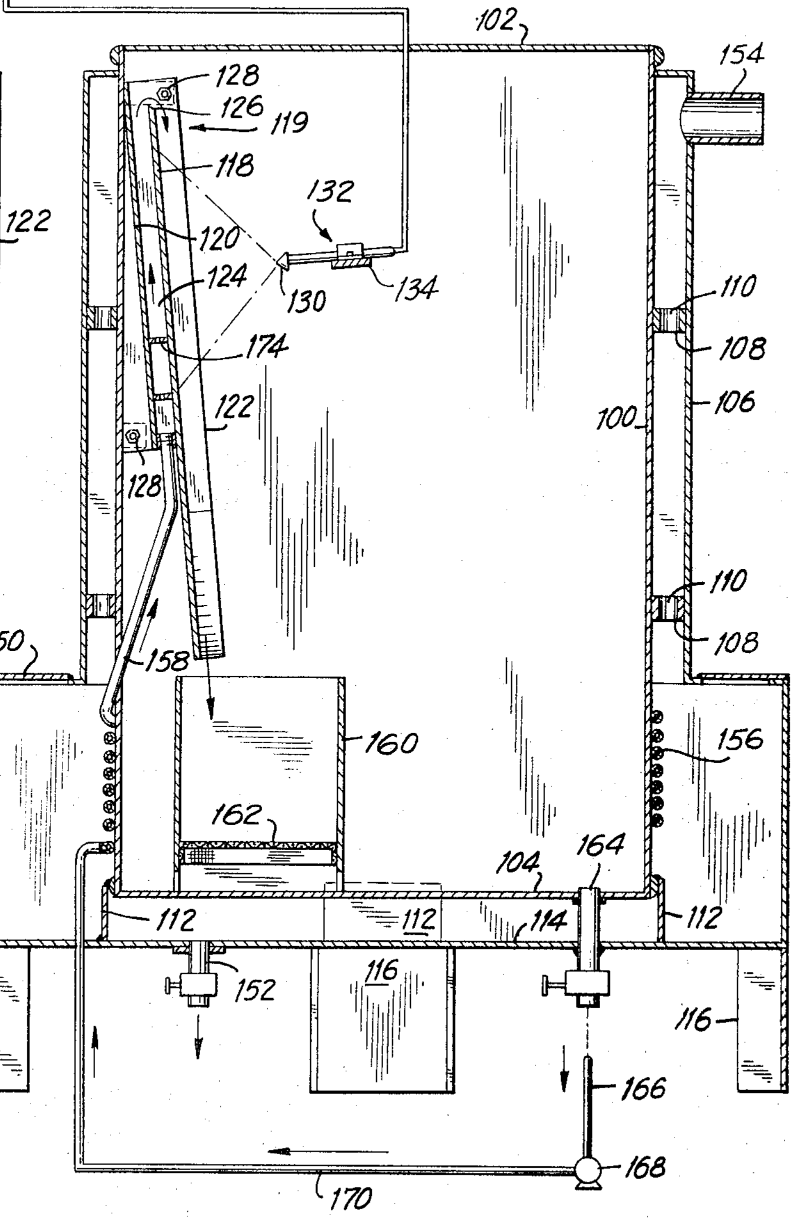

FIG. 4

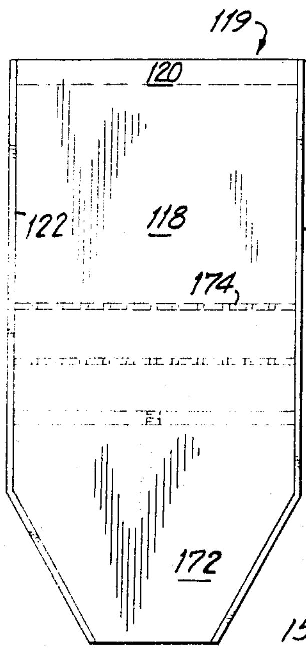

FIG. 5

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SPRAY-FREEZING APPARATUS AND METHOD

The present invention relates to the production of fine particles of solid materials by freeze-drying and, more particularly, to an improved apparatus and method for spray-freezing of droplets of a solution as a step in the production of submicron particles of the solute of the solution. The present method and apparatus have been found especially useful in the production of submicron size particles of ammonium perchlorate adapted to be used in th manufacture of solid propellants and will be illustratively described as used for this application. However, as the description proceeds, it will be apparent that the method and apparatus of the invention can equally apply to the production of ultrafine particles of other materials.

