

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 February 2003 (06.02.2003)

PCT

(10) International Publication Number
WO 03/009899 A1

- (51) International Patent Classification⁷: **A62B 21/00**
- (21) International Application Number: PCT/NL02/00506
- (22) International Filing Date: 25 July 2002 (25.07.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
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- (81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *with international search report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: COOL OXYGEN CHEMICAL GAS GENERATOR

(57) Abstract: The present invention is directed to a chemical oxygen generator to produce cool oxygen gas comprising: a. a charge housing, b. a solid but porous charge contained in the said housing, the charge being made of a chemical mixture that generates oxygen upon decomposition and that will undergo a self-sustained exothermal decomposition after initiation, the said charge containing at most 3.0 wt.% of binder material, the said porous charge allows the generated oxygen to pass through the charge without damaging the virgin material and without creating volumetric burning, the said charge is mounted in the housing in such a way that the generated oxygen passes through the charge and under the pressure difference flows from the moving decomposition front towards the vent, c. an ignition device mounted at one end of the cartridge in such a way that it is capable to initiate a self-sustained decomposition of the charge at the charge surface adjacent to the initiator, d. one or more vents mounted in such a way that the generated oxygen that has passed through the generating porous charge leave the gas generator through the said vents.



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Cool oxygen chemical gas generator

Field of the invention

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This invention relates to a chemical oxygen gas generator.

Background of the invention

Chemical oxygen (pyrotechnic) gas generators have been
10 developed and used already for long periods. Self-controlled, continuously
ready to operate for many years without any verification tests, easy
activation from low-power electric sources, small size, safe, a rather high
yield of oxygen on a per-unit volume and unit mass and a number of other
advantages make them irreplaceable in case of emergencies and in
15 accidents. They are used and applied, for instance, for the emergency
supply of oxygen to the passengers in aircraft in case of cabin
depressurization, in submarines if the other emergency oxygen supply
systems fail, in space stations in case of emergency if the basic oxygen
supply systems fail, and in many other conceivable emergency cases. A
20 typical example of the use of oxygen generators on-board aircraft is
presented in US patent - 4,840,171.

An operational application is the supply of oxygen for
firefighters. Other cases to provide oxygen to satisfy operational
requirements are e.g. for divers, or for driving rocket engines on-board
25 spacecraft. In all these cases oxygen has to be provided independently of
the ambient or surroundings.

In general, oxygen may be provided from oxygen stored in
bottles or from oxygen generators. The latter in many cases are lighter
and less voluminous for the same amount of oxygen than bottles. Chemical

oxygen generators are the subject of this invention. Chemical oxygen generators are well known to those versed in the art. As a rule, chemical compounds, which release oxygen during thermal decomposition, are used in chemical oxygen generators. The following compounds are commonly used:

- Alkali metal chlorates and alkali metal perchlorates, especially Lithium perchlorate (LiClO_4), Lithium chlorate (LiClO_3), Sodium perchlorate (NaClO_4), Sodium chlorate (NaClO_3), Potassium perchlorate (KClO_4) or Potassium chlorate (KClO_3);

- Peroxides, especially Sodium peroxide (Na_2O_2) and Potassium peroxide (K_2O_2)

- Superoxides, especially Potassium superoxide (KO_2) and Sodium superoxide (NaO_2)

Special additives are used in small amounts to assure self-sustained decomposition (combustion) while releasing oxygen. These additives also control the reaction rate, and form a heat resistant slag with a high-melting point and scavenge harmful gases (i.e. impurities, e.g. chlorine, its compounds and others) that may be released by side reactions.

Typical examples of these additives are:

- Metals: Aluminum, Magnesium, Zinc, Manganese, Molybdenum, Cobalt, Nickel, and in particular Iron;

- Cobalt oxides (Co_2O_3 and Co_3O_4), Chromium oxide (Cr_2O_3), Copper oxide (CuO), Iron oxide (Fe_2O_3), Zinc oxide (ZnO), Manganese oxide (MnO), Manganese dioxide (MnO_2), Magnesium oxide, (MgO), Silicium dioxide (SiO_2)

- Alkali peroxides, specifically Sodium peroxide (Na_2O_2), Potassium peroxide (K_2O_2), Barium peroxide (BaO_2)

- Alkali super-oxides, specifically Sodium superoxide (NaO_2) and Potassium superoxide (KO_2)

US patent 6,126,854 mentions a number of combinations and specifically mentions magnesium oxide to control the decomposition

reaction, suppress chlorine formation, improve the rheology and facilitate the mixing. One reason for improving the rheology and the mixing, is the way in which the oxygen candle according to US patent 6,126,854 has been made. The present invention avoids several of these difficulties. US patent
5 3,868,225 discusses another oxygen generator (or oxygen candle).

