PATENT SPECIFICATION

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(54) METHOD OF PREPARING A SUBTERRANEAN CAVITY FOR STORAGE OF LIQUEFIED GAS

(71) We, SOCIETE FRANCAISE DE STOCKAGE GEOLOGIQUE "GEOSTOCK" a French Corporation organised under the laws of France, of Tour Aurore—Cedex no 5—92080 Paris La Defense, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of preparing a subterranean cavity for the storage of liquefied gas.

It is known to store liquefied gases, for example natural gas, at very low temperature in reservoirs placed on the surface of the ground or in partly buried reservoirs, excavated in the ground and covered by an arch, for example of metal. For safety reasons these techniques have the drawback of a limited unitary capacity of the reservoirs.

Storage techniques are also known in which a liquefied gas is stored in the earth, in cavities where it is at the temperature of the ambient medium and under relatively high pressure; the depth of the cavity is then selected so that the hydrostatic pressure of the earth exceeds that of the stored liquid, but these techniques are expensive, in particular in the case of substances with high vapour pressure.

Various methods have been proposed to store liquefied gases and in particular gases liquefied at very low temperature, such as natural gas, in subterranean cavities, the sealing of the latter being produced by freezing of the earth. The liquefied gas is then at a pressure close to atmospheric pressure. Hitherto these methods have encountered various difficulties, principally connected with fissures which either existed in the earth before the excavation of the cavity, or appeared at the beginning or during the course of the installation operation. In some cases these fissures resulted in the entry of water which is difficult to arrest, especially if these fissures appeared only after the beginning of cooling, that is to say at a time when such problems had not been expected. In some cases, even leakages of gas to the surface occurred, which also are only generally detected after the beginning of cooling or of the installation operation.

In French patent application No. 2,240,165 a method of cryogenic storage is proposed in which the rock is previously cooled to a temperature below the temperature to be used during the storage. Fissures in the rock are created or widen with this precooling, they are plugged with a substance freezing at low temperature and then the cavity is heated to the temperature of use. In this way there is created in the rock a zone of compression which ensures sealing. There is provided, around the zone where the rock contains plugging material solidified in its fissures, a zone where the plugging material is liquid, and this zone should therefore constitute a safety zone which should arrest a newly appearing fissure.

In summary, the fluid-tightness of the subterranean cavity is ensured by the freezing of a substance artificially introduced into the surrounding formation and penetrating into the fissure created by the shrinkage of the rock under the effect of freezing. The freezing substance used is an organic compound, which increases the cost of the method, all the more as one is sometimes obliged to place considerable amounts of it around the reservoir.

In USP 3,392,532, it is proposed to plug the fissures of the rock surrounding the