The conventional method of producing fine particles of ammonium perchlorate for use in propellants involves the mechanical grinding of ammonium perchlorate powders in various types of grinders, e.g., ball mills. Such mechanical grinding processes are subject to a number of disadvantages. Thus since a certain amount of heat is created by friction during such grinding processes, a serious hazard of explosion exists. Morever, there is a certain amount of abrasion of the grinding surfaces which introduces undesirable impurities into the material being ground. Also it generally has not been possible by conventional grinding methods to achieve the submicron particle sizes that arre desirable for propellant applications.

Because of the disadvantages of the mechanical grinding methods, a number of alternative processes have been proposed. Among these alternatives is a freeze-drying process which involves, as a first step, preparing a solution of ammonium perchlorate or another solute, which is desired in small particle size, and spraying the solution into an appropriately refrigerated apparatus where it is frozen rapidly into small droplets. The droplets are then subjected to vacuum sublimation to evaporate the solvent and recover the solute in the form of small particles. A discussion of a freeze-drying method of this general type is contained in an article entitled; "Production of Submicronic Powder by Spray-Freezing" by Werly and Bauman contained in the November, 1964 issue of *Archives of Environmental Health*.

The fineness of the particles obtained in such a process depends upon the manner in which the freezing step is carried out, i.e., upon such factors as the spray droplet size, the nature of the refrigerated environment into which the solution is sprayed and the rate at which the solution droplets are frozen. As the droplets are frozen, the solute tends to crystallize out and if a slow freezing rate is used, the particles of solute tend to agglomerate within the frozen droplet. However, if freezing is sufficiently rapid and the proper type of refrigerated medium is used, the solute particles formed are separated by ice crystals and do not have an opportunity to agglomerate.

It is evident, that the sprayed droplets should be as fine as possible to insure that each solution droplet is uniformly and rapidly frozen. To attain this result, it is necessary to utilize a properly designed spray apparatus that takes into account the various controlling characteristics of the nozzle, such as internal shape and orifice size. However, assuming that a properly designed nozzle is used, the nature of the refrigerated environment into which the droplets are sprayed requires careful selection and control in order to achieve the desired small particle size of the solute.

It is accordingly a general object of the invention to provide an improved method and apparatus for spray-freezing droplets of a solution as a step in a freeze-drying process of the type described above for producing submicron particles of the solute. It is another object of the invention to provide a method and apparatus that permits more precise regulation and control of the spray-freezing operation than has heretofore been obtainable. It is still another object of the invention to provide a spray-freezing method and apparatus for producing spray-frozen droplets which upon vacuum sublimation of the solvent yield solute particles of exceptionally small size. It is a still further object of the invention to provide a spray-freezing apparatus which uses a liquid freezing medium ane provides for a more efficient utilization of the freezing medium and effective separation of the spray-frozen droplets therefrom. Other objects and advantages of the present invention will be in part obvious and in part apparent from the following discussion and accompanying drawings which illustrate a preferred embodiment and a modification of the invention capable of being used in carrying out the method of the invention.

In the drawings:

FIG. 1 is a vertical section, partly in elevation, through a spray-freezing apparatus in accordance with the present invention, showing the freezing surface of the weir and a basket for collecting the mixture of coolant and ice crystals formed;

FIG. 2 is an enlarged vertical section, partly in elevation, of the spray injector assembly shown in FIG. 1;

FIG. 3 is a detailed section of a portion of the apparatus of FIG. 1 showing the support for the basket for separating the frozen solution crystals from the coolant;

FIG. 4 is a vertical section of another embodiment of the invention wherein the weir has a flat freezing surface; and,

FIG. 5 is a front view of the weir shown in FIG. 4.

Referring first to FIG. 1, the freezing apparatus as shown comprises a vertically positioned cylindrical tank **10** in which a mixing weir **12** is centrally located. Mixing weir **12** is of generally cylindrical configuration and coaxial with tank **10**. It flares outward elliptically at its upper end **13** until the top edge of its wall is essentially horizontal. This upper end **13** rests on and is attached to an upper annular flange **14** that extends from the top of an inner cylindrical wall **16**. Wall **16**, of slightly less diameter than tank **10**, is suppoted at its lower end by a lower annular flange **18** that extends from the interior surface of tank **10**. The tank **10** is supported by four evenly spaced tank support legs **20**, only one of which is shown in FIG. **1**. The top of tank **10** is enclosed with a tank lid **22** that is circumferentially supported by an external upper tank flange **24**. A sight port **26** is provided in tank lid **22** to permit operators of the apparatus to view the spray-freezing process.