Materials, like asbestos, which are presently considered a health hazard, are used in this patent to obtain oxygen of breathing quality. The cool oxygen gas generator which is subject of this invention does not use asbestos.

10 US patent 5,336,470 and 5,322,669 discuss means to control the mass flow rate of the oxygen. This is done by introducing barriers of various shapes. These barriers on one hand create a specific path for the decomposition front, but also specifically serve to absorb heat from the decomposition reaction. This is certainly required if the chemical oxygen
15 generator has to provide oxygen for breathing purposes. For example, the decomposition of sodium chlorate is according to the reaction:



20 To maintain the decomposition reaction, fuel like iron (Fe) is added to the mixture. The decomposition temperature of the mixture is in the order of 1500 K. In a classical chemical oxygen generator heat is absorbed by the additives and the housing, but insulation material is required to prevent the outside of the housing becoming too hot and
25 additional heat sinks to cool the oxygen to acceptable temperatures. US patent 3,868,225 uses glass fiber as insulating material and a double wall through which coolant air may pass. Nevertheless, oxygen temperatures of 370 °C (700 °F) are reported. It is obvious that if the oxygen is to be used directly for breathing, it must be cooled down further, which usually is
30 done by large heat capacity filters. These serve the purpose of filtering the oxygen gas from particulate material and polluting chemicals, if present, but especially to cool the oxygen. Therefore, these filters are much larger

and heavier than would be the case if the only purpose was to filter and cleanse the oxygen. In fact, the filters are counterproductive for mass and volume reduction. The importance of low mass is specifically stressed in US patent 6,007,736.

5 The present invention circumvents the problems of the prior art, by making use of a technology that has been described in the Russian patent 2108282 and the International patent application PCT/NL00/00696, publication Number WO 0123327. Here the hot decomposition gas is passed through the not reacted material, thereby
10 raising the temperature of the virgin material and cooling the produced gas. However, to accomplish this it is necessary to make a porous charge that remains integer during the decomposition when oxygen is released. If that were not the case, particulate material might clog the porous charge and functioning of the gas generator would be impaired. US patent
15 4,981,655 teaches a chemical oxygen generator where also the hot oxygen passes through the virgin material. However, this virgin material consists of loose pellets held together and compressed by a spring load. The pellets themselves are specially manufactured and consist of a cylindrical center body and two hemispherical end caps. The cylindrical part can even be of a
20 different chemical composition than the hemispherical end caps. Although the dimensions of the pellets are not given in US patent 4,981,655, it can be inferred from the drawings that they are of macroscopic dimensions; therefore the specific surface area for contact with the hot oxygen is much smaller than the specific surface of the porous virgin material that is
25 subject of the present invention.

Summary of the invention

 The object of the invention is a chemical gas generator providing oxygen of low temperature, such as below 50°C, preferably below 30°C,
30 preferably also of very high purity.. The main object of the invention is a special oxygen-generating material and the technology of manufacturing

the porous, gas-permeable, mechanically strong charges of this material. When receiving a defined amount of (externally provided) heat, these charges are able to decompose exothermally (burn) while generating oxygen. They are also capable to pass hot oxygen through their own body without destruction or volumetric burning. The charge is placed in the gas generator in such a way that the oxygen generated in the reaction passes through the porous virgin charge in the same direction as the reaction front under a pressure difference. Because of this process, the oxygen is cooled down to the ambient temperature due to heat exchange with the charge. At the same time, the oxygen heats the charge near the reaction front up to the temperature required to sustain this reaction.

The slag formed after the reaction consists of substances with high melting and boiling points and remains within the gas generator.

To achieve an efficient exchange of heat and an unobstructed path for the oxygen, the charge has a porosity (ε_p) ranging from 41% to 61% and a relatively large specific surface $S_{pc}=(13\pm2)\cdot 10^8 \text{ m}^2/\text{kg}$. (The porosity is defined as $\varepsilon_p=1-\rho_{ch}/\rho_c$, where ρ_{ch} is the charge density and ρ_c is a charge composition density).

