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FIRE EXTINGUISHING METHODS UTILIZING HYDROFLUOROETHERS

FIELD OF THE INVENTION

The present invention is directed to hydrofluoroether fire extinguishing agents and methods for extinguishing fires using the hydrofluoroethers. More particularly, the present invention is directed to fire extinguishing agents and methods using saturated or unsaturated, fluorinated C_4 and/or C_5 hydrofuoroethers, and blends of one or more of the hydrofluoroethers with one or more other fire extinguishing agents.

BACKGROUND OF THE INVENTION AND PRIOR ART

The use of certain bromine, chlorine and iodine-containing halogenated chemical agents for the extinguishment of fires is common. These agents are in general thought to be effective due to their interference with the normal chain reactions responsible for flame propagation. The most widely accepted mechanism for flame suppression is the radical trap mechanism proposed by Fryburg in *Review of Literature Pertinent to Fire Extinguishing Agents and to Basic Mechanisms Involved in Their Action*, NACA-TN 2102 (1950). The finding that the effectiveness of the halogens are on a molar basis in the order Cl < Br < I supports the radical trap mechanism, as reported by Malcom in *Vaporizing Fire Extinguishing Agents*, Report 117, Dept. of Army Engineering Research and Development Laboratories, Fort Bevoir, VA, 1950 (Project- 8-76-04-003). It is thus generally accepted that compounds containing the halogens Cl, Br and I act by interfering with free radical or ionic species in

the flame and that the effectiveness of these halogens is in the order I > Br > Cl. In addition, it is generally thought that to be effective as a fire extinguishing agent, a compound must contain Cl, Br or I.

The use of iodine-containing compounds as fire extinguishing agents has been avoided primarily due to the expense of their manufacture or due to toxicity considerations. Until very recently, the three fire extinguishing agents presently in common use were all bromine-containing compounds, Halon 1301 (CF_3Br), Halon 1211 (CF_2BrCl) and Halon 2402 ($BrCF_2CF_2Br$). The effectiveness of these three volatile bromine-containing compounds in extinguishing fires has been described in U.S. Pat. No. 4,014,799 to Owens. Although not employed commercially, certain chlorine-containing compounds are also known to be effective extinguishing agents, for example Halon 251 (CF_3CF_2Cl) as described by Larsen in U.S. Pat. No. 3,844,354.

Although the above named bromine or chlorine-containing Halons are effective fire fighting agents, those agents containing bromine or chlorine are asserted by some to be capable of the destruction of the earth's protective ozone layer. Also, because the agents contain no hydrogen atoms which would permit their destruction in the troposphere, the agents may also contribute to the greenhouse warming effect.

More recently, hydrofluorocarbons have been proposed as fire suppression, for example in U.S. Pat. No. 5,124,053. However, a disadvantage of these compounds is their relatively high global warming potential.

It is therefore an object of this invention to provide a method for extinguishing fires that extinguishes fires as rapidly and effectively as the techniques employing Halon agents while avoiding the above-named drawbacks.

It is a further object of this invention to provide an agent for the use in a method of the character described that is efficient, economical to manufacture, and environmentally safe with regard to ozone depletion and greenhouse warming effects.

It is a still further object of this invention to provide blends of the new agents and other fire extinguishing agents that are effective and environmentally safe.

SUMMARY OF THE INVENTION

The foregoing and other objects, advantages and features of the present invention may be achieved by employing saturated or unsaturated, higher fluorinated hydrofluoroethers and blends thereof with other agents as fire extinguishants for use in fire extinguishing methods and apparatus. More particularly, the method of this invention involves introducing to a fire a saturated or unsaturated, fluorinated C_4 or C_5 hydrofluoroether in a fire extinguishing concentration and maintaining such concentration until the fire is extinguished. Specific saturated, fluorinated C_4 or C_5 hydrofluoroethers of this invention include:

$CF_3CHFCF_2OCH_3$, $CF_3CHFCF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_2CHCF_2OCHF_2$ and $(CF_3)_2CHCF_2OCF_3$.

Specific unsaturated, fluorinated C_4 or C_5 hydrofluoroethers of the present invention include:

$CF_3CF=CFOCH_3$, $CF_3CF=CFOCH_2F$, $CF_3CF=CFOCHF_2$, $CF_3CF=CFOCF_3$, $CF_2=CFCF_2OCH_3$, $CF_2=CFCF_2OCH_2F$, $CF_2=CFCF_2OCF_2H$, $CF_2=CFCF_2OCF_3$, $(CF_3)_2C=CFOCH_3$, $(CF_3)_2C=CFOCH_2F$, $(CF_3)_2C=CFOCF_2H$, $(CF_3)_2C=CFOCF_3$, $CF_2=C(CF_3)CF_2OCH_3$, $CF_2=C(CF_3)CF_2OCH_2F$, $CF_2=C(CF_3)CF_2OCF_2H$ and $CF_2=C(CF_3)CF_2OCF_3$.