An injector assembly **28**, shown in detail in FIG. **2**, is positioned through the center of tank lid **22** so that a spray nozzle **30** extends below the top edge of weir **12**. The spray nozzle **30** is attached to the lower end of an injector assembly pipe **31**. Pipe **31** is enclosed in a water jacket **32** through which hot water flows to prevent precrystallization of the solution. Hot water enters water jacket **32** through entrance **34** and flows downwardly into conduit **35** adjacent to pipe **31**. Returning water then flows upwardly in an outside annular conduit **36** and leaves water jacket at exit **37**. A portion of water jacket **32** is enclosed in a sleeve **38**, preferably of Teflon, and the entire assembly is held in lid **22** by a mounting cylinder **40** that is attached to the top of lid **22**.

The solution to be crystallized is contained in a solution storage tank **42** that is pressurized by gas stored in a pressurization tank **44**. The conduit **45**, between tanks **44** and **42**, contains a pressurization valve **46** that is used to control the pressurization of tank **42**. A solution flow conduit **48** connects tank **42** to pipe **31** of the injector assembly **28**. Adjustment of solution flow rate is controlled by a solution flow valve **50** that is located in conduit **48**.

An upper heat exchanger **52** is located between the inner cylindrical wall **16** and the wall of tank **10**. This heat exchanger consists of an upper refrigeration coil **54** that is supplied with a refrigerant through a refrigerant input conduit **56**. The refrigerant is cooled by a refrigeration unit **58** that supplies conduit **56**. The bottom turn of coil **54** is connected to the bottom turn of a lower refrigeration coil **60** by a refrigeration coil connecting conduit **62**. Coil **60** is positioned in the lower portion **64** of tank **10** and is covered by the coolant liquid that is maintained at a level **66** above the coil as shown in FIG. **1**. The uppermost turn of coil **60** is connected to a refrigerant return conduit **68** that directs the flow of the refrigerant back to refrigeration unit **58**.

A coolant exit port **70** is located at the bottom of tank portion **64** and is in communication with a coolant return conduit **72**. A cryogenic ball valve **74** is located in conduit **72** to provide appropriate control of the coolant flow. A second cryogenic ball valve **76** is connected to the coolant drain **78** that branches from a T-connection **79** in conduit **72**. Conduit **72** is connected to the input of a coolant circulating pump **80** that directs the coolant through a coolant feed conduit **82** to the bottom of heat exchanger **52**. The coolant then flows upwardly around the coil **54** which serves to further refrigerate it, and flows over the upper end **13** of weir **12**, forming a thin film on the inside surface of the weir. As the coolant film moves down, it is struck by the spray emitted from nozzle **30**. This contact with the coolant immediately freezes the spray droplets thereby forming a slurry of the frozen droplets in the coolant. This slurry then continues to flow down the inner surface of weir **12** and drops into a basket **86** positioned in a basket support **88**. Basket **86** is formed from a tightly woven screen, for example, 325 mesh, which holds the frozen droplets but permits passage of the coolant to the lower portion **64** of tank **10**. The basket support **88** extends through the wall of tank **10** and an insulation and vapor barrier **90**, which encloses the entire tank as well as the external various refrigerant and coolant conduits, for easy removal of basket **86**. The details of this basket support extension are shown in FIG. **3**, representing a partial side view of the embodiment in FIG. **1**. A horizontal basket support cylinder **92**, of slightly larger diameter than support **88**, is joined to the front of tank **10**. The outer end of support **88** is attached to an annular flange **94**, which in turn is welded to the outer edge of cylinder **92**. The internal diameter of flange **94** is such that basket **86** can be easily withdrawn from the interior of tank **10**. During the freezing process, an insulated cover **96** closes the end of the basket support extension.

In beginning the freezing process, it is first necessary to establish a constant flow of the coolant over the upper circumferential edge of weir **12**. The sight port **26** can be used to view this flow to ensure that the coolant only forms a thin film on the inner surface of the weir. As previously indicated, the coolant flows down the weir and is collected in the bottom portion **64** of tank **10**, where it is refrigerated by the refrigerant flowing in coil **60**. It should be noted that the flow pattern in coil **60** of the refrigerant starts in the bottom conduit and spirals upwardly to exit from the top conduit. This arrangement progressively lowers the coolant temperature as the coolant moves towards the bottom of tank **10**. Portions of the coolant near the bottom of tank **10** are then removed and pumped to the upper heat exchanger **52**. Since the upper refrigeration coils **54** spiral downwardly from the refrigerant input conduit **56**, the passage of the coolant upward in the heat exchanger **52** progressively lowers the coolant temperature until it approaches the temperature of the incoming refrigerant.

