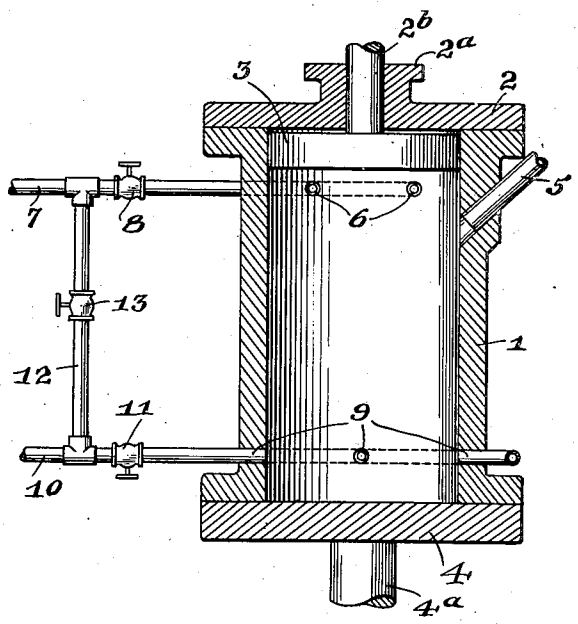
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PRODUCTION OF SOLID CARBON DIOXIDE

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PRODUCTION OF SOLID CARBON DIOXIDE

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This invention relates to certain improvements in the production of solid carbon dioxide; and the nature and objects of the invention will be clearly recognized and understood by those skilled in the art involved in the light of the following explanation and detailed description of the preferred method of the invention and the steps thereof from among equivalent or other steps within the spirit and the scope of our invention.

The invention is particularly directed to the production of solid carbon dioxide by the method in which cooling by partial expansion and evaporation of liquid carbon dioxide to initially produce a moist or wet carbon dioxide snow, is combined with mechanical compression to produce a block or cake of high density solid carbon dioxide; the expansion and evaporation of the liquid to form the moist snow being performed and carried out in the same chamber as the mechanical compression.

In the method to which this invention relates, liquid carbon dioxide is expanded into a chamber down to pressures at which gaseous carbon dioxide and a wet or moist carbon dioxide snow consisting of commingled crystals and liquid particles in the desired proportion are formed. The carbon dioxide gases so formed are withdrawn from the chamber at the upper end thereof above the forming mass of wet snow at a rate to maintain the chamber pressure during snow formation at wet or moist snow preserving pressure, that is, within a range of triple point pressure depending upon the proportion of liquid to crystals that it may be desired to form. After the formation of the desired quantity of wet snow under such conditions, the pressure in the chamber is reduced down to substantially atmospheric pressure by withdrawing or sucking off the gases resulting from the evaporation of the liquid in the moist snow as the pressure falls below the triple point range, from the lower end of the chamber downwardly through the snow mass with the result that the mass is solidified and congealed into a compact, dense, solid block or cake of carbon dioxide.

This method is capable of producing a block or cake of dense solid carbon dioxide without the application of mechanical pressure to complete and further densify and compact the block, but the method has the serious disadvantage of requiring a considerable period of time to form and complete the solid block or cake, particularly in carrying out and completing the second stage or step of reducing the chamber pressures and diffusing the gas downwardly through the congealing and solidifying snow mass.

In carrying out the second stage or step of this method, when the pressure in the chamber is reduced from the wet snow preserving or triple point pressures to atmospheric pressure by withdrawal of the gases from the lower end of the chamber and through the snow mass, the reduction in chamber pressure does not take place uniformly throughout the chamber, but occurs first at that part of the chamber near the gas outlets and then spreads slowly upwardly through the contents of the chamber. When the pressure at any given point in the chamber and in the snow mass falls definitely below the triple point pressure, the liquid carbon dioxide in the wet snow can no longer exist at that point, but the liquid carbon dioxide can and will exist as a liquid at points more remote from the gas outlet where the triple point pressures are maintained owing to the friction or retarding effect which opposes passage of liquid and gas through the pores or interstices of the solid. The pressures thus maintained in the upper portions of the mass urge the residual liquid carbon dioxide through the pores or interstices of the solid carbon dioxide to the points of lower pressure where the liquid can no longer exist, and this results in the formation of further solid in the interstices so as to ultimately and finally produce a hard dense block or cake of solid carbon dioxide.

