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HABITABLE COMBUSTION-SUPPRESSANT ATMOSPHERE COMPRISING AIR, A PERFLUOROALKANE AND OPTIONALLY MAKE-UP OXYGEN

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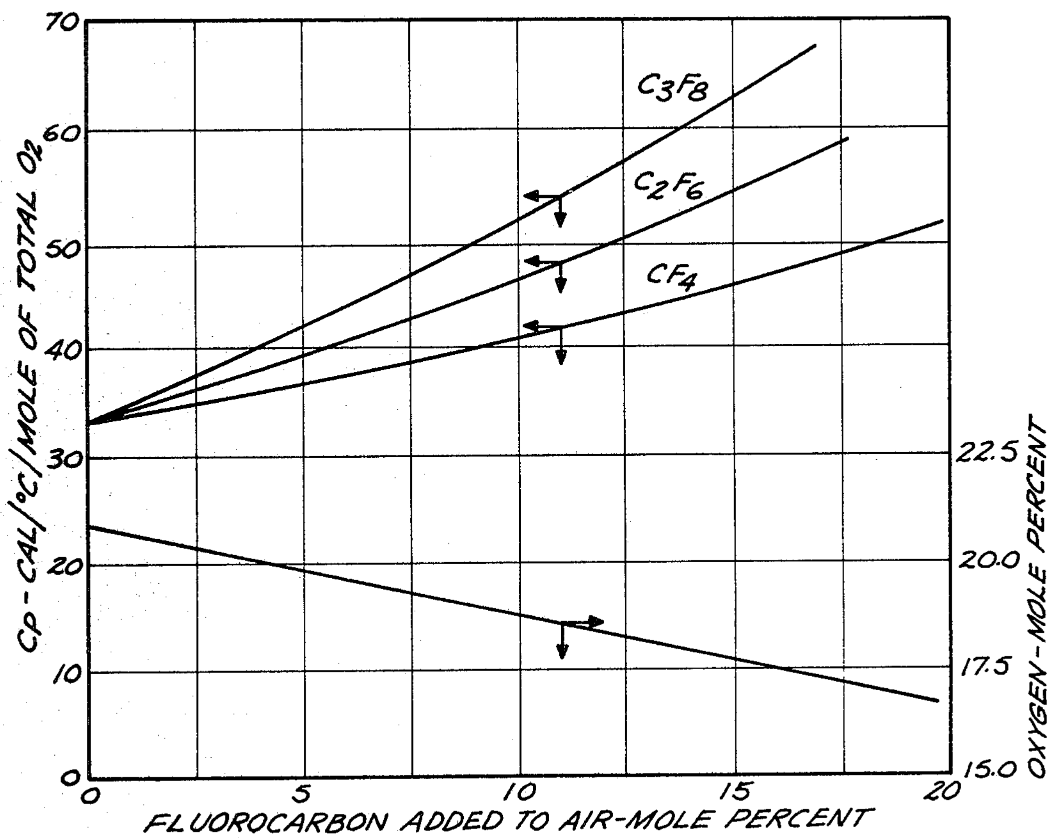

INVENTOR

CLAYTON M. HUGGETT

BY Martha L. Ross

AGENT

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HABITABLE COMBUSTION-SUPPRESSANT ATMOSPHERE COMPRISING AIR, A PERFLUOROALKANE AND OPTIONALLY MAKE-UP OXYGEN

Clayton M. Huggett, Burke, Va., assignor to The Susquehanna Corporation, Fairfax County, Va.

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ABSTRACT OF THE DISCLOSURE

Habitable atmospheres which do not sustain combustion and which are capable of sustaining mammalian life, consisting essentially of air, a perfluoroalkane gas, which is carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6), octafluoropropane (C_3F_8), or mixtures thereof, and make-up oxygen, as required, to provide, together with the oxygen present in the air, sufficient total oxygen to sustain mammalian life.

A method for preventing and controlling fire in enclosed air-containing, mammalian-habitable compartments comprising introducing CF_4, C_2F_6, C_3F_8, or mixtures thereof, and additional make-up oxygen as required.