These hydrofluoroethers may be used alone, in admixture with each other or as blends with other fire extinguishing agents. Generally, the agents of this invention are employed at concentrations lying in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis . The agents of this invention are suitable for use in both total flooding and portable fire suppression applications. Suitable extinguishing agents ('blends') for admixture with the hydrofluoroethers include CF_3CHFCF_3, $CF_3CF_2CF_2H$, $CF_3CH_2CF_3$, CF_3CF_2H, and CF_3H.

The hydrofluoroethers of this invention may be produced via numerous routes. For example, $CF_3CHFCF_2OCF_2H$ may be prepared via a three step process comprising

(i) reaction of methanol with commercially available hexafluoropropene ($CF_3CF=CF_2$) in the presence of base to produce $CF_3CHFCF_2OCH_3$;

(ii) chlorination of $CF_3CHFCF_2OCH_3$ with Cl_2 to produce $CF_3CHFCF_2OCHCl_2$; and

(iii) fluorination of $CF_3CHFCF_2OCHCl_2$ with HF to produce the final product $CF_3CHFCF_2OCF_2H$.

By further reacting with a strong base like sodium or potassium hydroxide the corresponding unsatured C_4 or C_5 hydrofluoroethers may be prepared.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, saturated and unsaturated C_4 and C_5 hydrofluoroethers have been found to be effective fire extinguishants at concentrations safe for use. However, because such hydrofluoroethers contain no bromine or chlorine, they have an ozone depletion potential of zero. Furthermore, since the compounds are characterized by short atmospheric lifetimes they are susceptible to breakdown in the lower atmosphere and hence do not pose a threat as greenhouse warming gasses.

Specific hydrofluoroethers useful in accordance with this invention are:

$CF_3CHFCF_2OCH_3$, $CF_3CHFCF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_2CHCF_2OCHF_2$, $(CF_3)_2CHCF_2OCF_3$, $CF_3CF=CFOCH_3$, $CF_3CF=CFOCH_2F$, $CF3CF=CFOCHF_2$, $CF_3CF=CFOCF_3$, $CF_2=CFCF_2OCH_3$, $CF_2=CFCF_2OCH_2F$, $CF_2=CFCF_2OCF_2H$, $CF_2=CFCF_2OCF_3$, $(CF_3)_2C=CFOCH_3$, $(CF_3)_2C=CFOCH_2F$, $(CF_3)_2C=CFOCF_2H$, $(CF_3)_2C=CFOCH_3$, $CF_2=C(CF_3)CF_2OCH_3$, $CF_2=C(CF_3)CF_2OCH_2F$, $CF_2=C(CF_3)CF_2OCF_2H$ and $CF_2=C(CF_3)CF_2OCF_3$.

These hydrofluoroethers may be used alone, in admixture with each other or as blends with other fire extinguishing agents. Generally, when a single hydrofluoroether of this invention is employed, concentrations lying in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis, are used; when employed in admixture, concentrations lying in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis, are used. Where the hydrofluoroethers of this invention are employed in admixture with other fire extinguishing agents ('blends'), the hydrofluoroethers desirably comprise of at least about 10 percent by weight of the blend, and the overall concentration of the blend lies in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis. The agents of this invention are suitable for use in both total flooding and portable fire suppression applications. Suitable extinguishing agents for admixture with the hydrofluoroethers include CF_3CHFCF_3, $CF_3CF_2CF_2H$, $CF_3CH_2CF_3$, CF_3CF_2H, and CF_3H.

The C_4 or C_5 hydrofluoroethers of this invention may be effectively employed at substantially any minimum concentrations at which fire may be extinguished, the exact minimum level being dependent on the particular combustible material, the particular hydrofluoroether and the combustion conditions. In general, however, best results are achieved where the hydrofluoroethers or mixtures and blends thereof are employed at a level of at least about 3% (v/v). Where hydrofluoroethers alone are employed, best results are achieved with agent levels of at least about 5% (v/v). Likewise, the maximum amount to be employed will be governed by matters of economics and potential toxicity to living things. About 15% (v/v) provides a convenient maximum concentration for use of hydrofluoroethers and mixtures and blends thereof in occupied areas. Concentrations above 15% (v/v) may be employed in unoccupied areas, with the exact level being determined by the particular combustible material, the hydrofluoroether (or mixture or blend thereof) chosen

and the conditions of combustion. The preferred concentration of the hydrofluoroether agents, mixtures and blends in accordance with this invention lies in the range of about 5 to 10% (v/v).

