

## UNITED STATES PATENT OFFICE

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## ANHYDROUS CALCIUM CHLORIDE PROCESS

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This invention relates to a new process for the manufacture of solid calcium chloride, and more particularly to a new and improved method for the dehydration of relatively concentrated solutions of calcium chloride.

The process in commercial operation for the manufacture of calcium chloride employs a dilute liquor as starting point, which is available as a by-product of the ammonia-soda process. This liquor is evaporated in a steam heated or other type of evaporator until a concentration of about 40% to 50%  $\text{CaCl}_2$  is reached, if desired under vacuum, and any deposited solids are removed. From this stage onwards it is not convenient to use a reduced pressure as at high concentrations this results in deposition of solid in the evaporator and generally blockage thereof. It is therefore customary in commercial practice to carry out the further evaporation by direct heating in pots at atmospheric pressure, during which process the concentration and temperature rise progressively to 70 to 72%  $\text{CaCl}_2$  and 170° C. At this point the solution is cooled, conveniently as a thin surface on a cooled rotating drum which dips into the liquor, to yield flakes, or in a cooled granulating machine to yield granules, and the solid so obtained contains 70 to 72%  $\text{CaCl}_2$ . In another method, the solution is cooled to 160° C. with agitation while preventing any further evaporation, to give a mush of crystals and liquor, which is then cooled further to give lumps.

In some commercial practice this solid is further dehydrated by putting it in an oven or by passing it through a rotating drier which is heated either through the walls or by a current of hot air, to give a product containing 76 to 78%  $\text{CaCl}_2$ . This product requires less packing and transport than 70 to 72%  $\text{CaCl}_2$  and is also less liable to cake on storage. Another method of making a substantially anhydrous product is to spread the 70%  $\text{CaCl}_2$  solution on a conveyor which takes it through a furnace at 350° to 450° C. to raise it to 85 to 90%  $\text{CaCl}_2$ , and then through a furnace at 500° to 600° C. to give substantially anhydrous calcium chloride.

Evaporation in direct-fired pots is a relatively inefficient way of employing heat, compared for example with multiple effect evaporation which can be employed for solutions of lower concentrations. In addition, the heat efficiency of such a pot is low, being only of the order of 40 to 50%. Furthermore, the large floor space occupied by such an installation and the relatively large amount of repairs makes pots unattractive. Most of this difficulty is due to the last stages of evap-

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oration of liquor to give 70 to 72%  $\text{CaCl}_2$ , as although the evaporation up to about 65% can be effected easily and efficiently, it is the further concentration which involves the inefficiencies of pot working. Moreover it is clear that the conversion of 70%  $\text{CaCl}_2$  liquor to a solid containing 75%  $\text{CaCl}_2$  or higher has hitherto been a difficult operation. It involves the preparation and handling of the intermediate solid, and the transfer thereto of at least 65 ton calories per ton 75%  $\text{CaCl}_2$  in order to effect the dehydration. Such heat can only be transferred through the walls with difficulty because of the deplorably poor heat transfer to a solid in this way. It is therefore usually supplied from the current of hot air, which has to be bled off to remove the evaporated water at a low partial water vapour pressure, and therefore far more heat is in fact used up in this process than would appear from this theoretical figure.

One object of the present invention is to provide an improved process for the manufacture of 75 to 77%  $\text{CaCl}_2$ . Another object is to decrease the amount of heat which must be supplied in the manufacture of commercial calcium chloride, and to provide an improved evaporation process. Yet another object is to provide a new and useful form of commercial calcium chloride.

I have found that there are certain conditions of concentration and temperature which, if properly chosen, can be employed for the conversion of concentrated calcium chloride solution to solid calcium chloride and water vapour with a considerable saving of heat over the customary process. Solutions of calcium chloride which are nearly saturated at their boiling point at or near atmospheric pressure, when subjected to reduction of partial water vapour pressure, can be made to undergo separation into water vapour and solid 70 to 76% calcium chloride by a process which continues to completion adiabatically.

