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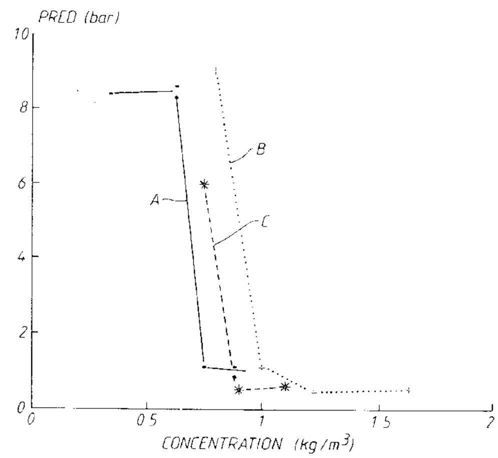
(54) Fire extinguishing and explosion suppression substances.

(57) A fire extinguishing and explosion suppression agent is disclosed comprising perfluorohexane discharged in atomised form, such as, for example, by means of a pressurising gas which may, for instance, be nitrogen at least partially dissolved in the perfluorohexane. Another agent disclosed comprises a mixture of trifluoromethane dissolved in perfluorohexane. The agents disclosed have zero ozone depletion potential and low toxicity.



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The invention relates to fire extinguishing and explosion suppression agents. In the following specification and claims, the term "fire suppression" will be used to cover both fire extinguishing and explosion suppression.

According to the invention, there is provided a fire suppression agent, comprising a non-flammable partially or fully fluorinated hydrocarbo having a boiling point above 0C in combination with discharge means for discharging it in atomised form into an area to be protected.

According to the invention, there is further provided a method of suppressing a fire, comprising the step of discharging into the fire, in atomised form, a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above OC.

According to the invention, there is still further provided a fire suppression agent comprising a mixture of a liquid component and a gaseous component, the liquid component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point above OC, and the gaseous component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point below OC.

Fire suppression agents embodying the invention will now be described, by way of example only, with reference to certain Examples and to the accompanying drawing which is a Figure showing graphical test results.

Fire suppression agents need to satisfy a number of different requirements. In the first place, of course, they must have efficient fire extinguishing ad explosion suppressing capabilities. Secondly, however, they should be environmentally friendly; known extinguishing and suppression agents based on bromofluorocarbons or bromochlorofluorocarbons (Halons) are environmentally damaging and, under the Montreal protocol on ozone-depleting chemicals and its subsequent amendments, their production has to be phased out by 1st January 1994. There is therefore a great need for effective and environmentally acceptable extinguishing and suppression agents. Thirdly, in many cases fire suppression agents have to be used in areas where people are present, such as, for example, in industrial areas or in transport. It is therefore important that the agents to be used should be as harmless as possible to humans.

One Example (Example 1) of a fire suppression agent comprises perfluorohexane, C_6F_{14}, used in atomised form. The boiling point of perfluorohexane is +58C. It is known for use as a fire suppression agent in the form of a streamed liquid. However, standard laboratory tests of its fire suppression capability when used in this way, against a two-dimensional or surface-type fire, have shown that, in order to produce the same fire suppression capability as a give quantity of Halon 1301, early three times as much perfluorohexane is required (when measured in mass or volume terms). Unexpectedly, however, it has been found that, when applied in atomised form, perfluorohexane is particularly effective against three dimensional fires - explosions and rapidly developing fires. When used in this way and in these circumstances, it has been found that a given mass or volume of perfluorohexane can achieve substantially the same suppression capability as substantially the same quantity of Halon 1301.

preferably, the droplets of perfluorohexane in the atomised discharge have a distribution lying in the region 20 - 200 micrometres. Droplets with this size distribution are large enough to have sufficient momentum to reach the seat of the fire or the developing fire ball in as short a time as possible (typically a few tens of milliseconds). However, they are still small enough to evaporate in the flame so as to absorb its heat. Atomisation is achieved by forcing the perfluorohexane through a suitably selected nozzle by means of a propellant gas. A suitable propellant gas is nitrogen. Nitrogen is very soluble in perfluorohexane. This solubility aids the atomisation process because, upon discharge of the perfluorohexane under pressure of the gas, the pressure release causes the dissolved nitrogen to come out of solution and this enhances the atomisation process.