The rate at which this infiltration of the liquid carbon dioxide will take place is obviously proportional to the porosity of the solid that has been already formed and the pressure that is acting on the liquid, and in producing blocks of dense solid carbon dioxide by this method, where the porosity is low, the rate of infiltration and of the completion of this stage or step of the method is slow and consumes a considerable period of time.

One of the main objects and results of the method of our invention is to materially and very substantially reduce the period of time necessary to carry out this final pressure reduction and solidification stage or step of such methods, while increasing the efficiency of the method in operation and making it possible to not only produce a solid carbon dioxide of higher density, but also to insure the production of cakes or blocks in which such high density is substantially uniform through each block or cake.

Our method is characterized and featured by the application of mechanical pressures to the formed moist or wet snow mass in the chamber concurrently with the reduction of chamber pressures by the diffusion of gas through the mass and withdrawal from the chamber, and at points on the mass remote from the points of gas withdrawal from the chamber, so that the congealing and solidifying mass is simultaneously compacted and densified and the liquid is forced therethrough to lower pressure regions for evaporation and dispersion and diffusion of the gases through the mass whereby the solidification step can be completed in a relatively short period of time, the time for completion of the step being proportional to the degree of mechanical pressure applied.

A further object and feature of the method of our invention resides in the combination and cooperative incorporation of mechanical pressures into the second stage or step of the general solidification methods referred to, in such a manner that mechanical pressures are applied during and concurrently with the pressure reduction on the wet snow mass in the chamber and are continuously applied to the congealing mass as the liquid particles therein are evaporated until the mass is in the dry state, and the mechanical pressures may then be increased and their application on the dry and congealed mass continued to complete the formation and increase the density of the solid block or cake.

With the foregoing general objects, features and characteristics in view, as well as certain others that will be readily apparent from the following explanations and description, the invention consists in certain novel steps forming the method of our invention as will be more fully and particularly referred to and specified hereinafter.

In the accompanying drawing, one form of apparatus capable of operation to carry out our method is more or less diagrammatically disclosed, and is shown partly in vertical section.

Referring to the accompanying drawing, the apparatus may consist of a conventional or other type of press that includes the press chamber 1, of cylindrical, rectangular or other desired or suitable cross-section, having the upper end or top closure 2, formed with an axial vertical bearing or gland 2*a*, which reciprocally receives the actuating rod 2*b* for the press piston or plunger 3 reciprocally confined within the press chamber 1. The mechanical pressure applying plunger 3 is actuated by the rod 2*b* from any suitable source of mechanical or hydraulic power (not shown) in the usual or any other desired manner familiar in the art.

The lower end or bottom of the press chamber 1, is normally closed by the closure plate or platform 4, which forms a sealing fit with and against the lower end of the press chamber wall. This lower closure plate 4, is vertically movable to and from chamber closing position by a rod or column 4*a* which is vertically reciprocal by any suitable hydraulic or mechanically operable means (not shown). The arrangement is such that the bottom closure plate may be lowered from its chamber closing and sealing position shown in the drawing, to position opening the press chamber for removal of the chamber contents.

For forming the wet or moist snow mass in the press chamber 1, there is provided a downwardly inclined liquid carbon dioxide expanding nozzle and diffuser 5, that is connected to and supplied with liquid carbon dioxide from any suitable or usual source of liquid carbon dioxide, which source it is not deemed necessary to here show. The mouth or discharge of this nozzle and diffuser 5, by which the moist snow and gases are discharged into the chamber 1, is located in a wall of the chamber 1, at a point below the normal raised or uppermost position of the press piston or plunger 3, as will be clear by reference to the drawing.