BACKGROUND OF THE INVENTION

Fluoroalkanes of the type containing one or more Cl and/or Br substituents have been used very effectively as fire extinguishing agents, namely as agents to put out fires after combustion is actively under way. The chloro- and/or bromo-substituted fluoroalkanes, such as bromochlorodifluoromethane, bromotrifluoromethane and dibromotetrafluoroethane, are generally, in fact, considerably more effective as fire extinguishing agents than the perfluoroalkane gases because, unlike the stable lower-perfluoroalkanes, the former decompose at elevated temperatures and form products, such as chlorine and bromine atoms, which are highly effective in quenching combustion by such mechanisms as interrupting free radical reaction propagation. Care, however, must be exercised in the storage and use of the chloro- and/or bromo-fluoroalkanes, particularly in a confined environment, such as aircraft, because of their undesirable side effects on mammalian life, such as anaesthetic action in relatively small concentrations, and toxicity at higher concentrations. The undesirable side effects and toxicity of the chloro- and/or bromo-fluoroalkanes make them impossible to utilize in a habitable atmosphere.

Although the perfluoroalkanes have fire extinguishing properties, they have generally been discarded as fire extinguishing materials, despite their non-toxicity and freedom from undesirable side effects, because of their substantially lesser effectiveness as compared with the chloro- and/or bromofluoroalkanes.

The perfluoroalkanes, because of their non-toxicity, have found principal use as aerosol-forming vehicles in the food and cosmetic art and as refrigerants. Inhalation tests have been made to determine and demonstrate the non-toxicity of the perfluoroalkanes for such uses. W. S. Clayton et al., Toxicity Studies With Octafluorocyclobutane, Industrial Hygiene Journal, October 1960, pp. 382–8, reports on the non-toxicity of octafluorocyclobutane on mammalian test animals. W. S. Clayton, Fluorocarbon Toxicity: Past, Present, Future, Journal of the Society of Cosmetic Chemists, May 27, 1967, pp. 333–50, reports on the non-toxicity of carbon tetrafluoride, hexafluoroethane and octafluorocyclobutane.

None of the known art has taught or suggested the present discovery that perfluoroalkane gases can be utilized to convert normal air into a still-habitable atmosphere which prevents combustion of normally ignitable materials of the non-self-sustaining type present in the environment, thus substantially eliminating the hazard of fire. A "non-self-sustaining" material is one which does not contain an oxidizer component capable of supporting combustion.

By "habitable" atmosphere is meant an atmosphere which supports mammalian life and permits the normal activities of such life for extended periods of time without disabling side effects or other forms of acute toxicity.

The object of this invention is to suppress the normal combustion-sustaining properties of air in an enclosed environment while maintaining its mammalian life-sustaining properties without substantial interference with the normal activities of such life.

Still another object is to provide a habitable atmosphere which comprises air so modified that it does not sustain the burning of ignitable non-self-sustaining combustible materials and, thereby, substantially eliminates fire hazards.

Another object is to provide a method for preventing and controlling fire in an enclosed compartment which can nevertheless sustain mammalian life.

Other objects and advantages will become obvious from the following detailed description.

DRAWING

The figure is a graph showing the relationship between fluorocarbon concentration added to air, the heat capacity of the modified air in cal./° C. per mole of total oxygen at 25° C. and constant pressure, and the mole percent of oxygen in the fluorocarbon-modified air.

SUMMARY OF THE INVENTION

The invention comprises a habitable atmosphere, which does not sustain combustion of combustible materials of the non-self-sustaining type and which is capable of sustaining mammalian life, consisting essentially of air; a perfluoroalkane selected from the group consisting of carbon tetrafluoride, hexafluoroethane, octafluoropropane, and mixtures thereof; and make-up oxygen in an amount from 0 to the amount required to provide, together with the oxygen present in the air, sufficient total oxygen to sustain mammalian life. The perfluoroalkane should be present in an amount sufficient to impart to the atmosphere a heat capacity per mole of total oxygen which is sufficient to suppress combustion of the flammable materials present in an enclosed compartment containing said atmosphere.