Perfluorohexane does not cotain chlorine or bromine and does not destroy stratospheric ozone. It has an ozone depletion potential (ODP) of zero. Tests on perfluorocarbons similar to perfluorohexane have shown that they have essentially very low toxicity. Perfluorohexane, when used in the atomised form described above, is thus particularly suitable as a suppression agent for use in crew bay compartments if military vehicles, but is not restricted to such appliances. Other applications could include engine compartments of military vehicles, machinery rooms and compartments in ships, off-shore oil and gas platforms, rail vehicles, civil and military aircraft, aircraft shelters and hangars and the like.

Although in this Example reference has been made to perfluorohexane, the substance used may be a mixture not only of isomeric perfluorohexanes but also of other perfluorocarbons.

Thus, more generaly, perfluorohexane and other perfluorocarbons (i.e. fully fluorinated hydrocarbons) or mixtures and isomers of them, having boiling points above O C, and preferably in the range +20 to +150 C, are included within Example 1 and can be used in the manner explained above. Suitable perfluorocarbons are:-

TABLE 1

perfluoropentane	$CF_3(CF_2)_3CF_3$	(+29C)
perfluoroheptane	$CF_3(CF_2)_5CF_3$	(+83C)
perfluoroctane	$CF_3(CF_2)_6CF_3$	(+105C)
perfluorononane	$CF_3(CF_2)_7CF_3$	(+125C)

Another possibility (Example 2) is to use partially fluorinated hydrocarbons (i.e. high boiling point hydrofluorocarbons), or mixtures or isomers of them, again having boiling points above OC and again preferably in the range +20 to +150C. Suitable hydrofluorocarbons are:

TABLE 2

1H-tridecafluoro-n-hexane	$CF_3(CF_2)_4CHF_2$	(+72)
1-trifluoromethyl-2H-decafluoro-n-heptane	$CF_3CH(CF_3)CF_2CF_2CF_3$	(+55)
1H-pentadecafluoro-n-heptane	$CF_3(CF_2)_5CHF_2$	(+94)
1H-heptadecafluoro-n-octane	$CF_3(CF_2)_6CHF_2$	(+118)
4H,5H-hexadecafluoro-n-octane	$CF_3(CF_2)_2(CHF)_2(CF_2)_2CF_3$	(+112)

These substances would be used in the same way as explained for Example 1 and mixtures of substances from Tables 1 and 2 can be used.

In Tables 1 and 2, the figures in brackets represent the respective boiling points. The substances of Tables 1 and 2 all have zero ODP and are believed to have low toxicity when used in the applications referred to.

Instead of nitrogen as the pressurising gas, another inert gas could be used, such as argon, helium or carbon dioxide.

A third Example (Example 3) of a suppression agent embodying the invention comprises a mixture of a high boiling point perfluorocarbon, such as perfluorohexane, with a low boiling point fluorinated. hydrofluorocarbon. A suitable hydrofluorocarbo is trifluoromethane (CHF_3). Trifluoromethane has a boiling point of -82C and, as a gas, is very soluble in perfluorohexane. It is found that such a mixture has very effective suppression capabilities. A mixture containing perfluorohexane and trifluoromethane in a mole ratio of 2:1 (i.e. about 9% by weight of trifluoromethane) has been found to have a suppression capability of the same order as Halon 1301. However, it is not believed that the dissolved gaseous trifluoromethane acts in the same way as the pressurising gas (e.g. nitrogen) referred to above (for atomising the perfluorohexane). It is believed that the trifluoromethane primarily acts, upon discharge of the mixture, by the resultant evaporation effect which causes the perfluorohexane to be rapidly and significantly cooled, and it is this cooling effect which primarily provides the beneficial suppression ability. In other words, the trifluoromethane directly contributes to the fire suppression process.

In other forms of Example 3, the perfluorohexane in the mixture described could be replaced by (or mixed with) one or more other partially or fully fluorinated hydrocarbons with boiling points above O C and preferably in the range +20C to +150C, such as those listed in Tables 1 and 2 above. Furthermore, the trifluoromethane could be replaced by (or mixed with) one or more other hydrofluorocarbons and/or with one or more perfluorocarbons having a boiling point below O C. Possible other hydrofluorocarbons and perfluorocarbons are:-

TABLE 3

difluoromethane	CH_2F_2	(-52C)
pentafluoroethane	CF_3CHF_2	(-49C)
perfluoroethane	CF_3CF_3	(-78C)
perfluoropropane	$CF_3CF_2CF_3$	(-37C)
perfluorobutane	$CF_3CF_2CF_2CF_3$	(-2C)
perfluorocyclobutane	cyclo-C_4F_8	(-6C)
1,1,1,2-tetrafluoroethane	CF_3CH_2F	(-27C)
1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3	(-17C)

Again, the temperature figures in brackets indicate the respective boiling points of the substances.

