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(54) **Process for generating a gas for providing energy**

(57) The present invention is directed to a process
for generating a gas for providing energy to a system,

comprising providing a gas having a temperature of at
most 100°C, by using the endothermal decomposition
of a product made of gas penetrable solid material.

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Description

[0001] The invention relates to applied chemistry, more specifically to the generation of gases of low temperature for providing energy to a system.

[0002] Transfer of energy to all kinds of systems using the kinetic energy of (compressed or high pressure) gas is a well-known method. Usually these systems are either based on compressed gases stored in cylinders, or on compressors driven by external power, such as gasoline or electricity. The latter approach is not useful in case the power/energy has to be provided on locations where such facilities are not available. Examples thereof can be found in all kinds of emergency systems, rescue and salvage systems and the like. Also the use of compressed gas has disadvantages, as these systems require maintenance and cannot be relied on in situations where only occasionally need exists for its use. Further, the use of compressed gases may have the disadvantage of temperature decrease due to adiabatic expansion. Especially when relatively large amounts of gas are expanded to low pressure, temperatures may drop to -50°C , with the result of icing-up, or even blocking the opening by freezing.

[0003] The weight and size of the system for providing the gas for power generation is also an important consideration.

[0004] Gas generating processes based on the decomposition or burning of chemical propellants and other compositions are frequently being used for a number of purposes. It is known that gas for inflation can be generated by decomposition or burning of solid materials, such as azides. However, these materials have the disadvantage that they generate a very hot gas, which is often unwanted, because of the hazards thereof to the environment or the object to be inflated.

[0005] Accordingly there is a need for a system for generating a gas for energy transfer, which system is reliable, does not require maintenance, and that can be used in isolated situations, without the need for external supervision. Further, such a system should be generating gas of a relatively low temperature, which is preferably not harmful to the environment.

[0006] The present invention is based on the use of a generator of cold gas by using the endothermal decomposition of a product made of gas penetrable solid material.

[0007] The invention accordingly provides for a process for generating a gas for providing energy to a system, comprising providing a gas having a temperature of at most 100°C , by using the endothermal decomposition of a product made of gas penetrable solid material.

[0008] The hot gas generated by the burning of a solid material passes through the porous material. The heat of decomposition needed is given off by the hot gas, which cools as a consequence thereof.

[0009] The decomposition can consist of an endothermal reaction, or of a phase transition of the solid porous

material. Examples of phase transition are melting, evaporation and sublimation.

[0010] The present invention can be used especially for all kinds of systems, that are carried out at difficult locations, such as in unpopulated areas, on sea or under the water, for rescue and salvage operations, and the like.

[0011] More in particular it is possible to use the invention for all kinds of applications where now compressed gas, air, nitrogen, oxygen, etc., are being used. In general the applications comprise the activation of valves, and other pneumatic systems.

[0012] Examples thereof are the opening and/or closing of pneumatic valves, especially for emergency situation, in the petrochemical industry, including the oil industry and oils wells. The system of the invention can for example be used for emergency valves that can be activated when an emergency occurs, for example closing a valve in an oil well under sea, which might not be necessary for years. As the present system does not require maintenance, it can be installed in the well, and stay there forever, without supervision. Systems based on compressed gas need regular maintenance, which makes them rather expensive and difficult to use at such locations. Other emergency systems that may benefit from the present invention include emergency brakes for trains or lifts.

[0013] Other uses of the invention include the expulsion and/or dispersion of liquids or solids, such as water or powder for fire extinguishing purposes, materials for generating smoke or clouds (mono- or multispectral, depending on the temperature). This smoke or cloud may be useful in rescue and salvage work, for example in locating lost objects or persons. Also for other situations the generation of smoke may be useful, such as in case of riots or disturbances.

[0014] Also the use of pneumatic tools can be contemplated in the scope of this invention, more in particular those tools that are only used occasionally, for example for rescue work (shears for cutting open wrecks).

[0015] Within the scope of the present invention also the provision of an impulse to an object can be considered. For example braking, accelerating or expelling an object can suitable be accomplished with the present invention. Examples of objects to be expelled are all kinds of projectiles, including smoke canisters, sonar buoys, line throwers, bird scaring, fire works and the like.

[0016] All these applications have in common that they require a relatively cold and harmless gas to be generated at short notice at locations where no external power is available. Important in these applications is also that the equipment is relatively compact and remains reliable even after long periods of storage, without maintenance or testing. Especially the use of compressed gas requires continuous maintenance activities. For example in remote locations this may be difficult to arrange.