The invention also comprises a method for preventing and controlling fire in a confined air-containing compartment while maintaining the compartment habitable by mammalian life, which comprises, introducing into the air carbon tetrafluoride, hexafluoroethane, octafluoropropane, or mixtures thereof, in an amount sufficient to provide a heat capacity per mole of total oxygen which is sufficient to suppress combustion of the flammable materials present in the compartment and additionally introducing oxygen, if and as required, to make up with the oxygen available in the air, sufficient total oxygen to sustain mammalian life.

PREFERRED EMBODIMENTS

The perfluoroalkanes CF_4, C_2F_6, and C_3F_8, when added in adequate amounts to the air in a confined space, eliminate the combustion-sustaining properties of the air and suppress the combustion of flammable materials, such as paper, cloth, wood, flammable liquids, and plastic items, which may be present in the enclosed compartment, without detriment to normal mammalian activities.

The perfluoroalkanes CF_4, C_2F_6, and C_3F_8 are extremely stable and chemically inert. They do not decompose at temperatures as high as 400° C. to produce corrosive or toxic products and cannot be ignited even in pure oxygen so that they continue to be effective as flame suppressants at the ignition temperatures of the combustible items present in the compartment. They are also physiologically inert. Although they may cause some discomfort due to the increased density and reduced thermal conductivity which they impart to the air, such discomfort is not such as substantially to impair normal activity and can be counteracted by physical means, such as air cooling, or by the addition of an inert low-molecular weight gas, such as helium.

The C_1 to C_3 prefluoroalkanes are additionally advantageous because of their low boiling points, the highest being that of C_3F_8, which has a boiling point at normal atmospheric pressure of −36.7° C. Thus, at any low environmental temperature likely to be encountered, these perfluoroalkane gases will not liquify and will not, thereby, diminish the fire preventive properties of the modified air.

To eliminate the combustion-sustaining properties of the air, the perfluoroalkane gas should be added in an amount which will impart to the modified air a heat capacity per mole of total oxygen present, including any make-up oxygen required, sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials present in the enclosed environment. The minimum heat capacity required to suppress combustion varies with the combustibility of the particular flammable materials present in the confined space. It is well known that the combustibility of materials, namely their capability for igniting and maintaining sustained combustion under a given set of environmental conditions, varies according to chemical composition and certain physical properties, such as surface area relative to volume, heat capacity, porosity, and the like. Thus, thin, porous paper such as tissue, is considerably more combustible than a block of wood.

In general a heat capacity of about 40 cal./° C. and constant pressure per mole of oxygen is more than adequate to prevent or suppress the combustion of materials of relatively moderate combustibility, such as wood and plastics. More combustible materials, such as paper, cloth, and some volatile flammable liquids, generally require that the perfluoroalkane be added in an amount sufficient to impart a higher heat capacity. It is also desirable to provide an extra margin of safety by imparting a heat capacity in excess of minimum requirements for the particular flammable materials. A minimum heat capacity of 45 cal./° C. per mole of oxygen is generally adequate for moderately combustible materials and a minimum of about 50 cal./° C. per mole of oxygen for highly flammable materials. More can be added if desired but, in general, amounts imparting a heat capacity higher than about 55 cal./° C. per mole of total oxygen add substantially to the cost and may create unnecessary physical discomfort without substantial further increase in the fire safety factor.

Heat capacity per mole of total oxygen can be determined by the formula:

$$C_p^* = (C_p)_{O_2} + \sum_x \frac{P_x}{P_{O_2}} (C_p)_x$$

wherein:

C_p^*=total heat capacity per mole of oxygen at constant pressures;
P_{O_2}=partial pressure of oxygen;
P_x=partial pressure of other gas;
$(C_p)_x$=heat capacity of other gas at constant pressure.