Hydrofluoroethers may be applied using conventional application techniques and methods used for Halons such as Halon 1301 and Halon 1211. Thus, these agents may be used in a total flooding fire extinguishing system in which the agent is introduced to an enclosed region (e.g., a room or other enclosure) surrounding a fire at a concentration sufficient to extinguish the fire. In accordance with a total flooding system apparatus, equipment or even rooms or enclosures may be provided with a source of agent and appropriate piping, valves, and controls so as automatically and/or manually to be introduced an appropriate concentrations in the event that fire should break out. Thus, as is known to those skilled in the art, the fire extinguishant may be pressurized with nitrogen or other inert gas at up to about 600 psig at ambient conditions.

Alternatively, the hydrofluoroether agents may be applied to a fire through the use of conventional portable fire extinguishing equipment. It is usual to increase the pressure in portable fire extinguishers with nitrogen or other inert gasses in order to insure that the agent is completely expelled from the extinguisher. Hydrofluoroether containing systems in accordance with this invention may be conveniently pressurized at any desirable pressure up to about 600 psig at ambient conditions.

The compounds of the present invention are nondestructive agents, and are especially useful where cleanup of other media poses a problem. Some of the applications of the hydrofluoroethers of this invention are the extinguishing of liquid and gaseous fueled fires, the protection of electrical

equipment, ordinary combustibles such as wood, paper and textiles, hazardous solids, and the protection of computer facilities, data processing equipment and control rooms.

The invention will be further described with reference to the following specific Examples. However it will be understood that these Examples are illustrative in nature and not restrictive in nature.

EXAMPLE 1

This example demonstrates the desirable "throw" obtainable with the fire suppression agents of the present invention when employed in portable ("streaming") applications. The throw is the distance the stream of agent can be discharged; the longer the throw the better, as this allows extinguishment without approaching the fire at too close a distance, which can lead to exposure of the operator to fire and toxic fumes from the combustion process.

A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 50 grams of $CF_3CHFCF_2OCF_2H$ and then pressurized with nitrogen to the desired pressure. The cylinder contents were completely discharged and the throw distance noted (Table 1).

TABLE 1

Throw vs. Pressure for $CF_3CHFCF_2OCF_2H$ System

Pressure, psig	Throw, feet
25	10
80	15
120	17
150	18

EXAMPLE 2

This example demonstrates the extinguishment of Class B fires with the agents of the present invention. A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 30 grams of $CF_3CHFCF_2OCF_2H$ and then pressurized with nitrogen to 120 psig. A 2 inch x 4 inch x 0.5 inch SS pan was filled with 20 mL of methanol. The methanol was ignited and allowed to burn for 30 seconds; the agent was then discharged from a distance of 4 feet onto the fire. The methanol fire was extinguished in 1.5 seconds; a total of 16 grams of agent was discharged.

EXAMPLE 3

The method of Example 2 was employed with acetone, isopropanol and heptane fuels. All fires were rapidly extinguished (see Table 2).

TABLE 2

Extinguishment with $CF_3CHFCF_2OCF_2H$

Fuel	Extinguishing Time, seconds	Agent discharged, grams
acetone	2.0	25
isopropanol	1.5	21
heptane	1.8	11

EXAMPLE 4

This example demonstrates the extinguishment of deep-seated Class A fires with the agents of the present invention. A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 30 grams of $CF_3CHFCF_2OCF_2H$ and then pressurized with nitrogen to 120 psig. A wood crib was constructed of six layers of 6 inch x 2 inch by 0.125 inch strips of kiln dried fir, each layer consisting of 4 pieces. The crib was soaked with heptane, ignited, and allowed to burn for five minutes. The agent was then discharged onto the fire, resulting in rapid (< 2 seconds) extinguishment; a total of 25 grams of agent was discharged. Immediately after extinguishment the wood crib was cold to the touch, demonstrating the efficient suppression afforded by the agent.