[0017] In the present invention a method of generat-

ing cold gases, specifically nitrogen, oxygen, hydrogen, or a gas-mixture, is used, based on the endothermal decomposition of a product made of gas penetrable solid material. The gas penetrable solid material comprises a nitrogen (or other gas) source and a heat absorbing mixture, whereby the gaseous reaction products are cooled by passing the hot gases through the porous body of the product in the moving direction of the reaction front. The hot gases heat the porous body to a temperature necessary to support the endothermic chemical reaction taking place. The heating of the porous body is necessary to enable the main reaction. The decomposition of the cooling agent is also an endothermic chemical reaction.

[0018] The type of gas generating material can be freely selected among the suitable propellant or other gas generating materials. Generally the gas to be generated will be nitrogen, but it is also possible to use oxygen, hydrogen or a suitable mixture of gases.

[0019] The high temperature burning gases are passed through the layer of the cooling agent or the heat exchanger and the temperature of the gases decreases as a result of the endothermal decomposition process of, or heat absorption by the cooling agent.

[0020] The degree of cooling of the generated gas depends on the nature of the cooling agent, the mass of the cooling agent, which can sometimes exceeds the mass of the gas-generating composition. Generally the gas is cooled to a temperature below 100°C, but a value within the range of 25 to 75°C is preferred.

[0021] When sodium compounds are used as the gas source for the low temperature gas production, the decomposition reaction generally results in Na and the gas. The formed gas is blown off and the slag remains. This slag comprises of the remains of cementing agent and cooling agent and metallic sodium. Under these conditions of gas generation the highly chemically reactive sodium is thus generated. This highly reactive material will accumulate in the condensed burning products and thus provides a potential hazard for persons involved. When moisture is present this can result in vigorous and dangerous reactions taking place in combination with the generation of the highly flammable and explosive hydrogen.

[0022] According to a preferred embodiment this problem can easily be overcome by the use of a gas generator comprising a first body, comprising means for the generation of gas, and a second body, comprising means for the generation of a neutralisation agent, wherein means are present for contacting the neutralisation agent with the reaction products formed in the generation of gas in the first body, and wherein means are present for operating the means in the second body at a temporal and/or spatial interval with the means in the first body.

[0023] The principle encompasses two gas generators in one housing. A first gas generator with the primary task of generating gas of low temperature, and a

second gas generator with the primary task of generating neutralising compounds for the slag obtained from the first gas generator.

[0024] The first gas generator contains a composition from which gas of low temperature can be obtained by the decomposition of a gas generating composition in the form of a gas penetrable solid material wherein the generated gaseous products are passed through the porous body in the moving direction of the reaction front.

[0025] The second gas generator (the neutraliser) is another composition, comprising a gas generating composition together with an effective neutraliser compound, for instance sulphur. With the neutraliser composition gas and vaporised sulphur is generated at a time and space interval with the first gas generator. The gas and vaporised sulphur is generated at a rate and a manner that the effective neutralisation of slag is accomplished and the vaporised sulphur is not emitted. The vaporised sulphur reacts with the reaction products from the first gas generator such that the products are effectively neutralised.

Claims

1. Process for generating a gas for providing energy to a system, comprising providing a gas having a temperature of at most 100°C, by using the endothermal decomposition of a product made of gas penetrable solid material.
2. Process according to claim 1, wherein a combustible gas generating material is combusted and the generated hot gas is passed through the gas penetrable solid material.
3. Process according to claim 1 or 2, wherein a gas generator is used, comprising a first body, comprising means for the generation of gas, and a second body, comprising means for the generation of a neutralisation agent, wherein means are present for contacting the neutralisation agent with the reaction products formed in the generation of gas in the first body, and wherein means are present for operating the means in the second body at a temporal and/or spatial interval with the means in the first body.
4. Process according to anyone of the claims 1-3, wherein the gas is selected from the group of nitrogen, oxygen, hydrogen and gas mixtures.
5. Process according to claim 1-4, wherein the gas is used for opening and/or closing of pneumatic valves.
6. Process according to claim 1-4, wherein the gas is used for activating emergency brakes for trains or lifts.

7. Process according to claim 1-4, wherein the gas is used for expulsion and/or dispersion of liquids or solids, such as water or powder for fire extinguishing purposes, as well as materials for generating smoke or clouds. 5
8. Process according to claim 1-4, wherein the gas is used for operating pneumatic tools.
9. Process according to claim 1-4, wherein the gas is used for the provision of an impulse to an object. 10
10. Process according to claim 9, wherein the gas is used for braking, accelerating or expelling an object. 15
11. Process according to claim 10, wherein the gas is used for expelling projectiles, including smoke canisters, sonar buoys, line throwers, bird scaring, fire works and the like. 20

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Application Number
EP 00 20 1611