The charge is composed of fine-granules as an oxygen source; the main ingredients are compounds from the groups:

- chlorates and perchlorates of alkali metals, particularly Lithium perchlorate (LiClO_4), Lithium chlorate (LiClO_3), Sodium perchlorate (NaClO_4), Sodium chlorate (NaClO_3), Potassium perchlorate (KClO_4) or Potassium chlorate (KClO_3);
- peroxides, particularly Sodium peroxide (Na_2O_2) and Potassium peroxide (K_2O_2);
- Superoxides, particularly Potassium superoxide (KO_2) and Sodium superoxide (NaO_2).

Small amounts of special substances are introduced into the charge composition to:

- provide a self-sustaining decomposition (combustion) generating oxygen,

- control the reaction rate,
- form a heat-proof slag with a high-melting and -boiling point, and
- scavenge harmful contaminants (e.g. chlorine and its compounds) which may appear in small amount as a result of side reactions.

5 These substances are selected from the following groups:

- metals: Aluminum (Al), Magnesium (Mg), Zinc (Zn), Manganese (Mn), Molybdenum (Mo), Cobalt (Co), Nickel (Ni), Particularly Iron (Fe);
- Oxides: Cobalt oxides (Co_2O_3 and Co_3O_4), Chrome oxide (Cr_2O_3), Copper oxide (CuO), Iron oxide (Fe_2O_3), Zinc oxide (ZnO), Manganese
10 oxide (MnO), Manganese dioxide (MnO_2), Silicium dioxide (SiO_2), Magnesium oxide (MgO);
- alkali and alkaline-earth metal peroxides: particularly sodium peroxide (Na_2O_2), Potassium peroxide (K_2O_2) and Barium peroxide (BaO_2);
- superoxides: particularly Sodium superoxide (NaO_2) and Potassium
15 superoxide (KO_2).

To achieve the proper burning and cooling characteristics, it is preferred that the porous material has a very high specific surface. It is important that at the substantial porosity and relatively high specific surface of the pores, a rather high charge strength is assured (the
20 minimum compression strength is at least 0,67 MPa and the modulus of elasticity is over 50 MPa). These mechanical characteristics assure when assembling, operating and transporting the gas generator, that the charge does not deform, remains integer and doesn't crack or crumble.

The selection and amount of special binder material and the
25 process of charge manufacturing is an important aspect of this invention. It is an aspect of the invention that the amount of binder material is less than 3.0 wt.% of the charge, thereby assuring a high purity, while at the same time maintaining sufficient porosity. It provides a sufficient level of mechanical properties at a substantial porosity of the charge with a very
30 small amount of binder in the composition. The binder is selected from the following group:

- Inorganic binders: particularly Sodium silicate (Na_2SiO_3) or Potassium silicate (K_2SiO_3) or a mixture thereof.

- Organic binders:, particularly Sodium polyvinyl tetrazole ($\text{C}_3\text{H}_3\text{N}_4\text{Na}$)_m. or, alternatively:

5 - Nitrocellulose, a mixture of pentaphtalic anhydride and pentaerythrite, epoxy resins, or water soluble proteins.

In case organic binders are used, and this is preferred, the amount thereof is preferably less than 1.5 wt.%.

According to the method to generate cool gases (Russian Patent
10 No2108282) the charge design and its arrangement in the generator must create a decomposition front and ensure that the generated oxygen flows through the charge in the direction: from the igniter to the vent. In relation to this, the design and shape of the charge are limited only by the fact they must provide a suitable propagation of decomposition front and
15 oxygen flow through the charge.

Vibration-tamping the granular mass into a processing die is used to manufacture the porous charges. This technology involves the following main stages:

- preparation of ingredients,
- 20 • mixing of dry powdered ingredients,
- mixing of the mass,
- granulation of the mass,
- molding of the granular mass and solidification of a charge.

25 Preparation of the solid ingredients involves:

- drying,
- grinding, and
- sieving or screening, to separate particle fractions of defined sizes.

30 Preparation of the binder involves:

- mixing of a solution of the binder in a defined concentration in an intermediate processing solvent,
- mixing of the powdered ingredients in the required ratio until a homogeneous mass is obtained.

5 Mixing of the mass involves the following: thorough agitation of the binder solution (or parts of it) and mixing of the dry powdered ingredients in the required ratios.

Granulation comprises manufacturing of solid granules of defined sizes from the obtained mass such that it guarantees the required porosity and specific surface area of the charge pores. The granules are moistened with the binder solution in the intermediate processing solvent or directly with the intermediate processing solvent and are molded by vibration tamping into a processing die of the required dimensions and shape. Vibration tamping is carried out to provide homogenous density, porosity and strength of the complete charge. The charge, cast into a processing die, is subjected to solidification.