In one method of carrying out this invention, I take a solution containing about 70 to 72%  $\text{CaCl}_2$  and the rest water except for small amounts of impurities which may amount to 1 to 2% taken together. The temperature of this solution is adjusted to about 170° to 175° C. The solution is then subjected to conditions in which the partial water vapour pressure above the solution is kept below atmospheric, e. g. is kept at 100 to 400 mm. of mercury, and a large surface area of solution is provided e. g. by spraying the solution down an empty tower. This permits autoevaporation of the water, and calcium chloride is thus deposited as a granular, dry solid containing 75%

to 76%  $\text{CaCl}_2$  by these operations alone. The above description represents the optimum case where it is unnecessary to introduce any heat whatsoever, and the only heat precautions which must be taken are that undue losses to the atmosphere must be avoided.

Another method of operation is to spray an appropriate solution down a tube in which there is an ascending current of air to carry off the water vapour and thus maintain a low water vapour partial pressure. This method also gives dry granular calcium chloride. The air should be warm to avoid undue heat losses from the solution, and it may if desired be hot enough to supply some heat to the process.

The method of providing a large surface area may be by any of the standard methods normally adopted for this purpose, e. g. spraying, exposing as a film, agitating a solution or distributing it on previously produced granular calcium chloride as carrier for the solution in a creeper mixer. In any of these processes the time involved in autoevaporation is much less than is normally taken in evaporating calcium chloride solutions or in further dehydrating solid 70%  $\text{CaCl}_2$ . In addition, we avoid the consumption of much of the heat hitherto required, more especially the transmission of heat to a solid which is a difficult operation, and also avoid the need for superheating or supersaturating at raised pressure as a means of reaching higher concentrations.

Thus it will be seen that my invention comprises adiabatic or substantially adiabatic conversion of an appropriately chosen solution into vapour and solid merely by subjecting it to the necessary reduction of partial water vapour pressure. In the ideal case this adiabatic process is also an isothermal one.

The success of my invention is due in a large extent to the discovery that the heat required for vaporising the water from a calcium chloride solution of certain specific concentrations can be provided by the heat liberated from crystallisation of calcium chloride dihydrate from such solutions. Thus, I have found that the crystallisation of calcium chloride dihydrate from highly concentrated solutions liberates considerable heat notwithstanding the well known fact that the dissolution of calcium chloride dihydrate in water liberates a very large amount of heat. Moreover, I have discovered that with specific conditions this crystallisation liberates enough heat to vaporise all of the water from these concentrated solutions. By operating in this fashion, calcium chloride dihydrate can easily be obtained even though it is extremely deliquescent. In other words, this discovery makes possible production of calcium chloride by overcoming many of the difficulties and peculiar problems associated with the dehydration of calcium chloride, e. g. the complicated problems of heat transfer are dispensed with since by operating under my conditions the heat required is actually generated internally as required.

The ideal case is represented by the use of about 72% calcium chloride solution at about 170° to 175° C., but there are other conditions within the immediate vicinity of this point where the operation though adiabatic is not isothermal in that some change of the temperature occurs during the autoevaporation. As the higher limit, solutions can be used containing as much as 75%  $\text{CaCl}_2$  at a temperature not exceeding 200° C. As a lower limit I may use liquor containing 67% calcium chloride with an initial temperature as

low as 150° to 160° C., which will autoevaporate adiabatically to give solid 70% calcium chloride by reducing the partial vapour pressure of water down to about 50 mm. of mercury. Alternatively, the same effect can be achieved by starting with 65% calcium chloride solution at a higher temperature and subjecting it to the same process, but this does not give the same thermal advantage. Thus there is a comparatively restricted range of concentrations in which my process operates without the introduction of any heat. Within this general range of 65% to 75%  $\text{CaCl}_2$  the preferred concentrations lie between 68% and 72%  $\text{CaCl}_2$ , and for the 68% liquor it has been found preferable to start with a temperature between 150° and 170° C., and for the 72% liquor it has been found preferable to start at a temperature between 170° and 180° C.