The boiling points of CF_4, C_2F_6, and C_3F_8 and the mole percents of each required to impart to air heat capacities (C_p) of 40 and 50 cal./° C. at 25° C. and constant pressure while maintaining a 21% oxygen content are tabulated in Table I:

TABLE I

	Boiling point, ° C.	C_p=40, percent	C_p=50, percent
CF_4	−128.0	19.0	46.5
C_2F_6	−78.2	8.0	19.5
C_3F_8	−36.7	5.2	12.6

C_2F_6 and C_3F_8 are preferred embodiments because of the relatively small amounts of each required to impart fire suppressant properties to air. C_2F_6 is particularly preferred because its boiling point is sufficiently low to make it usable under the most extreme temperature conditions. It has the additional advantages of substantial commercial availability and relatively low cost.

The concentration of oxygen available in the confined air space should be sufficient to sustain mammalian life. The amount of make-up oxygen, if required, is determined by such factors as degree of air dilution by the perfluoroalkane gas and depletion of the available oxygen in the air by respiration. The amount of oxygen required to sustain human, and therefore mammalian life in general, at atmospheric, subatmospheric, and superatmospheric pressures, is well known and the necessary data are readily available. See, for example, Paul Webb, Bioastronautics Data Book, NASA SP–3006, National Aeronautics and Space Administration, 1964, p. 5. The minimum oxygen partial pressure is considered to be about 1.8 p.s.i.a., with amounts above about 8.2 p.s.i.a. causing oxygen toxicity. At normal atmospheric pressures at sea level, the unimpaired performance zone is in the range of about 16 to 36 volume percent O_2. Preferably the amount of oxygen maintained is at or close to that which maintains optimum comfort, namely at least about 18% and preferably about 21% at normal atmospheric pressure with adjustments as required for different pressures, particularly if the confined space is maintained or subjected to reduced pressures.

In some applications, little, if any, make-up oxygen will be required initially, particularly where the perfluoroalkane volume requirement, e.g. C_2F_6 and C_3F_8, is relatively small. However, habitation for extended periods of time will generally require addition of oxygen to make-up depletion caused by respiration.

The figure shows the heat capacity per mole of total oxygen imparted to air by different mole percentages of CF_4, C_2F_6, and C_3F_8 without the addition of make-up oxygen. The resulting percentages of oxygen present in the fluorocarbon-modified air is also shown.

It will be seen that between about 4 to 9 mole percent C_3F_8 provides a heat capacity in the 40 to 50 cal. range and the oxygen content drops only to about 20.1 to 19%. This is well within the habitable range. Similarly, for C_2F_6, from about 5.5 to 12.3 mole percent are required for a heat capacity range of 40 to 50 cal. and the corresponding oxygen concentrations are about 19.8 to 18.3%, again well within the habitable range. In the case of CF_4, the concentrations required for a heat capacity range of 40 to 50 cal. are about 9.3 to 18.7%. The corresponding oxygen concentrations are about 18.9 to 17.1%. At concentrations appreciably above a 10% addition of CF_4, it is desirable to introduce make-up oxygen initially.

Introduction of the perfluoroalkane gas and make-up oxygen as required is easily provided for by metering appropriate quantities of the gas or gases into the enclosed air-containing compartment.

The air in the compartment can be treated at any time that it appears desirable. The modified air can be used continuously if a threat of fire is constantly present or the particular environment is such that fire hazard must be kept at an absolute minimum, or it can be used as an emergency measure if a threat of fire develops.

Example I

A closed chamber with a transparent plastic front and a volume of about 12 cubic feet was fitted with gas inlet and outlet connections and an oxygen meter. A small electric fan was placed in the bottom of the chamber to promote gas mixing. Samples of filter paper, cotton cloth and polyurethane foam, approximately one inch wide by six inches long, were suspended vertically from a metal rod in the center of the chamber. A small crucible containing JP–5 hydrocarbon liquid and a filter paper wick was placed nearby. Ignition sources, consisting of small pieces of solid rocket propellant wrapped in short lengths of electric resistance wire and connected to an external power source, were placed at the base of the solid samples and on top of the wick in the JP–5.