One part of the invention is that the housing of the gas generator has one or more filters. These filters are installed between the charge and the vent of the gas generator. The filters have the following objectives:

- they catch slag particles, which may be carried with the oxygen flow;
- they scavenge other gas impurities that contaminate the oxygen, and that were not scavenged by the special additives in the charge;
- they catalytically convert contaminating compounds in less harmful compounds, e.g conversion of CO in CO₂
- they cool the oxygen flow towards the end of reaction, when the last small part of the charge is heated and may have insufficient heat capacity to cool this final flow of oxygen down to the required temperature.

Another part of this invention is a thermal protection on the oxygen generator housing to prevent heating of its outer surface during the burning of a charge.

5 This thermal protection may be applied on the inner side or the outer side of the housing or on both sides.

The inner thermal protection may be made of glass or silicon fibers impregnated with the same binder as used in charge.

10 Alternatively, the housing itself, if that is made of composite and low heat-conducting material, may serve as a thermal protection material.

If there is no thermal protection on the housing, the outer side of the charge may be provided with a thermal protection, or the outside surface of the charge itself may serve as thermal insulation. The outside of charge with a thickness $\sim 1,5$ mm adjacent to the wall of the housing will not burn due to cooling by the wall and then serves as a thermal insulator.

All these approaches may also be used in combination.

Brief description of the Figures

20 Figure 1 is the schematic of the cold oxygen generator, consisting of an igniter (1), a porous oxygen generating charge (2), one or more filters (3); these filters (3) are optional; the housing (4), the (optional) thermal protection (5); this thermal protection may also be formed by the charge itself; and the vent or exit (6).

25 Figure 2 is a schematic of the burning porous charge: a decomposed part of the charge (7) is at the left-hand-side; the decomposition front (8) separates the decomposed part of the charge and the virgin charge material (9). The temperature profile (10) in the charge has been schematically indicated and the temperature rapidly drops from the decomposition temperature of 1500 K to ambient temperature. Oxygen

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(11) flows from the decomposition front (8) to the right through the porous charge and leaves the porous charge at the right hand side.

Detailed description of the preferred embodiments of the invention

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The chemical cool oxygen generator (Figure 1) includes a housing, 4, wherein a porous charge, 2, made of the oxygen generating material is mounted. The self-sustaining decomposition (combustion) of the charge, 2, is initiated by means of the igniter, 1. The reaction starts on the charge surface adjacent to the igniter and the reaction front runs through the charge body to the opposite end in direction to the vent, 6. Under the pressure difference the oxygen generated as a result of the reaction passes through the body of the virgin porous charge, is cooled there and passes through vent, 6, to the user, or to a storage bottle.

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In one of the preferred embodiments, the housing is protected from the heat of the decomposing charge by a thermal protection 5, preferably made from silica or glass fiber impregnated with the same binder as used for the charge 2. In another preferred embodiment, the charge 2 itself provides the thermal protection of the housing. In this case a layer of ~1,5 mm thickness adjacent to the wall of the housing does not burn due to cooling of the outside of the charge by the wall of the housing, 4.

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In the preferred embodiment, the housing, 4, is made of metal such as steel, aluminum or titanium. In another preferred embodiment, the housing, 4, is made of a composite material (plastic composite).

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Between the charge, 2, and the vent, 6, a filter, 3, is installed. The given filter serves:

- to prevent any particles to be carried away with oxygen, 11;
- to scavenge any chemical impurity that has not been removed during the reaction by the charge composition;

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- to convert any CO present in the gases into CO₂ by a catalytic action
- to cool the last portion of the oxygen, 11, that may be of a slightly higher temperature than the oxygen during the major period of the burning.

Filter, 3, can consist of four separate filters: the first is for preventing carrying particles away with the oxygen, 11, the second is for removing harmful gaseous impurities, the third is for converting any CO into CO₂, the fourth filter is for additional oxygen cooling.

Sand can be a material of the filter to cool the very last portion of the oxygen, 11. In a second preferred embodiment, all the filter functions are combined in two or three separate filters, 3. In another preferred embodiment, the various filter functions are combined in one filter, 3.

In other preferred embodiment the number of filters is reduced, as in many cases no filters or only specific filters are required. If no additional cooling is required, the sand filter is omitted.

In another preferred embodiments, the sand filter combines the functions of cooling and preventing any particle matter to be expelled with the oxygen.

The housing, 4, in a preferred embodiment has handles or grips for easy transportation. In another preferred embodiment, the housing, 4, has attachment fixtures, that provide easy mounting of the oxygen generator in different devices. Such fixtures encompass threaded ends, flanges, screw connections or other standard connections that are known in the field.