The press chamber 1, is provided with the gas off-take or discharge ports 6, of which there may be any suitable or desired number, located at a relatively high level in the wall of the press chamber 1, but below the normal raised, inoperative and uppermost position of the plunger 3 in the chamber, these ports 6 being also located preferably above the mouth or discharge point from the nozzle and diffuser 5. The ports 6, are in communication with a pipe line 7 that leads to that stage of a suitable or usual liquefying compressor (not shown) at which the suction pressures and resulting gas withdrawal will substantially maintain the pressures in the press chamber 1, at approximately the triple point or at wet snow preserving pressures. The pipe line 7, has the gas flow therethrough controlled by a suitable valve 8, located in the line 7 and by which the flow of gas therethrough can be cut off and stopped when desired. Adjacent the lower end of the press chamber 1, and above lower closure plate 4, a series of gas off-take ports 9 are located by which the diffusion gases from the chamber 1 are withdrawn. These ports 9 are in communication with a pipe line 10 that leads preferably to the low pressure or atmospheric suction intake of any suitable or desired and familiar type of liquefying compressor (not shown). The gas flow through the pipe line 10 is controlled by a suitable valve 11 through the medium of which, the flow of gas can be stopped and the communication of the ports 9 with the compressor can be cut off. In the example hereof, the pipe lines 7 and 10 that are in communication with the ports 6 and 9, respectively, are connected by a pipe 12 at points therein between the valves 8 and 11 and the respective compressors or compression stages. A valve 13 is provided in the line 12 for closing the line and shutting off communication therethrough between pipe lines 7 and 10.

It will be understood, of course, that the pipe lines 7 and 10 can be coupled with the proper compression stages, respectively, of a suitable stage compressor, or to separate compressors, which compressors serve to recompress and bring the gases up to liquefaction pressures. It is not considered necessary to disclose these compressors here as they may be of the usual and familiar types for this purpose.

Now, with such apparatus, a solidification method in accordance with and embodying our invention, is carried out in the following manner and includes the following steps.

In the first stage or step of the method, the press chamber 1 is closed and sealed by hydraulically or mechanically raising the closure plate 4 into position sealing and closing the lower open end of the press chamber 1, as shown in the accompanying drawing. The press plunger 3, is raised or elevated by its hydraulic or mechanical operating means to the uppermost position in the press chamber 1, above

the expansion nozzle and diffuser 5, and the gas off-take ports 6. This normal raised position of the plunger 3 is shown in the accompanying drawing. The valve 11 in the pipe line 10, that communicates with the press chamber ports 9, is closed to cut off discharge and flow of gas from the chamber through line 11, while the valve 8 in pipe line 7 is opened to place the upper end of the press chamber in communication with the compression stage with which line 7 is coupled. Liquid carbon dioxide is then expanded in the nozzle 5 and discharged into the press chamber 1, down to a pressure within the triple point pressure range, with the resulting formation and conversion of the liquid carbon dioxide into gaseous carbon dioxide and into a wet snow mixture composed of crystals of solid and particles of liquid carbon dioxide. The pressure within the press chamber 1, is maintained at a wet snow preserving pressure, that is, pressure within the triple point range of pressures by the rate of off-take of the gases formed through the ports 6 by the stage of compression with which the pipe line 7 is coupled, and in relation to the liquid discharge and expansion from nozzle 5. These pressure conditions are maintained during expansion of the liquid through the nozzle 5 and discharge of the moist snow and gases into the press chamber 1, and are continued while a mass of the moist or wet snow is forming and collecting in the chamber on the lower closure plate 4 and until the desired charge or quantity of moist or wet snow has been formed or built up in the press chamber 1.