5	cavity by the injection into the latter of gas at a temperature below the freezing point of water, at a pressure balancing the hydrostatic pressure. The gas employed has a vapour pressure higher than or equal to that of butane. Since this substance has a melting point of -0.5C, it is not understood how it is possible to keep it under pressure at a sufficiently low temperature to freeze water which may contain much dissolved salts. In any case, after the freezing of the water in the walls, if it desired to store a liquefied gas at low temperature it would be necessary to proceed with	5
10	considerable additional cooling and nothing is provided in this patent to prevent or treat the fissures which appear during this further cooling period. Moreover, in this patent, the walls of the cavity are not mentioned during cooling, and it is only said that the circulation of the cooling gas is continued until the walls are completely plugged by the ice (column 4, lines 74—75). It is possible, for example to assure it by lowering the gas pressure somewhat and by observing the flow rate of the exhaust pump.	10
15	In summary, in this method, the walls of the cavity and the surrounding mass are not monitored during the period of cooling, and modifications to the programme only take place during the inital freezing, which is the concern of the present invention. Thus, the method of USP 3,392,532 does not overcome the problem of	15
20	overcoming the fissures which appear in the course of the whole of the cooling and the duration of the storage life. In addition, it requires the use of large amounts of butane or similar gas, with which there is the further complication of hindering possible manual intervention in the cavity.	20
25	The present invention seeks to provide a method of preparing a subterranean cavity for the storage of liquefied gas, whose fluid-tightness is essentially obtained by the freezing of the earth, and in which, during the whole life period of storage, the drawbacks due to the entry of water, or gas leakages, are minimized. The studies which gave rise to the present invention enabled us to observe that	25
30	the drawbacks which has just been mentioned had their origin principally in the process of cooling the cavity, before its filling or at the beginning of the latter. According to this invention we provide a method of preparing a subterranean cavity for the storage of liquefied gas wherein the fluid tightness of the cavity is substantially obtained by freezing of the earth, comprising the steps of:	30
35	providing a suitable cavity and determining, prior to cooling, the mechanical and thermal characteristics of the rock in which the cavity is formed; gradually cooling the cavity under conditions selected dependent on the said mechanical and thermal characteristics to a desired final temperature below the	35
40	temperature of freezing of the earth suitable for the storage of liquefied gas, whereby the formation of unwanted fissures during cooling is reduced; monitoring the physical condition of the walls of the cavity and the surrounding rock during the cooling so as to detect formation of fissures and which will interfere with fluid tightness of the cavity; and	40
45	modifying the cooling of the cavity so as to cause the fissures to become plugged and/or plugging the fissures by external means at temperatures sufficiently low that subsequent cooling will not destroy the fluid tightness of the plugs but above the desired final temperature. The studies on which the present invention is based have also shown the	45
50	existence of a risk of gas leakage during the period of exploitation of the reservoir, and hence it was appropriate to take certain precautions. According to the invention, preferably, the cavity is hollowed to a depth calculated so that, up to the end of the planned utilisation, the frozen zone is below the phreatic level. The reason for operating in this manner will be explained below.	50
55	Preferably, as will be explained in more detail in the following description, during the application of cooling, a temperature variation relationship is followed obeying the two criteria of maintaining in the compression zone existing around the cavity a width capable of arresting the propagation of the majority of those fissures capable of causing an entry of water into the cavity, and of obtaining in the earth	55
60	only stress gradients that do not cause the appearance of such fissures. It is preferred that at least certain of the preparing steps in the course of the cooling be done by a human operator, for example the repair of certain disturbances, like exceptional fissures, or even the systematic plugging of the fissures.	60
65	In fact, according to a preferred emnodiment of the invention, in the course of the cooling, the fissures opening in the wall of the cavity are plugged, this operation being carried out on, or in the vicinity of this wall at a temperature where these	65

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	fissures have a size such that their subsequent movements cannot break the fluid- tightness of the plug. Preferably, these plugs are produced by spraying water which freezes on the walls and forms a substantially continuous layer at least in certain	
5	Preferably also, the initial cooling is done by the introduction of cold gas, such	5
	as air, into the cavity. The terms employed above and the whole of the invention will now be explained in more detail with the assistance of the single Figure, which is a diagram of stresses in rock, as a function of temperature.	
10	The studies which have resulted in the present invention were directed firstly to the nature of the stresses which appear in rock during its cooling, as a function of the temperature reached.	10
15	In the appended diagram, there are drawn as ordinates upwards the theoretical tractive stresses, and downwards the compressive stresses, in rock saturated with water, during cooling between ambient air and -160°C. This diagram was obtained by calculation from experimental determination of the thermo-mechanical characteristics of various types of rock. The curve in full line, which represents the stresses in the rock enables the	15
20	following observations to be made: Between ambient temperature and a temperature T ₂ the rock is in compression. At ambient temperature, the value of the latter corresponds to the initial stresses in the earth: geostatic stress (weight of the ground), and hydrostatic	20
25	pressure, the thermal stress being nil. Between ambient temperature and T ₁ , equal to about +4°C, cooling reduces the compressive stress, which corresponds to contraction of the matrix and of the water in the pores.	25
30	On the contrary between T ₁ and a point A the compression increases. This phenomenon corresponds to the anomaly of the expansion of water which produces maximum density at +4°C, then the gradual solidification of the water in the pores. It is known that, due to the effect of capillary forces, the solidification of water in the finest pores is not reached before the region of -100°C; so that the temperature of the point A can vary fairly widely, for example, between -0 and	30
35	-40 °C or even beyond as a function of the porosity of the rock and of the amount and nature of the salts dissolved in the water. In the same way, the temperature T_2 can also vary between about -10 and -50 °C. At temperatures below that of the point A, compression diminishes and then is annulled at T_2 and is then replaced by a tractive stress of the whole of the rock and of the ice that it contains.	35
40	The curve of the tensile strength of the rock is drawn in dashed line on the diagram. The position of this curve is obviously very variable according to the nature of the rock. It cuts the curve of the stresses at a point B at a temperature T_3 comprised between -20 and -100 °C. It is at this temperature that, in the earth, the fissures	40
45	The theoretical curve of the stresses beyond B are extended in mixed lines, which gives an idea of the development of the size of the fissures which have appeared from point B. It is observed that this curve tends towards a maximum, that is to say the size of the fissures tends itself towards a maximum.	45
50	The number and distribution of the fissures are connected with the stress gradient in the earth in the zone which is in the neighbourhood of temperature T_3 , and it is understood that, in the course of the cooling of a reservoir, the moment when the wall of the reservoir reaches this temperature T_3 is a moment when it is appropriate to act with maximum precautions, since an open fissure at this time	50
55	has then a tendency to propagate in the earth. Moreover, it is appropriate to observe that the existence of a range of temperatures wherein the rock is in compression is, a priori, a favourable element: a reservoir maintained at low temperature is thus surrounded, at a certain distance, by a compressed zone where the fissures are closed on themselves and rendered	55
60	fluid-tight on condition that they do not exceed a critical size. There will now be described, by way of example, a sequence of operations for the placing in operation of a reservoir: In the first stage, the reservoir is excavated in conventional manner and is fitted out. The stage can comprise notably the plugging of fissures and entries of	60
65	water by injections of cement or the like. The fitting out comprises in addition, the plugging of the cavity so that it is	65