Figure 2 is a schematic of the charge during quasi steady state burning. At the left, there is a decomposed part of the charge, 7, (slag). The decomposition front, 8, moves from left to right. The decomposition temperature does not exceed 1500 K. The released oxygen, 11, passes through the virgin porous charge, 9, under the pressure difference, thereby raising the temperature, 10, of the virgin charge and reducing the

oxygen temperature. At a short distance behind the decomposition front (about 5-10 mm), the temperature drops to a value close to the initial charge temperature. The oxygen flow leaves the charge at the right-hand-side. The temperature profile, 10, as a function of distance of the charge length is shown schematically.

In the preferred embodiment, the oxygen releasing composition involves chemicals selected from the following list as oxygen sources:

- Lithium perchlorate (LiClO_4),
- Lithium chlorate (LiClO_3),
- 10 - Sodium perchlorate (NaClO_4),
- Sodium chlorate (NaClO_3),
- Potassium perchlorate (KClO_4),
- Potassium chlorate (KClO_3),
- Sodium peroxide (Na_2O_2),
- 15 - Potassium peroxide (K_2O_2),
- Sodium superoxide (NaO_2),
- Potassium superoxide (KO_2).

The chemicals from the following list are added in small proportion (up to 5%) to the composition to maintain the self-sustaining decomposition of the oxygen releasing material, to control the reaction rate, to form a slag with a high melting point, and to remove impurities (i.e.harmful gases) that can be formed as a result of side reactions:

- metals:
- Aluminium (Al), Magnesium (Mg), Zinc (Zn), Manganese (Mn),
- 25 Molybdenum (Mo), Cobalt (Co), Nickel (Ni), and especially Iron (Fe)
-
- Compounds (oxides):
- Barium peroxide (BaO_2),
- Cobalt oxides (Co_2O_3 or Co_3O_4),
- 30 - Chromium oxide (Cr_2O_3),
- Copper oxide (CuO),

- Iron oxide (Fe_2O_3),
- Silicium dioxide (SiO_2),
- Zinc oxide (ZnO),
- Manganese oxide (MnO),
- 5 - Manganese dioxide (MnO_2),
- Sodium peroxide (Na_2O_2),
- Potassium peroxide (K_2O_2),
- Sodium superoxide (NaO_2),
- Potassium superoxide (KO_2).

10 The binder for the oxygen generating composition is selected from the following group of materials:

- Inorganic adhesives, especially, Sodium silicate (Na_2SiO_3), or Potassium silicate (K_2SiO_3) or a mixture thereof.
- organic adhesives or lacquers, especially the Sodium salt polyvinyl
- 15 tetrazole ($\text{C}_3\text{H}_3\text{N}_4\text{Na}$)_m
- Nitrocellulose, a mixture of pentaphtalic anhydride and pentaerythrite, epoxy resins, or water soluble proteins.

20 In the preferred embodiment, the porous charge of oxygen generating composition has a specific surface area of $11 \cdot 10^8$ - $15 \cdot 10^8$ m^2/kg , a porosity within the range from 41% to 61%, a compression strength over 0,67 MPa, a modulus of elasticity more than 50 MPa and a density between 1020 to 1150 kg/m^3 .

 In the first preferred embodiment, the charge has the following composition:

- | | | | |
|----|---|--|----------------|
| 25 | - | NaClO_3 | 87.5% (weight) |
| | - | BaO_2 | 3.5%(weight) |
| | - | Fe | 4.0%(weight) |
| | - | MnO_2 | 3.5%(weight) |
| | - | ($\text{C}_3\text{H}_3\text{N}_4\text{Na}$) _m | 1.5%(weight) |

30

The measured characteristics of the decomposition products
(without a filter) are:

Composition of the gas:

- O₂ 95.4 % (volume)
- 5 - CO₂ 0.92 % (volume)
- N₂ 2.10% (volume)
- H₂O 1.58% (volume)

The gas temperature (at the exit of the gas generator) is 293 °C
(566 K).

10 In the second preferred embodiment, the charge has the
following composition:

- NaClO₃ 87.5% (weight)
- BaO₂ 3.5(weight)
- Fe 4%(weight)
- 15 - Co₃O₄ 3.5%(weight)
- (C₃H₃N₄Na)_m 1.5%(weight)

The measured characteristics of the decomposition products
(without a filter)are:

- Composition of the gas:

- 20 - O₂ 95.35 % (volume)
- CO₂ 0.93 % (volume)
- N₂ 2.12% (volume)
- H₂O 1.60% (volume)

25 The gas temperature (at the exit of the gas generator) is 293 °C
(566 K).

The technology of vibration-tamping the granular mass of the
oxygen generating composition in a processing die is used to manufacture
porous charges. The technology involves the following main stages:
preparation of ingredients, mixing of the mass, granulation of the mass,
30 molding the granular mass and solidification of the charge.