WHAT IS CLAIMED IS:

1. A method for extinguishing a fire comprising the steps of introducing to the fire a fire extinguishing concentration of a composition comprising a compound selected from the group consisting of $CF_3CHFCF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_3CHCF_2OCHF$, $(CF_3)_2CHCF_2OCF_3$, $CF_3CF=CFOCH_2F$, $CF_3CF=CFOCHF_2$, $CF_3CF=CFOCF_3$, $CF_2=CFCF_2OCH_3$, $CF_2=CFCF_2OCH_2F$, $CF_2=CFCF_2OCF_2H$, $CF_2=CFCF_2OCF_3$, $(CF_3)_2C=CFOCH_2F$, $(CF_3)_2C=CFOCF_2H$, $CF_2=C(CF_3)CF_2OCH_3$, $CF_2=C(CF_3)CF_2OCH_2F$, $C(CF_3)CF_2OCF_2H$, and $CF_2=C(CF_3)CF_2OCF_3$ and maintaining the concentration of the compound until the fire is extinguished.

2. The method of claim 1, wherein the compound is selected from the group consisting of $CF_3CHFCF_2OCH_3$, $CF_3CHFF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_2CHCF_2OCHF_2$, $(CF_3)_2CHCF_2OCF_3$.

3. The method of claim 1, wherein the compound is employed at a level of at least about 3% (v/v).

4. The method of claim 1, wherein the compound is employed in a total flooding system.

5. The method of claim 1, wherein the compound is employed in a portable extinguishing system.

6. The method of claim 1, wherein the composition comprises a blend with other fire extinguishing agents.

7. The method of claim 6, wherein the other fire extinguishing agents are selected from the group consisting of CF_3CHFCF_3, $CF_3CF_2CF_2H$, $CF_3CH_2CF_3$, CF_3CF_2H, and CF_3H.

8. A fire extinguishing agent comprising a compound selected from the group consisting of $CF_3CHFCF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_3CHCF_2OCHF_2$, $(CF_3)_2CHCF_2OCF_3$, $CF_3CF=CFOCH_2F$, $CF_3CF=CFOCHF_2$, $CF_3CF=CFOCF_3$, $CF_2=CFCF_2OCH_3$, $CF_2=CFCF_2OCH_2F$, $CF_2=CFCF_2OCF_2H$, $CF_2=CFCF_2OCF_3$, $(CF_3)_2C=CFOCH_2F$, $(CF_3)_2C=CFOCF_2H$, $CF_2=C(CF_3)CF_2OCH_3$, $CF_2=C(CF_3)CF_2OCH_2F$, $C(CF_3)CF_2OCF_2H$, and $CF_2=C(CF_3)CF_2OCF_3$.

9. A method of making $CF_3CHFCF_2OCF_2H$ comprising the steps of:

reacting methanol with hexafluoropropene in the presence of base to produce $CF_3CHFCF_2OCH_3$;

chlorinating $CF_3CHFCF_2OCH_3$ with Cl_2 to produce $CF_3CHFCF_2OCHCl_2$; and

fluorinating $CF_3CHFCF_2OCHCl_3$ with HF to produce $CF_3CHFCF_2OCF_2H$.

10. A method of making a saturated, fluorinated C_4 or C_5 hydrofluoroether selected from the group consisting of $CF_3CHFCF_2OCH_2F$, $CF_3CHFCF_2OCF_2H$, $CF_3CHFCF_2OCF_3$, $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2CHCF_2OCH_2F$, $(CF_3)_3CHCF_2OCHF_2$, $(CF_3)_2CHCF_2OCF_3$, $CF_3CF=CFOCH_3$, $CF_3CF=CFOCH_2F$, $CF_3CF=CFOCHF_2$, $CF_3CF=CFOCF_3$, $CF_2=CFCF_2OCH_3$, $CF_2=CFCF_2OCH_2F$, $CF_2=CFCF_2OCF_2H$, $CF_2=CFCF_2OCF_3$, $(CF_3)_2C=CFOCH_3$, $(CF_3)_2C=CFOCH_2F$, $(CF_3)_2C=CFOCF_2H$, $(CF_3)_2C=CFOCH_3$, $CF_2=C(CF_3)CF_2OCH_3$, $CF_2=C(CF_3)CF_2OCH_2F$, $C(CF_3)CF_2OCF_2H$ and $CF_2=C(CF_3)CF_2OCF_3$ comprising the steps of

reacting a C_1 alcohol with a fluorinated C_3 or C_4 alkene in the presence of a base to form a first reaction product;

chlorinating the first reaction product with Cl_2 to form a second reaction product; and

fluorinating the second reaction product with HF to form a saturated, fluorinated C_4 or C_5 hydrofluoroether.

11. The method of claim 10, wherein the base is selected from the group consisting of sodium and potassium hydroxide.

12. The composition comprising $CF_3CHFCF_2OCF_3$.