Whilst this invention has hitherto been described as an adiabatic process which in the ideal case is also an isothermal process, I include within the present invention the substantially adiabatic process where some heat is added but only a small amount relative to that which has hitherto been thought necessary. The known conversion of solid 70%  $\text{CaCl}_2$  to solid 76%  $\text{CaCl}_2$  and water vapour by the conventional hot air drying process involves the transfer to it of about 65 ton calories per ton of product, and a wastage of several times this amount in the discharged air. I have shown that I can make this 76% product from the 70% liquor without the introduction of any heat and without having to handle the intermediate product, by working under specified conditions, but for simplification in operation it is sometimes desirable to use a weaker solution and to add an amount not exceeding 30 and generally not exceeding 10 ton calories per ton of product. This is conveniently applicable when the process is carried out in a creeper mixer. I also include the case where a small amount of heat is lost, for example by radiation from the substance or from the walls of the vessel, or by transmission to cool air used to effect autoevaporation.

In one method of carrying out the process as a continuous process in a creeper mixer I employ a paddle creeper which is open at the top for access of air. The paddle creeper contains granular calcium chloride, and a 68% to 72% calcium chloride liquor at a temperature of 150° to 180° C. is fed in at one end of this creeper. A pool of liquor thus forms at the feed end, and further along the creeper the contents become mushy and subsequently become dry, and eventually free-flowing granular calcium chloride runs off at the far end. Although theoretically there is no need to introduce heat into this creeper process, yet we find it convenient to heat the walls of the creeper, and/or to see that the air which passes freely over the surface of the solid in the creeper and thus removes the water vapour is hot, e. g. at 100° to 200° C. In practice, of course, the amount of heat which can be transferred through the metal surface to a mushy solid or to a substantially dry or free-flowing solid as is present in the creeper is extremely small because of the resistance to heat flow from the creeper walls to the solid. In the case where I do not use strictly adiabatic operation but provide some heat either through the walls or by contact with hot air, I can with a rather longer time of operation manage to use a feed liquor containing as little as 60%  $\text{CaCl}_2$  at a temperature of 120° to 150° C.

According to the present invention, therefore, I provide a process for producing solid calcium chloride from a highly concentrated solution at an elevated temperature, preferably between 120° and 200° C., by providing a large surface area of the liquor and a low partial water vapour pressure to facilitate vaporisation of the water, and substantially adiabatically allowing the vaporisation to yield solid calcium chloride. The solution employed is of a concentration at or near saturation at these temperatures. The process may be carried out, for example, by spraying a 67% to 72%  $\text{CaCl}_2$  solution at 150° to 175° C. into a vacuum, or by spraying a 65% to 70%  $\text{CaCl}_2$  solution at 150° to 170° C. through a current of hot air, or by feeding a 60% to 72%  $\text{CaCl}_2$  solution into a vessel containing granular calcium chloride which is being agitated while air passes over it, or by spreading the liquor as a thin film.

The characteristic feature of the invention is the substantially adiabatic nature of the operation, thereby avoiding the difficult process of heat transfer to a solid, viscous solution or slurry.

By way of explanation of the fact that ideal conditions of adiabatic autoevaporation exist under which I carry out my process, I believe that the ideal conditions are those at which saturated aqueous solutions of calcium chloride show a maximum in the curve of vapour pressure against temperature. It has already been known that the vapour pressure of saturated calcium chloride solutions rises with increasing concentration up to about 72%  $\text{CaCl}_2$  and then falls again. At this maximum vapour pressure, the heat required to convert a saturated solution to water vapour and solid calcium chloride dihydrate at the same temperature is nil. In respect of this vapour pressure of saturated aqueous solutions, calcium chloride differs from most other inorganic substances. Only a few substances have such a maximum, and without this maximum there can be no adiabatic isothermal autoevaporation. In addition, calcium chloride dihydrate has such a maximum near to atmospheric pressure. This vapour pressure is low enough to give a dense product without using closed pressure vessels and yet is high enough to cause a high rate of evaporation in my process without the need for large volumes of carrier fluid such as air to remove the water vapour. Those factors which I have determined have been found by me to be requisite in practice for the ready operation at high rates of an adiabatic evaporation process under the conditions I have described herein.

This presents yet a further advantage of the process in that all the final and difficult dehydration is carried out without, in the ideal case, any fall in vapour pressure from this maximum figure. That is to say, the last of the water present exerts a vapour pressure of about 800 mm. of mercury and thus is readily removed.