The preparation of solid ingredients involves drying, grinding
and separation to separate out fractions with particles of specific sizes.

Subsequently, the powdered ingredients are agitated in the required ratio until a homogeneous mixture is obtained.

The mixing of the mass is obtained by agitation of the binder (or a part of it) with the dry powdered ingredients and an intermediate solvent in the required ratio.

Granulation involves the manufacturing of solid grains from the obtained mixture with well-defined sizes, that guarantees the required porosity and specific surface area of the pores in the charge. The grains are moistened with a mixture consisting of a part of the binder and the intermediate processing solvent, or they are only moistened with processing solvent. They are molded by vibration-tamping into a processing die of the required dimensions and shape of the charge. Vibration-tamping is carried out to provide a homogenous density, porosity, and strength through the complete body of the charge. After this, the charge in the processing die is left to harden at the appropriate solidification temperatures.

After solidification the charge is removed from the processing die and placed in the housing of a chemical gas generator. In some cases, the processing die itself can be a part of the generator housing and after the solidification, the charge can be connected with the other generator elements.

In accordance with the method to generate cool gases by decomposition in porous charges, according to the Russian Patent No2108282, the design of a charge and its installation in the gas generator provides a proper propagation of the decomposition front and oxygen flow through the porous-charge body.

It is understood that the foregoing description is that of the preferred embodiments of the invention and that various changes and

modifications may be made thereto without departing from the spirit and scope of the invention as defined in the appended claims.

Claims

1. A chemical oxygen generator to produce cool oxygen gas comprising:
 - 5 a. a charge housing,
 - b. a solid but porous charge contained in the said housing, the charge being made of a chemical mixture that generates oxygen upon decomposition and that will undergo a self-sustained exothermal decomposition after initiation, the said charge containing at most 3.0 wt.%
10 of binder material,
the said porous charge allows the generated oxygen to pass through the charge without damaging the virgin material and without creating volumetric burning,
the said charge is mounted in the housing in such a way that the
15 generated oxygen passes through the charge and under the pressure difference flows from the moving decomposition front towards the vent,
 - c. an ignition device mounted at one end of the cartridge in such a way that it is capable to initiate a self-sustained decomposition of the charge at the charge surface adjacent to the initiator,
 - 20 d. one or more vents mounted in such a way that the generated oxygen that has passed through the generating porous charge leaves the gas generator through the said vents.
2. A chemical oxygen generator according to claim 1 with
 - a. an inert porous mass (filter) to cool the oxygen towards the end of
25 burning,
 - b. a filter to prevent particulate matter to be expelled from the said cartridge,
 - c. a filter containing a catalyst that converts any CO present in the decomposition gases into CO₂,
 - 30 d. a filter to prevent polluting chemicals to be expelled from the said cartridge.

3. A chemical oxygen generator according to claims 1 or 2 where two or more of the filters mentioned under 2a, 2b, 2c and 2d are combined.

4. A chemical oxygen generator according to any of the claims 1, 2 and 3 where the temperature of the vented oxygen gas is less than 50 °C, but preferably less than 30 °C.

5. A chemical oxygen generator according to any of the claims 1-4, where the said charge is made from granular material bonded together by a bonding agent and having a porosity between 41% and 61%.

6. A chemical oxygen generator according to claim 1-5, wherein the binder is an organic binder and present in an amount of 1.5 wt.% or less.

7. A chemical oxygen generator according to claim 1-6, containing a charge with a compression strength larger than 0,67 MPa and a Modulus of Elasticity under compression larger than 50 MPa.