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	fluid-tight to water at its temperature before the application of cooling, and the installation of pipes for the introduction of fluids.	************
	In another stage, which can take place before, during or after the first stage, the	
5	mechanical and thermal characteristics of the rock are determined, and in	_
3	particular the exact shape of the stress curve as a function of temperature, and that of the tensile strength curve as a function of temperature, as defined in the	5
	appended Figure.	
	Also the thermal characteristics are determined, the utility of which will be	
	seen below.	
10	Then, an initial cooling programme is established taking into account the	10
	following conditions:	
	It is known that the size of the fissure is connected with that of the temperature	
	gradients, that is to say the speed of cooling. In order that a fissure should not be	
1.5	able to result in a penetration of water inside the reservoir, it is necessary that the	
15	water which penetrates should freeze there before entering the reservoir. This	15
	freezing depends, notably, on the shape of the fissure and its potential delivery rate,	
	and on the amount of cold that it can receive from the surrounding rock. It hence depends also on the distance which separates it from the reservoir. It is understood	
	that it is at the beginning of the cooling or of the utilisation of the reservoir that the	
20	ice front is closest to the latter. It is possible to calculate, approximately, the	20
20	maximum dimension of acceptable fissures, knowing in particular the heat capacity	20
	and the thermal conductivity of the rock.	
	It is hence understood that it is possible to determine the speed of cooling	
	which corresponds to a given size of the fissures. This determination can, in theory,	
25	be done purely by calculation. However, it is only possible to obtain acceptable	25
	results if the rocks are extremely homogeneous. In practice, the preferred method	
	consists of establishing an initial cooling programme, by means of the data	
	collected, then of observing the size of the fissures which are formed, for example,	
30	visually or by means of television cameras placed in the reservoir, or alternatively	20
30	by extensometry, and of accelerating or slowing down the cooling with respect to the initial programme as a function of the size of the fissures.	30
	Schematically, four types of fissures can be encountered, regardless of	
	whether they have been produced by cooling, or whether they preexisted and had	
	only been reopened by the cooling.	
35	1) Fissures giving water at a sufficiently low flow rate for the contribution of	35
	frigories from the cavity or from the frozen rocky zone to be sufficient to freeze the	
	water and to self-plug the fissure. Such a fissure is acceptable.	
	2) Fissure giving water at a flow rate such that self-plugging does not occur.	
40	Such a fissure must, obviously, be plugged, if this has not been previously done,	40
40	by conventional means such as the injection of cement, before the application of cooling. Preferably, it is sealed by self-plugging with ice. For this, the flow rate is	40
	slowed down to a value compatible with the contribution of frigories, either by	
	injecting beyond the frozen zone a suitable sealing product for use under these	
	conditions, for example polyurethanes, silica gels, SiF ₄ etc, or, preferably and more	
45	simply, by temporarily increasing the pressure in the cavity to counterbalance in	45
	part the hydrostatic pressure.	
	3) Fissure not giving water but reaching the aerated zone of the earth situated	
	above the hydrostatic level.	
50	Such fissures, creating gas leakages towards the atmosphere, are to be	50
50	avoided at any price, for reasons of safety at the surface. For this purpose, the appropriate depth for the reservoir must be defined so that the "ice front" is below	50
	the phreatic level during the whole life span of the reservoir. It is known that,	
	during the whole time that the reservoir is in service, as a result of the continual	
	application of cold, the ice front, which is comprised between isotherms at about 0	
55	and -20°C, recedes constantly from the reservoir, at a speed which depends on the	55
	thermal properties of the terrain. The hydrostatic level, on the other hand, is	
	subject to seasonal variations and to development in time. The termination of the	
	appropriate depth is hence possible as a function, notably, of the complete	
60	exploitation of the program. It is however preferable to provide temperature and	60
60	hydrostatic level checking probes. In the case where the ice front and the	60
	hydrostatic level approach each other more quickly than planned, it would be appropriate to react, for example by modifying the conditions of exploitation and	
	by raising the water level by limiting pumping or by resupplying the water level.	
	4) Fissures not giving water and not passing through the ice front.	
65	These fissures do not offer any drawback in the course of the application of	65