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	FR 1 099 904 A (ETAT FRANCAIS) 14 September 1955 (1955-09-14) * page 1, left-hand column, line 30 - page 2, left-hand column, line 43 * * page 4, left-hand column, line 37 - page 5, right-hand column, line 3 *	1,2,4-11	C06B23/04 C06B45/00 C06D5/06 C06B23/02
Y	WO 00 06424 A (AUTOLIV ASP, INC.) 10 February 2000 (2000-02-10) * page 13, line 12 - line 27 * * page 18, line 15 - line 35 * * page 20, line 5 - line 20; claims *	1,2,4-11	
Y	US 4 298 412 A (R.A. BIDDLE ET AL.) 3 November 1981 (1981-11-03) * column 1, line 21 - line 44 *	1,2,4-11	
Y	US 2 744 816 A (A. CANTLAY HUTCHISON) 8 May 1956 (1956-05-08) * column 5, line 22 - line 43 *	4-11	
Y	CHEMICAL ABSTRACTS, vol. 132, no. 7, 12 February 2000 (2000-02-12) Columbus, Ohio, US; abstract no. 80495x, V.A. SHANDAKOV ET AL.: "Cold gas generators multiple use in hazardous situations" page 845; XP002140538 * abstract * & NATO Sci. Ser., I 1999, 26(Prevention of Hazardous Fires and Explosions), 341-346 --- -/--	1-11	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C06B C06D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 June 2000	Examiner Schut, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1611

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	DATABASE WPI Section Ch, Week 199847 Derwent Publications Ltd., London, GB; Class E36, AN 1998-554999 XP002140541 & RU 2 108 282 C (ALTAI SCI PRODN ASSOC), 10 April 1998 (1998-04-10) * abstract *	1-11	
A	EP 0 767 155 A (MORTON INTERNATIONAL, INC.) 9 April 1997 (1997-04-09) * page 3, line 14 - line 47 * * page 5, line 9 - line 30; claims *	1-4	
A	WO 96 40541 A (TAKATA MOSES LAKE, INC.) 19 December 1996 (1996-12-19) * page 9, line 4 - line 16; claims *	1-4	
A	DE 43 18 883 A (TRW INC.) 9 December 1993 (1993-12-09) * column 13, line 55 - column 14, line 41 *	1-4	
A	US 4 758 287 A (J.F. PIETZ) 19 July 1988 (1988-07-19) * column 10, line 14 - line 30 * * column 11, line 21 - line 35; claims *	1,2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 June 2000	Examiner Schut, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1611

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	CHEMICAL ABSTRACTS, vol. 132, no. 1, 3 January 2000 (2000-01-03) Columbus, Ohio, US; abstract no. 4539z, A.M. TELEGATOR ET AL.: "Ignition analysis of a porous energetic material: II. Ignition at a closed heated end." page 525; XP002140539 * abstract * & COMBUST. THEORY MODELL. , vol. 3, no. 3, 1999, pages 433-445, ---	1-4	
A	DATABASE COMPENDEX 'Online! ENGINEERING INFORMATION, INC., NEW YORK, NY, US KOMAROV V F ET AL: "Propellants, their properties, and regions of application" Database accession no. EIX99464805134 XP002140540 * abstract * & FIZ GORENIYA VZRYVA;FIZIKA GORENIYA I VZRYVA MAR-APR 1999 MEZHDUNARODNAYA KNIGA, MOSCOW, RUSSIA, vol. 35, no. 2, March 1999 (1999-03), pages 30-34, ---	1-4	
Y	GB 2 184 719 A (YEDA RESEARCH AND DEVELOPMENT COMPANY LIMITED) 1 July 1987 (1987-07-01) * page 1, line 99 - page 2, line 2; claims * ---	4-11	
Y	US 5 511 481 A (W.D. STEPHENS) 30 April 1996 (1996-04-30) * claims * ---	4-11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 June 2000	Examiner Schut, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1611

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 3 066 014 A (W.W. WHITE) 27 November 1962 (1962-11-27) * column 5, line 1 - line 47 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 June 2000	Examiner Schut, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 1611

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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22-06-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 1099904 A	14-09-1955	NONE	
WO 0006424 A	10-02-2000	US 6051158 A	18-04-2000
US 4298412 A	03-11-1981	US 4407119 A	04-10-1983
US 2744816 A	08-05-1956	NONE	
RU 2108282 C		NONE	
EP 767155 A	09-04-1997	US 5670740 A JP 9118582 A	23-09-1997 06-05-1997
WO 9640541 A	19-12-1996	NONE	
DE 4318883 A	09-12-1993	JP 6048880 A US 5507890 A	22-02-1994 16-04-1996
US 4758287 A	19-07-1988	DE 3820443 A FR 2616428 A GB 2205826 A,B IT 1226696 B JP 1052485 A JP 2824769 B	29-12-1988 16-12-1988 21-12-1988 04-02-1991 28-02-1989 18-11-1998
GB 2184719 A	01-07-1987	NONE	
US 5511481 A	30-04-1996	NONE	
US 3066014 A	27-11-1962	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82