8. A chemical oxygen generator according to claim 1-7, where the oxygen generating chemical is from the group of alkali chlorates of perchlorates, more specifically Lithium perchlorate (LiClO_4), Lithium chlorate (LiClO_3), Sodium perchlorate (NaClO_4), Sodium chlorate (NaClO_3), Potassium perchlorate (KClO_4) or Potassium chlorate (KClO_3) and preferably Sodium chlorate (NaClO_3), or from the group of alkali peroxides and superoxides, specifically sodium peroxide (Na_2O_2), potassium peroxide (K_2O_2), specifically sodium superoxide (NaO_2), potassium superoxide (KO_2), additives selected from the group Aluminium (Al), Magnesium (Mg), Zinc (Zn), Molybdenum (Mo), Manganese (Mn), Cobalt (Co), Nickel (Ni), Iron (Fe), Barium peroxide (BaO_2), Cobalt oxides (Co_2O_3 and Co_3O_4), Chromium oxide (Cr_2O_3), Copper oxide (CuO), Iron oxide (Fe_2O_3), Silicium dioxide (SiO_2), Zinc oxide (ZnO), Manganese Oxide (MnO) and Manganese Dioxide (MnO_2), or from the group of alkali peroxides, specifically sodium peroxide (Na_2O_2), potassium peroxide (K_2O_2), and alkali superoxides specifically sodium superoxide (NaO_2), potassium superoxide (KO_2) and as binder material from agents from the group of inorganic adhesives, specifically: Na_2SiO_3 , K_2SiO_3 , or mixtures thereof, from the group of organic lacquers and adhesives, preferably

Sodium Polyvinyl Tetrazole ($C_3H_3N_4Na$)_m, and furthermore Sodium Carboxyl Cellulose, Polyvinylacetate, Nitrocellulose, a mixture of pentaphtalic anhydride and pentaerythrite, epoxy resin, and water soluble proteins.

- 5 9. A chemical oxygen generator according to claim 1-8 that is made with the vibration-tamping technology to load a granular mass into a processing die involving the following main stages:
- preparation of solid ingredients: comprising drying, grinding and separation into the required fractions; preparation of binder solutions of
 - 10 the required concentrations with an intermediate processing solvent;
 - mixing of the dry powdered ingredients in the required ratio until a homogeneous mixture is obtained;
 - mixing the mixture of dry powdered ingredients with the binder (or a part of it) and the intermediate processing solvent in the required ratio;
 - 15 - manufacturing grains of defined sizes with the mixture of the binder and powdered ingredients;
 - molding grains moistened with a mixture comprising a part of binder and processing solvent in the required ratio by vibration-tamping into a processing die;
 - 20 - solidification of the molded charge.

10. A chemical oxygen generator according to claims 1 to 9 where the tooling to cast the charge in is part of the housing of the gas generator.

11. A chemical oxygen generator according to claim 1-10, where the composition is Sodium chlorate > 80%, Barium peroxide > 2%, Iron powder

25 > 3%, Cobalt oxide (Co_3O_4) < 5%, Manganese dioxide < 5% and Sodium Polyvinyl Tetrazole < 3%.

12. chemical oxygen generator according to claim 1-11, where the binder is Sodium Polyvinyl Tetrazole and amount of Sodium Polyvinyl Tetrazole $\leq 1,5\%$.

30 13. A chemical oxygen generator according to claim 1-12, where the velocity of the decomposition reaction is determined by the composition of the charge and in particular by the amount and kind of additives.

14. A chemical oxygen generator according to claim 1-13, where the particle size of the granular ingredients has been selected such that a porosity between 41% and 61% is obtained.

15. A chemical oxygen generator according to claim 1-14 where the particle size of the granular ingredients has been selected such that the charge density is between 1000 kg/m³ and 1150 kg/m³.

16. A chemical oxygen generator according to claim 1-15 where the composition of the charge and the granular properties of the ingredients is such that the velocity of the decomposition front lies between 0.2 and 0.3 mm/s.

17. A chemical oxygen generator according to claim 1-16 where the filter to cool the oxygen gas towards the end of burning consists of sand.

18. A chemical oxygen generator according to claim 1-17, where the housing has been made from metal.

19. A housing for a chemical oxygen generator according to claim 18, where the metal is aluminium, titanium or steel.

20. A chemical oxygen generator according to claim 1-17, where the housing has been made from plastic composite material.

21. A housing according to the claim 17-20, where the said housing has fixtures allowing the housing to be mounted in devices or to attach the housing to equipment or walls.

22. A housing according to the claim 17-21 where the said housing has fixtures allowing the housing to be carried and transported.

23. A chemical oxygen generator according to claim 1-17, where the housing, via the vent or exit is connected to a buffer or storage vessel.

24. A chemical oxygen generator according to claim 1-17 or 23, where the outer layer of the charge acts as a thermal insulator.

25. A chemical oxygen generator according to claim 1-17, 23 or 24, where thermal protection material has been placed between the charge and the wall of the housing.

26. A chemical oxygen generator according to claim 25 where the thermal protection material consists of glass fiber impregnated with the same binder as used in the charge.