a.	5	cooling, that is to say as long as the cavity is filled with gas. This is not the same when the latter is filled with liquid, since this, penetrating into these fissures, suddenly disturbs the system of isotherms and creates considerable local thermal gradients of the nature to open these fissures and to extend them beyond the ice front, through the compression zone, which would be disturbed. It is hence imperative to close these fissures before the filling of the reservoir by liquid.	5
, n	10	According to an important feature of the method, these fissures are plugged at the moment when they are in the neighborhood of their maximum opening. According to an advantageous feature, the plugging is carried out simply by spraying water on the walls, so as obtain a homogeneous coating of ice. It is also possible to provide a coating of ice charged with particles such as glass fiber. In this way advantage is taken of the helpful mechanical properties of this material at the	10
· .	15	temperature concerned. If the temperature is not too low, for example -80°C, the ice coating is formed by suitably equipped human operators. If not, it is possible to raise the temperature temporarily to a level enabling human intervention. By way of example, there is given below the program of cooling a reservoir, excavated in a terrain of which the properties had previously been determined. The results of the preliminary examination is as follows:	15
	20	 a) petrophysical properties of the matrix. Composition: pseudo-oolitic calcereous, with about 100% of CaCO₃ Apparent density dry: γd=2.58 t/m³ Apparent density saturated: =2.62 t/m³ Particle density: γs=2.69 t/m³ 	20
	25	Average porosity: η=5% (from 2% to 11%) Existence of 2 facies: one with fine particles the other coarser, very intermeshed Water permeability: K≈50. 10 ⁻⁹ cm/s for coarse particles	25
	30	K≥10. 10 ⁻⁹ cm/s for fine particles b) mechanical properties of the matrix (tests carried out at ambient temperature on saturated material, cores sampled at the storage level):	30
	35	strengths $ \begin{cases} \text{CS from 950 to 1500 bars (average 1150 bars)} \\ \text{TS about 85 bars} \\ \text{TS (Brasilian) about 110 bars} \\ \text{deformability} \end{cases} $ $ \begin{cases} \text{E between 400,00 and 600,000 bars} \\ \text{ν from 0.25 to 0.30} \end{cases} $	35
		intrinsic rupture curve $\begin{cases} \text{linear for } \tau_{\rho} \leq 100 \text{ bars (C=about 150 bars, } \varphi=60^{\circ}) \\ \text{parabolic beyond} \end{cases}$	
	40	Anisotropy weak c) behavior in cooling: study of the speed of sound and of the coefficient of expansion enables it to be estimated than water freezes at about -10°C in the material. the mechanical characteristics improve regularly with lowering of the	40
	45	temperature. The initial cooling program adopted is as follows: Passage from +15°C to θ 1, with -10°C \leq θ 1 \leq -5°C, in 1 day maximum. It is possible to adopt, for example, as in the calculations, θ 1=-6°C.	45
	50	Ist Level at θ 1. Passage to θ 2 in a maximum of 1 day. θ 2 is approximately the temperature at which the material recommences to contract under the effect of cold; in the calculations it has been taken that $\theta 2 \simeq -20^{\circ}$ C. 2nd Level at $\theta 2 \simeq -20^{\circ}$ C Drop to -40° C	50
	55	3rd level at -40°C. Drop to -70°C 4th Level at -70°C Drop to -100°C 5th Level at -100°C Final gradual drop to -160°C	. 55
	60	The total program lasts about 7 months and can include at any moment fairly brief rises in temperature, for example for repairs by personnel. It should be	60