The invention also provides a further characteristic feature in the form of the product. The product is generally obtained as a granular dust-free material somewhat resembling in appearance a coarse sand or aggregates thereof. Depending on the type of process employed, the bulk density of the solid product may vary between 0.4 and 1.3 gm./cc. When I carry out the evaporation by spraying the solution into an evacuated tower the evaporation takes place by rapid disintegration of the sprayed drops and consequent formation of hollow or porous granules whose packing density is between 0.3 and 0.8 and is generally 0.4 to 0.6 gm./cc. For commercial and domestic

purposes a low density is often an attractive feature. When I spray the liquor down a tower countercurrent to an upflowing stream of warm or hot air the granules so obtained are approximately the size of sand and their packing density is generally 0.7 to 0.9 gm./cc. When I carry out the process in a granulator in contact with air the product is in dust-free granules which may even exceed 2 mm. in diameter, and the bulk density is 0.9 to 1.5 and generally about 1.1 to 1.3 gm./cc. All such products are themselves novel and useful. They are all readily handled, measured and dissolved.

The process can clearly be carried out as a batch process, but in industrial operation it is much more convenient to carry it out as a continuous process as, for example, in apparatus of the creeper type. The process is operated at a relatively low temperature and therefore the attack on materials of which the plant is constructed is not serious. For example, mild steel can be used for the construction of the plant, and cast iron is also eminently satisfactory. In addition, attack on the vessels during the present process can readily be avoided by producing a thin layer of scale on the surface of the vessel and any stirrers or other metallic parts. The thin layer of scale may be readily deposited from the solution used in the process by filling the vessels with this solution and causing slight cooling. The scale so formed is adherent and permits the manufacture of white calcium chloride.

The invention is illustrated but not restricted by the following examples.

#### Example 1

The apparatus used in this example consists of a vertical tower 3 feet in diameter and 15 feet high, equipped at the bottom with a tray which can be emptied through a doorway, and at the top with a spray nozzle fed through a control valve from a stock tank. Apart from these features, the tower is empty and is closed to the atmosphere and connected through a condenser to a vacuum pump. In the process, the absolute pressure inside the tower is reduced to 5 lbs. per square inch by means of the vacuum pump. The stock tank is filled with a liquor containing 70%  $\text{CaCl}_2$ , 28%  $\text{H}_2\text{O}$  and 2% of sundry impurities principally  $\text{NaCl}$ , which is at 175° C. The control valve is then opened to admit liquor at a rate of 200 litres per hour. The liquor may be observed through windows in the walls of the tower and is seen to emerge from the spray nozzle as multitudinous droplets. As these droplets fall in the tower they change to a solid and collect on the tray in the manner of snowfall. When the tray is full, the liquor feed valve is closed, the vacuum is released, the tray is emptied into a container and the operation restarted. The product so obtained is much too hot to handle manually when removed from the tower, and when cold is found to contain 76%  $\text{CaCl}_2$ . It has a bulk density of .4 to .5 gram per cc. Microscopically the structure of the solid can be observed to be jagged and shredded.

#### Example 2

In this example the apparatus consists of a vertical tower of 5 feet diameter and 30 feet high, equipped with a band conveyor at the bottom for removal of the product, atomising spray nozzles at the top for introduction of the liquor as fine droplets, an inlet pipe near the base for introduction of hot air, and an outlet at the top

for removal of the moisture-laden air. The spray nozzles are fed by a pump from a stock tank. The stock tank is filled with liquor containing 70%  $\text{CaCl}_2$ , 28%  $\text{H}_2\text{O}$  and the remainder impurities principally  $\text{NaCl}$ . This liquor is kept at 170° C. and is pumped through the spray nozzles into the tower at a rate of 250 litres per hour. Simultaneously, air is blown into the bottom of the tower at 180° C. and at a rate of 150  $\text{m}^3$  per hour, and evacuated from the top along with the water vapour evolved. Hot, granular 76% calcium chloride collects on the band conveyor and is removed and packed. It has a bulk density of 0.8 gm. per cc.