The interior of tank **10** is maintained at such a low temperature that there is danger of precrystallization of the solution while still in the injector assembly **28**. The hot water jacket **32** is therefore installed about the injector assembly to provide means for maintaining the temperature of the solution above its freezing point prior to emission from nozzle **30**. Further isolation of the injector assembly and water jacket from the tank lid **22** is provided by the sleeve **38**, which is preferably constructed of Teflon or other similar material. This sleeve also protects the assembly from metal fatigue caused by temperature cycling and temperature gradiants.

Referring now to FIG. **4** wherein a second embodiment of a freezing appartus is shown. This embodiment comprises a cylindrical tank **100** which is enclosed at opposite ends by an upper tank cover **102** and a lower tank cover **104**. An outer housing **106** begins slightly below the upper tank cover **102** and encloses the remainder of tank **100**. Two annular flange separators **108** maintain the lateral position of tank **100** with respect to outer housing **106**. Several holes **110** in the flange separators **108** provide means for venting an evaporated cooling medium which will be discussed later. Tank **100** is supported vertically in outer housing **106** by tank support legs **112** which are attached to the bottom **114** of outer housing **106**. In turn, the outer housing is supported by legs **116**.

A flat mixing weir plate **118** is shown as part of a weir assembly **119** formed by the weir plate **118**, a back plate **120**, and sides **122**. Weir plate **118** and back plate **120** are positioned parallel and separated so that the space between them constitutes a weir conduit **124**. The upper edge of weir plate **118** is beveled at about 45° sloping downwardly towards the center of tank **100**. The weir assembly **119** is supported in tank **100** by weir support bolts **128** at an angle of approximately 5° from the vertical.

A nozzle **130**, forming part of a nozzle assembly **32**, is positioned opposite the front portion of weir plate **118** such that the center axis of the nozzle is perpendicular to the front surface of plate **118**. The nozzle assembly **132** is mounted in tank **100** on a nozzle assembly support **134** which extends between the opposite sides of the tank walls. The solution to be crystallized is contained in a solution storage tank **136** which is pressurized by gas stored in a pressurization tank **138.** The conduit **140,** between tanks **138** and **136,** contains a pressurization valve **142** used to control the pressurization of tank **136.** A solution flow conduit **144** connects tank **136** to the nozzle assembly **132.** Adjustment of solution flow rate is controlled by a solution flow valve **146** located in conduit **48.**

The lower portion **148** of outer housing **106** is of a larger diameter than the upper portion and constitutes a heat exchange section of the apparatus. A series of hinged inlet ports **150** are positioned along the horizontal top of lower housing portion **148** to provide means whereby a cooling medium may be inserted in the heat exchanger. A drain **152** is located on the bottom **114** of the outer housing to provide an exit for the liquefied cooling medium. As previously mentioned, holes **110** in flange separators **108** provide conduit means whereby evaporated portions of the cooling medium may rise and exit through an exhaust vent **154.** Several turns of a coolant coil **156** surround the lower portion of tank **100** to form a portion of the heat exchanger. The uppermost turn of coil **156** is connected to the bottom of weir conduit **124** by conduit **158.** Coolant flows through coils **156** and up through conduits **158** and **124** exiting over the upper beveled edge **126** of weir plate **118.** The coolant then flows in a thin film down the sharp incline on the front surface of weir plate **118** whereupon droplets of the solution are sprayed against it and are immediately frozen thereby forming a slurry frozen droplets of the solution in the coolant. The slurry then continues to flow down to the bottom of the weir and drops into the top of a collector tube **160** which supports a collector basket **162** formed of fine screen mesh. The crystallized solution particles are separated from the coolant by the screen in basket **162** and the coolant continues to flow to the bottom of tank **100** where it exits through port **164** to the coolant return conduit **166.** Conduit **166** is connected to the input of a coolant circulating pump **168** which pumps the coolant through a conduit **170** back to coils **156.**

After a sufficient quantity of solution has been frozen, the process is discontinued and cover **102** is removed to permit the apparatus operator to retrieve basket **162.**

In the front view of the weir assembly **119,** shown in FIG. **5,** it can be seen that the lower portion **172** of weir plate **118** coverges to ensure proper delivery of the slurry into collector tube **160.** This view also shows that a plurality of holes are formed in the two baffles **174** which separate weir plate **118** from back plate **120,** thus enhancing distribution of the coolant stream across the width of the conduit **124.**

There are several possible coolants which may be used with the preceding embodiments. Of course, it is essential that any liquid, selected as a coolant, be a nonsolvent for the particular solution utilized. In cases where ammonium perchlorate is the desired product and an aqueous solution thereof is used as the feed to the spray, Freon 12 has proven to be a preferable coolant although other coolants, such as n-butyl alcohol, may also be used effectively. To prevent loss of the coolant during operation of the freezing apparatus, it is desirable to construct the apparatus to withstand pressures of at least 100 psi.