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	understood that the temperatures mentioned are those of the wall of the excavation; those of the inner gaseous temperature can be deduced therefrom by	
5	thermal calculation. In the 1st part of the cooling, the cold generating fluid is dehumidified air. The equipment of the cavity enables one to know at any moment, during the	5
-	application of cooling: the temperature distribution in the earth over a thickness of the order of 10 meters around the cavity,	
10	the stress condition in the surface zone of the wall; the deformations of the cavity; and	10
10	the inflows of water and appearance of fissures. At the end of the -40°C stage an accurate oscultation in the cavity takes place with personnel and the camera to determine if possible the fissures due to exceeding the tractile strength of the earth.	
15	An identical oscultation takes place before -100°C in order to judge the opportune moment to spray water on the walls. Lin to -100°C the cooling is done by circulation of dehumidified cold air.	15
20	Beyond -100°C, once the cavity has been osculted and after the spraying of water for plugging the fissures, any human intervention is excluded except in the case of absolute necessity. The cooling is continued by the spraying of liquid nitrogen, so as to purge the oxygen of the air progressively, until its content in the atmosphere of the cavity is less than about 5%. It is then possible to introduce liquefied natural gas to continue the cooling between about -130°C and -160°C, and then to fill the cavity.	20
25	WHAT WE CLAIM IS: 1. A method of preparing a subterranean cavity for the storage of liquefied gas wherein the fluid tightness of the cavity is substantially obtained by freezing of the earth, comprising the steps of:	25
30	providing a suitable cavity and determining, prior to cooling, the mechanical and thermal characteristics of the rock in which the cavity is formed; gradually cooling the cavity under conditions selected dependent on the said mechanical and thermal characteristics to a desired final temperature below the temperature of freezing of the earth suitable for the storage of liquefied gas,	30
35	whereby the formation of unwanted fissures during cooling is reduced; monitoring the physical condition of the walls of the cavity and the surrounding rock during the cooling so as to detect formation of fissures which will intefere with fluid tightness of the cavity; and modifying the cooling of the cavity so as to cause the fissures to become	35
40	plugged and/or plugging the fissures by external means at temperatures sufficiently low that subsequent cooling will not destroy the fluid tightness of the plugs but above the desired final temperature. 2. A method according to Claim 1 wherein the cavity is excavated to a depth calculated so that up to the end of the planned utilization of the cavity, the frozen zone is below the hydrostatic level.	40
45	3. A method according to Claim 1 or 2, wherein during cooling, a temperature variation relationship is followed obeying the two criteria of maintaining in the compression zone existing around the cavity a width capable of arresting the propagation of the majority of those fissures capable of causing entry of water into the cavity, and of obtaining in the earth only stress gradients that do not cause the	45
50	appearance of such fissures. 4. A method according to any one of the preceding claims wherein at least some of the preparing steps in the course of the cooling are affected by a human operator.	50
55	5. A method according to any one of the preceding claims wherein during the cooling, the fissures opening into the wall of the cavity are plugged, this operation being carried out on, or in the vicinity of this wall at a temperature where the fissures have a size such that their subsequent movements cannot break the fluid tightness of the plug.	55
60	6. A method according to Claim 5, wherein the fissures opening into the wall of the cavity are plugged by the spraying of water which freezes on said walls. 7. A method according to any one of the preceding claims wherein in the course of cooling, exceptional fissures resulting in the entry of water into the cavity are plugged by reducing the flow rate of water from these fissures until self-plugging by the formation of ice is obtained.	60

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8. A method according to Claim 7 wherein to reduce the flow rate in said exceptional fissures, the pressure inside the cavity is raised.

9. A method according to any one of the preceding claims wherein the cooling of the cavity is effected at least until the fissures opening into the cavity are plugged, by sending cold gas into the latter, said cold gas being a breathable gas.

10. A method according to Claim 9 wherein the breathable gas is dehumidified

air.

11. A method of preparing a subterranean cavity for the storage of liquefied gas substantially as hereinbefore described.

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COMPLETE SPECIFICATION

1 SHEET

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