With the fan turned on, hexafluoroethane was admitted to the chamber, displacing air through the exit tube, until the oxygen content of the atmosphere dropped to 16%. Pure oxygen was then admitted, displacing the air, fluorocarbon mixture until the oxygen content returned to 20.9%. At this point the composition of the atmosphere was approximately 20.9% oxygen, 57% nitrogren and 22.1% hexafluoroethane and small amounts of the other normal air components. The heat capacity of the modified air was approximately 52.5 cal./° C. per mole of total O_2.

At this point a rabbit was introduced into the chamber. The fan was stopped and an electric current was applied to each of the ignition circuits in sequence. The solid propellant pellets burned vigorously, charring the solid samples in close proximity and melting a portion of the polyurethane foam, but no sustained fires were obtained and the samples were undamaged at a short distance from the ignition source. The rabbit showed no signs of alarm or discomfort from the fluorocarbon-containing atmosphere during the approximately 15 minutes required to perform the experiment.

The chamber was opened and thoroughly purged with air and fresh fuel samples and igniters were introduced. The chamber was closed and the ignition sequence was repeated. This time sustained fires were obtained with each of the fuel samples. The samples were completely consumed except for a small amount of carbonaceous ash. The rabbit showed considerable alarm at the fire and smoke produced. The rabbit was observed for a period of thirty days following the experiment and showed no ill effects.

Example II

Tests were made to determine the flammability limits of various flammable materials in fluoroalkane-modified air. A 3.2 cu. ft. test chamber was employed. The materials tested included 2″ x 7″ strips of cotton flannel, 5″ x 8″ sheets of tissue paper, 1″ x 7″ strips of foamed plastic, and 1 cc. of kerosene in a small cup containing a saturated wick. Except for the kerosene, the samples were vertically suspended and ignition initiated from the bottom. The ignition sources were pieces of solid composite propellant that burned about 5 seconds. The test chamber contained an air atmosphere into which the fluoroalkane gas was introduced in varying amounts. No make-up oxygen was used.

All samples were first tested in the normal air atmosphere without fluoroalkane addition. All samples ignited readily and burned completely.

The following results were obtained with fluoroalkane addition:

COTTON FLANNEL

Mole percent of—				
CF_4	Air	O_2	C_p	Result
18.7	81.3	17.1	50.0	No flame propagation.
17.5	82.5	17.3	48.4	Weak flame propagation along edges, then self-extinguishment.
13.5	86.5	18.2	44.0	Burned completely.

Mole percent of—				
C_2F_6	Air	O_2	C_p	Result
12.0	88.0	18.5	49.5	No flame propagation.
11.0	89.0	18.7	48.0	Do.
9.1	90.9	19.1	45.1	Flame propagated slowly, high residue.
6.6	93.4	19.6	41.5	Burned completely.

Mole percent of—				
C_3F_8	Air	O_2	C_p	Result
9.4	90.6	19.0	50.5	No flame propagation.
8.1	91.9	19.3	47.8	Weak edge flame for 1 second.
6.75	93.25	19.6	45.1	Burned for several seconds, then self-extinguished.
5.4	94.6	19.9	42.8	Burned completely.

TISSUE PAPER

Mole percent of—				
C_2F_6	Air	O_2	C_p	Result
12.0	88.0	18.5	49.5	No flame propagation.
11.0	89.0	18.7	48.0	Burned slightly for short time.
9.1	90.9	19.1	45.1	Extinguished after ignition.
6.6	93.4	19.6	41.5	Burned completely.

FOAM PLASTIC

Mole percent of—				
C_2F_6	Air	O_2	C_p	Result
12.0	88.0	18.5	49.5	No flame propagation.
9.1	90.9	19.1	45.1	Do.
6.8	93.8	19.7	41.9	Do.
5.1	94.9	19.9	39.2	Do.
3.1	96.9	20.4	36.8	Do.
1.75	98.25	20.6	35.1	Burned completely.