#### Example 3

The equipment consists of an inclined trough 2 feet wide and 2 feet deep, fitted with a rotating paddle mixer, and insulated to prevent undue loss of heat through the walls. The liquor employed contains 65%  $\text{CaCl}_2$  and 33%  $\text{H}_2\text{O}$ , and is used at a temperature of 150° C. Air at 150° C. is allowed to circulate freely over the top of the open trough. The trough is substantially filled with solid granular calcium chloride (about 10 cwt.), and liquor is then run into the feed end of the trough continuously at a rate of .1  $\text{m}^3$  per hour. This causes the formation of a mushy puddle at the point where liquor is added, and the contents of the trough vary from this mush through a wet solid, a dry-looking solid, to a dry free-flowing solid at the discharge end. Dry solid calcium chloride in a form resembling coarse sand and aggregates thereof then leaves at the exit end of the trough. It contains 27%  $\text{H}_2\text{O}$ , has a bulk density of 1 to 1.1 grams per cc., and is free-flowing and free from dust.

#### Example 4

The apparatus consists of a polished drum 2 feet wide and 6 feet diameter, rotating slowly on a horizontal axis with the bottom portion immersed to a depth of 6 inches in a bath of liquor. The bath contains 72%  $\text{CaCl}_2$  liquor at 175° C. The drum rotates at one revolution per minute, and picks up a thin layer of solution on the surface which rises out of the solution. As the solution is exposed to warm air on the rotating drum, the water evaporates leaving a layer of solid 75% calcium chloride, which is scraped off as flakes on the downgoing side of the drum.

#### Example 5

In this example a batch process is illustrated. The apparatus consists of an open stirred pot which is heated gently. This pot is half-filled with 70%  $\text{CaCl}_2$  liquor. Hot air is blown over the top of the liquor, which becomes first a slurry and then a moist solid which gradually dries and crumbles. Within an hour a dry free-flowing granular solid of particle size chiefly between .2 mm. and .5 mm. is obtained, containing 76% calcium chloride.

What I claim is:

1. The process for the manufacture of solid hydrated calcium chloride from an aqueous solution thereof which comprises heating an aqueous calcium chloride solution of between 60% to 72% calcium chloride content to a temperature of between 120° and 200° C., then providing a large surface area of the heated solution, subjecting the solution to a partial water vapor pressure of less than one atmosphere and allowing the solution to yield solid hydrated calcium chloride by substantially adiabatic evaporation of water.

2. The process of the manufacture of solid hydrated calcium chloride from an aqueous solution thereof which comprises heating an aqueous calcium chloride solution of between 65% to 72% calcium chloride content to a temperature of between 150° and 175° C., then providing a large surface area of the heated solution, subjecting the solution to a partial water vapor pressure of less than one atmosphere and allowing the solution to yield solid hydrated calcium chloride by substantially adiabatic evaporation of water.

3. A process for the manufacture of solid hydrated calcium chloride from an aqueous solution thereof which comprises heating an aqueous calcium chloride solution of between 65% to 70% calcium chloride content to a temperature of 150° to 170° C., and then spraying the heated solution into a vacuum to provide a large surface area of the heated solution, allowing the solution to yield solid hydrated calcium chloride by substantially adiabatic evaporation of water and, thereafter collecting the resulting solid hydrated calcium chloride.

4. A process for the production of solid hydrated calcium chloride from an aqueous solution thereof which comprises heating an aqueous solution of calcium chloride containing between 65 to 70% calcium chloride to a temperature of 150 to 175° C., providing a large area of the heated solution by spraying the heated solution into a current of air heated to a temperature between 150 to 170° C., and collecting the resulting solid hydrated calcium chloride particles.

5. A process for the production of solid hydrated calcium chloride from an aqueous solution thereof which comprises heating an aqueous solution of calcium chloride containing between 60 to 72% calcium chloride to a temperature of 120 to 200° C., providing a large area of the heated solution by flowing the heated solution onto an agitated bed of granulated calcium chloride, circulating air of approximately the same temperature as the heated solution over the agitated bed, and removing particles of solid hydrated calcium chloride from said bed.

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