After the desired charge or quantity of wet or moist snow has been formed in the press chamber 1, under the conditions hereinbefore described, the expansion and discharge of liquid carbon dioxide through the nozzle 5 into the chamber 1 is cut off and stopped and the valve 8 in the pipe line 7 is shut, to cut off communication of the chamber with the compression stage to which pipe line 7 is coupled, and hence, to stop the withdrawal of the gases from the chamber above the formed mass of wet snow. The valve 11 is then opened in the pipe line 10 to place the lower end of chamber 1 in communication with the compressor intake, valve 13 and pipe 12 being normally closed, and suitable hydraulic or mechanical pressure is then applied to the press plunger 3 through the piston or plunger rod 2b, so that gases are then withdrawn by the compressor (not shown) from the lower end of the chamber through the ports 9, after being forced to diffuse or pass downwardly and outwardly through the mass of snow that has been formed and collected in the chamber 1, by the combined action of the downwardly moving pressure applying plunger 3, and the suction through the pipe line 10 by the compression stage with which this pipe line is coupled. This second stage or step of our method results first in a reduction of pressure in the press chamber 1, below the wet snow preserving or triple point pressures, and this pressure reduction takes effect first at the lower end of the chamber of the mass of moist or wet snow and then progressively works upwardly through the mass. As the pressure reduction drops below wet snow preserving or triple point pressures, the liquid content of the wet snow mass evaporates and a portion thereof freezes out as solid while the remainder is converted into gas. These evaporation gases are caused to diffuse downwardly through the congealing and solidifying mass, and further, due to the pressure applied at the upper end of the mass by the plunger 3, the liquid particles in those regions of the mass ahead of the pressure reduction, are forced through the interstices in the mass into the upwardly progressing regions of below triple point pressures so that they are not only more completely and thoroughly caused to infiltrate or disperse through the mass, but are also caused to be more rapidly and quickly evaporated to thereby materially reduce the time required to carry out and complete this solidification and densifying step.

The downward pressure applying movement of the press plunger 3, is continued along with the gas withdrawal through ports 9, until the liquid in the mass has all been evaporated under the reduced pressure conditions in the chamber 1, and the portions of the liquid have been frozen out as solid in and through the interstices of the mass, so that finally, the moist snow mass has been converted and changed into a relatively dense and congealed block of dry carbon dioxide snow or ice. However, we prefer to continue this application of mechanical pressure to the mass after it has reached its dry state, and to even increase the mechanical pressure applied by the plunger 3 to the block in the final step so as to obtain a high density in the block and a density that is substantially uniform throughout the block. At the proper time during the final step of pressure application, and after the mass has reached the dry and finished block form, we then relieve the mechanical or hydraulic pressure that has maintained the lower closure plate 4 in its chamber closing position, and permit this plate to slowly lower under the pressure exerted thereon by plunger 3, so that the finished block is expelled or forced from the press chamber by plunger 3, and lowered on the closure plate 4, for removal.

The time required to carry out the final stage of our process in which the mechanical pressures are applied concurrently with and during the chamber pressure reduction and liquid evaporation, is inversely proportional to the degree or amount of pressure applied by the plunger 3. Thus, by the application of sufficiently high mechanical pressure, this final step or stage of the process can be carried out within a very short period of time of only a few minutes, depending, of course, upon the size of the block being formed. Further, these higher mechanical pressures can be applied to the wet snow mass during the reduction of pressure in the chamber and the evaporation of the liquid without increasing the temperature of the mass above the triple point temperature range.

We also prefer, in carrying out our method, to so adjust and control the wet snow preserving pressures during the first stage or step of the method, as to produce a much greater proportion of solid, or snow crystals, to liquid particles in the snow mass, so that the greater part of the charge has been crystallized and solidified prior to the second stage or step of our method. In this way, the greater part of the solidification has been carried out and the time required for evaporation and freezing of the additional solid out of the liquid is further materially reduced.

With the prior methods to which our process relates, in this second stage, it is necessary to have a high proportion of liquid to solid in the wet snow mass in order that the required con-

gealing and cementing of the mass into the solid block or cake may be obtained without the use of mechanical pressures.

Attention is also directed to the fact that with the apparatus shown in the accompanying drawing, if desired or found expedient, the withdrawal of the gas from the press chamber through the ports 6 and 9, can be effected through pipe lines 7 and 70, alternately, by means of appropriate manipulations and settings of the valves 8, 11 and 13 in the pipe lines 7, 10 and 12, respectively.

It is also to be understood that a practically continuous out-put and production of solid carbon dioxide cakes or blocks can be obtained by using a plurality of units of apparatus such as shown in the drawing, arranged for operating in a cycle, with constant reliquefaction of the gas by the compressors and supplying such reliquefying gas to the liquid expansion nozzles in the press chambers of the units.