A mechanical refrigeration system, as shown in the embodiment of FIG. **1,** may also be used with the embodiment of FIG. **4,** provided a suitable heat exchanger is utilized. A refrigerant that may be used effectively with such a refrigeration system is Freon 113. The refrigeration unit must have sufficient cooling capacity to lower the temperature of the coolant to a point where it can crystallize the sprayed solution rapidly. It has been found that a 15 ton refrigeration unit is sufficient for an apparatus as shown in FIG. **1** where the diameter of tank **10** is 16 inches and the diameter of the cylindrical portion of weir **12** is 5 inches. In the embodiment of FIG. **4,** a refrigerant such as a mixture of methylene chloride and dry ice may be packed against the coolant coils **156** in the lower portion **148** of the outer housing **106.**

Similar nozzle pressurization systems have been shown in the embodiments. Preferably nitrogen is used as the pressurization gas in the pressurization tanks. It has been found desirable to maintain a pressure of at least 1,000 psig in the pressurization tanks to ensure proper spray emission from the nozzles. It will of course be understood that while only one nozzle and one weir have been shown in the described embodiments, multiple nozzles can be used with a single weir and more than one weir can be used in a single freezing apparatus.

Although illustrative embodiments of the present invention have been described herein with reference to the accompanying drawings, it is to be understood that the invention is not limited to those precise embodiments, and that various changes and modifications may be effective therein by one skilled in the art without departing from the scope or spirit of this invention.

I claim:

1. An appartus for forming fine frozen crystals of a solution by using a refrigerated liquid coolant which is a non-solvent for said solution comprising in combination, a stationary coolant tube having an upper and lower end, means for supplying said coolant to the upper end of said coolant tube in an amount to form a thin downwardly flowing film of said coolant on the inner surface of said tube, at least one spray nozzle located adjacent to said tube and positioned to spray droplets of said solution against the thin downwardly flowing film of said coolant, means for supplying said solution under pressure to said spray nozzle, whereby the spray droplets of said solution are frozen by said coolant and form a slurry with said coolant which flows from the lower end of said coolant plate, and means for progressively lowering the temperature of said coolant prior to supplying said coolant to the upper end of said coolant tube comprising a refrigerant and a coiled conduit in external contact with said coolant for conducting said refrigerant in a flow direction opposite to the flow direction of the adjacent coolant.

2. An apparatus as described in claim **1** wherein, said means for progressively lowering the temperature of said coolant includes a refrigerant enclosure and coiled conduit means for conducting said coolant within said refrigerant enclosure.

3. An apparatus as described in claim **1** wherein, said coolant tube has a cylindrical-shaped lower portion, and a downwardly converging convexly curved upper portion merging with said lower portion to form a smooth interior surface on which the coolant film is established.

4. An apparatus as described in claim 1 wherein, said means for supplying said coolant comprises, conduit means ending at the upper end of said coolant plate, regulating means for controlling the coolant flow rate in said conduit means, and pumping means for moving said coolant through said conduit means.

5. An apparatus as described in claim 1 including, means for separating said frozen crystals of solution from said coolant comprising a removable basket of fine mesh screen positioned below said coolant tube.

6. An apparatus as described in claim 1 including, means for heating said solution prior to spraying from said nozzle to prevent precrystallization of said solution in said nozzle.

7. Apparatus as described in claim 1 wherein said spray nozzle is located within said coolant tube.

8. An apparatus for forming fine frozen crystals of a solution by using a refrigerated liquid coolant which is a non-solvent for said solution comprising a housing, a stationary coolant tube having an upper and lower end mounted in said housing, a cylindrical partition positioned between said housing and tube and cooperating with the wall of said housing to define a passage for conducting coolant to the upper end of said coolant tube to cause said coolant to flow downwardly in a thin film on the inner surface of said coolant tube, means for supplying coolant to said passage and spray means positioned within the upper end of said coolant tube to spray droplets of said solution against said coolant film.

9. Apparatus according to claim 8 wherein said coolant tube has a cylindrical lower portion and a downwardly converging, convexly curved upper portion merging with said lower portion to form a smooth interior surface on which the coolant film is established.

10. Apparatus according to claim 8 including a refrigerant coil mounted in said passage and means for supplying refrigerant to the upper end of said coil to cause refrigerant to flow through said coil in a direction generally counter-current to the flow of coolant through said passage.

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