KEROSENE

Mole percent of—				
C_2F_6	Air	O_2	C_p	Result
12.0	88.0	18.5	49.5	No flame propagation.
9.1	90.9	19.1	45.1	Do.
7.3	92.7	19.5	42.5	Do.
6.8	93.8	19.7	41.9	Burned momentarily, then extinguished.
5.1	94.9	19.9	39.2	Do.
3.1	96.9	20.4	36.8	Burned readily.

It will be noted from the above results that the amounts of fluoroalkane required for flame suppression varied with the degree of flammability of the generally highly flammable samples used. The degree of flammability of some of the test materials was increased by their physical forms, e.g. the high surface area of roughly textured flannel, the thinness and high porosity of tissue paper, and the high porosity of the formed plastic. It should also be noted that at fluorocarbon concentrations below those which completely prevent ignition of the fuel material, there are ranges of concentration in which flamming is weak and quickly suppressed, thus providing an additional safety factor against conflagration.

I claim:

1. A habitable atmosphere which does not sustain combustion of combustible materials of the non-self-sustaining type and which is capable of sustaining mammalian life, consisting essentially of:

(a) air;

(b) a perfluoroalkane selected from the group consisting of carbon tetrafluoride, hexafluoroethane, octafluoropropane, and mixtures thereof in an amount sufficient to impart to said atmosphere a heat capacity per mole of total oxygen sufficient to suppress combustion of the combustible materials present in an enclosed compartment containing said atmosphere; and

(c) make-up oxygen in an amount from 0 to the amount required to provide, together with the oxygen present in said air, sufficient total oxygen to sustain mammalian life;

said atmosphere containing sufficient total oxygen to sustain mammalian life.

2. The habitable atmosphere of claim 1 wherein the heat capacity per mole of total oxygen is at least about 45 cal./° C. at 25° C. and constant pressure.

3. The habitable atmosphere of claim 1 wherein the heat capacity per mole of total oxygen is at least about 50 cal./° C. at 25° C. and constant pressure.

4. The habitable atmosphere of claim 1 wherein the perfluoroalkane is hexafluoroethane.

5. The habitable atmosphere of claim 2 wherein the perfluoroalkane is hexafluoroethane.

6. The habitable atmosphere of claim 3 wherein the perfluoroalkane is hexafluoroethane.

7. The habitable atmosphere of claim 1 wherein the perfluoroalkane is octafluoropropane.

8. The habitable atmosphere of claim 2 wherein the perfluoroalkane is octafluoropropane.

9. The habitable atmosphere of claim 3 wherein the perfluoroalkane is octafluoropropane.

10. A process for preventing and controlling fire in an enclosed air-containing mammalian-habitable compartment which contains combustible materials of the non-self-sustaining type, which comprises:

(a) introducing into the air in said enclosed compartment a perfluoroalkane selected from the group consisting of carbon tetrafluoride, hexafluoroethane, octafluoropropane, or mixtures thereof in amount sufficient to impart a heat capacity per mole of total oxygen sufficient to suppress combustion of the combustible materials present in said enclosed compartment; and

(b) introducing make-up oxygen in an amount from 0 to the amount required to provide, together with the oxygen present in said air, sufficient total oxygen to sustain mammalian life;

said atmosphere containing sufficient total oxygen to support mammalian life.

11. The process of claim 10 wherein the heat capacity per mole of total oxygen is at least about 45 cal./° C. and constant pressure.

12. The process of claim 10 wherein the heat capacity per mole of total oxygen is at least about 50 cal./° C. and constant pressure.

13. The process of claim 10 wherein the perfluoroalkane is hexafluoroethane.

14. The process of claim 11 wherein the perfluoroalkane is hexafluoroethane.

15. The process of claim 12 wherein the perfluoroalkane is hexafluoroethane.

16. The process of claim 10 wherein the perfluoroalkane is octafluoropropane.

17. The process of claim 11 wherein the perfluoroalkane is octafluoropropane.

18. The process of claim 12 wherein the perfluoroalkane is octafluoropropane.

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