While a vertical type of press is disclosed in the example of apparatus for carrying out our method, it will be understood that the method is not limited to the use of such vertical types of presses, but may be carried out in presses of the horizontally working plunger or other type, so long as the gas discharge ports and the liquid expansion nozzle are properly relatively disposed to each other and with respect to the press plunger operation.

It will also be evident that our method is not limited or restricted for operation in and with the particular apparatus here shown, but may be carried out and performed with a variety of other forms and types of apparatus; and it is further evident that the method of our invention is capable of variation in the steps as specifically described and explained hereinbefore, and hence, we do not wish to limit our invention in all respects to the exact and specific steps of the present disclosure, but desire and intend to include equivalent and other steps within the broad spirit and scope of the invention as defined by the appended claims.

What we claim is:—

1. The method of producing a block or cake of solid carbon dioxide that includes the steps of admitting liquid carbon dioxide to the pressing chamber of a plunger press, with expansion of liquid into the chamber and discharge of gas from the chamber so regulated that the chamber becomes charged with a mixture of solid carbon dioxide and liquid carbon dioxide; then after charging the chamber with the solid and liquid carbon dioxide mixture, reducing the chamber pressure and withdrawing from the chamber the gas that is evolved by evaporation of a part of the liquid as a result of the pressure reduction; and concurrently with the chamber pressure reduction and gas withdrawal from the chamber, applying mechanical pressures to the mixture in the press chamber at points remote from the part of the press chamber from which the gas is withdrawn.

2. The method of producing a block or cake of solid carbon dioxide that includes the steps of admitting liquid carbon dioxide into a chamber with expansion of the liquid into the chamber and withdrawal of gas from the chamber so regulated that the chamber becomes charged with a mixture of solid and liquid carbon dioxide; then reducing the chamber pressure and withdrawing from the chamber the gas evolved by evaporation of a part of the liquid in the mixture that results from the chamber pressure reduction; concurrently with the chamber pressure reduction and gas withdrawal from the chamber, applying mechanical pressures to the mixture in the chamber at points remote from the part of the chamber from which the gas is withdrawn; and continuing the application of mechanical pressures to the charge in the chamber after elimination of the liquid therein by the chamber pressure reduction to form the charge into a block of dense solid carbon dioxide.

3. The method of producing a block or cake of solid carbon dioxide that includes the steps of forming a mass of liquid and solid carbon dioxide in a chamber while maintaining a pressure in the chamber that will preserve the mixture of liquid and solid carbon dioxide; reducing the chamber pressure and withdrawing from the chamber the gas that is evolved by evaporation of a part of the liquid in the mass as a result of the chamber pressure reduction; concurrently with the chamber pressure reduction and gas withdrawal from the chamber, applying mechanical pressures to the mass in the chamber as the mass solidifies; and continuing application of mechanical pressures to the mass after elimination of the liquid carbon dioxide therefrom by the chamber pressure reduction, and increasing the mechanical pressures so applied to the mass after the liquid elimination in order to complete the dry solidified mass into a block of solid carbon dioxide.

4. The method of producing a block of solid carbon dioxide that includes the steps of charging a chamber with a mass of liquid and solid carbon dioxide; reducing the chamber pressure and withdrawing from the chamber the gas that is evolved by the evaporation of a part of the liquid in the mass as a result of the chamber pressure reduction; and concurrently with the chamber pressure reduction and gas withdrawal, applying mechanical pressures to the mass as the mass solidifies into the dry solid state.

5. In a method of producing a high density block of solidified carbon dioxide in a press having a press chamber with a press plunger therein; the steps of expanding liquid carbon dioxide into the press chamber to a pressure at which gas and wet carbon dioxide snow are formed while withdrawing the gases from the chamber at a rate to maintain wet snow preserving pressures in the chamber; stopping liquid expansion into the press chamber upon the completion of a desired quantity of wet snow in the chamber; then reducing the chamber pressure and withdrawing the gases therefrom evolved by the evaporation of a portion of the liquid forming the wet snow mass, such gas withdrawal being from a point in the chamber remote from the press plunger; and during and concurrently with such pressure reduction and gas withdrawal applying mechanical pressures to the solidifying wet snow mass by operation of said press plunger.

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