27. A chemical oxygen generator according to claim 25 where the
5 thermal protection material consists of silica fiber impregnated with the same binder as used in the charge.

Figures

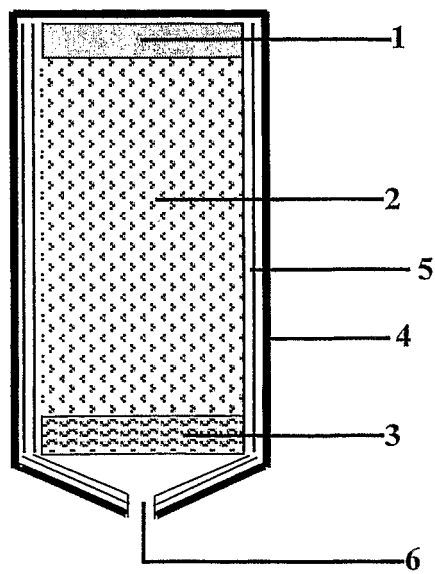


Figure 1

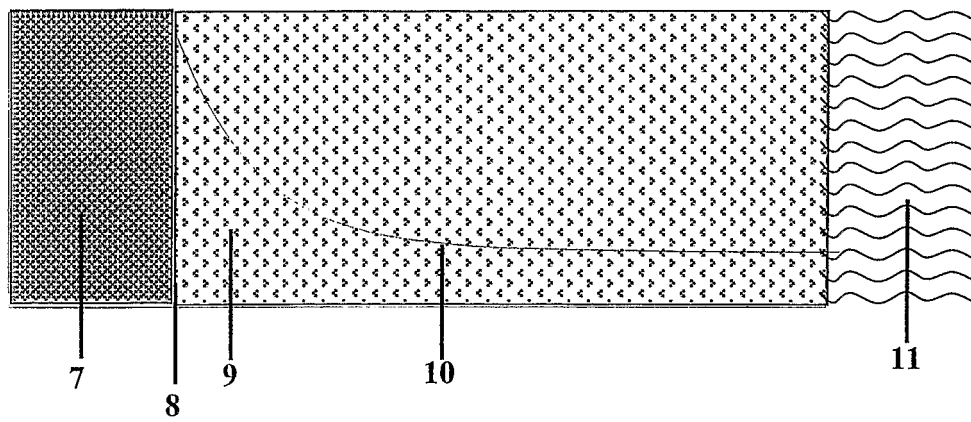


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 02/00506

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A62B21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A62B C06D A62C C01B C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 558 756 A (BOVARD ROBERT M ET AL) 3 July 1951 (1951-07-03) the whole document ----	1-27
A	SHANDAKOV V A ET AL: "Cold gas generators multiple use in hazardous situations" CHEMICAL ABSTRACTS + INDEXES, AMERICAN CHEMICAL SOCIETY. COLUMBUS, US, vol. 132, no. 7, 14 February 2000 (2000-02-14), page 845 XP002140538 ISSN: 0009-2258 abstract ----	1
A	US 3 736 104 A (CHURCHILL J P ET AL) 29 May 1973 (1973-05-29) column 4, line 16-46; figure 3 ----- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

17 September 2002

Date of mailing of the international search report

26/09/2002

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 02/00506

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 797 854 A (MARS J ET AL) 19 March 1974 (1974-03-19) column 5, line 10-22; figure 2 ----	
A	FR 1 099 904 A (MAURICE PIERRE; TAVERNIER PAUL; LE DIRECTEUR DU SERVICE DES PO) 14 September 1955 (1955-09-14) right-hand column, line 4-11 ----	
A	US 5 298 187 A (ZHANG YUNCHANG ET AL) 29 March 1994 (1994-03-29) -----	

INTERNATIONAL SEARCH REPORT

Inter al Application No

PCT/NL 02/00506

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2558756	A	03-07-1951	NONE	
US 3736104	A	29-05-1973	NONE	
US 3797854	A	19-03-1974	CA 975400 A1	30-09-1975
			DE 2229038 A1	21-12-1972
			FR 2141916 A1	26-01-1973
			GB 1392075 A	23-04-1975
			IT 958355 B	20-10-1973
			JP 55020891 B	05-06-1980
FR 1099904	A	14-09-1955	NONE	
US 5298187	A	29-03-1994	AU 3775493 A	05-10-1993
			DE 69310505 D1	12-06-1997
			DE 69310505 T2	18-12-1997
			EP 0630351 A1	28-12-1994
			HK 1006703 A1	12-03-1999
			WO 9317961 A1	16-09-1993