Like the perfluorocarbons, these hydrofluorocarbons have zero ODP and are believed to be relatively non-toxic when used in the applications referred to.

The Figure shows the results of performance tests carried out for comparing the explosion suppression capabilities of certain of the suppression agents described above with each other and with Halon 1301.

The tests were carried out using a test vessel of $6.2m^3$ in volume. A predetermined quantity, about 1 litre, of diesel fuel, prewarmed to 90C, is sprayed into the vessel and ignited. The incipient explosion is detected by the rise in pressure (although this can be done optically by means of optical flame detectors known to those skilled in the art). When the pressure from the steadily growing explosion fireball exceeds 0.025 bar, the contacts of a pressure switch are closed automatically, triggering discharge of the suppressant from one or more rapid-action suppressors into the test vessel. A measure of the suppressant action is given by the maximum pressure (Pred) attained in the vessel. The lower this. parameter, the better is the suppression. The horizontal axis plots the concentration of the injected suppression agent (in kilograms of agent per cubic metre of the test vessel). In all of these tests, the fluorinated hydrocarbons contained within the suppressors were pressurised to 52 bar with nitrogen gas.

Pred figures of less than 1 bar are considered to represent satisfactory suppression; figures over 1 bar are considered to represent failed suppression.

Curve A shows the results obtained using Halon 1301, while curve B relates to atomised perfluorohexane (Example 1) and curve C relates to the mixture of perfluorohexane and trifluoromethane (Example 3) in a 2:1 mole ratio (i.e. about 9% by weight of trifluoromethane). The Figure shows that the agents described give very effective suppression when used in concentrations only slightly greater than Halon 1301.

Similar results are obtained using other mixtures of perfluorohexane and trifluoromethane, for example 1:1 or 1:2 mole ratios.

Table 4 below tabulates the suppression performance, measured as described above, for perfluorohexane alone (Example 1 above) and for various mixtures of Example 3 above. Most of the mixtures shown are mixtures of perfluorohexane with a low boiling point fluorinated hydrofluorocarbon. For comparison, the Table also shows two known fire suppression agents, bromofluoromethane and bromochlorodifluoromethane.

The "minimum suppression concentration" in Table 4 is the minimum concentration required to obtain satisfactory suppression as defined above - that is, to produce Pred figures of less than 1 bar.

TABLE 4

Agent		Boiling Point °C	mol%	Minimum Suppression Concentration	
				kg/m³	L/m³
perfluorohexane	C_6F_{14}	+58	100	0.90	0.54
perfluorohexane	C_6F_{14}	+58	67		
(mixed with)				0.85	0.64
trifluoromethane	CHF_3	-82	33		
perfluorohexane	C_6F_{14}	+58	50		
(mixed with)				0.85	0.64
trifluoromethane	CHF_3	-82	50		
perfluorohexane	C_6F_{14}	+55	33		
(mixed with)				0.95	0.82
trifluoromethane	CHF_3	-82	67		
perfluorohexane	C_6F_{14}	+58	67		
(mixed with)				0.82	0.53
heptafluoropropane	CF_3CHFCF_3	-17	33		
bromotrifluoromethane	CF_3Br	-58	100	0.76	0.49
bromochlorodifluoromethane	CF_2BrCl	-4	100	0.75	0.42

Claims

1. A fire suppression agent, characterised by a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above 0C in combination with discharge means for discharging it in atomised form into an area to be protected.

2. An agent according to claim 1, characterised in that the discharge means comprises a pressurising gas.

3. A method of suppressing a fire, characterised by the step of discharging into the fire, in atomised form, a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above OC.

4. A method according to claim 3, characterised by the step of atomising the non-flammable partially or fully fluorinated hydrocarbon by means of a pressurising gas.

5. An agent or method according to claim 2 or 4, characterised in that the pressurising gas is at least partially dissolved in the non-flammable partially or fully fluorinated hydrocarbon.

6. An agent or method according to any one of claims 2,4 and 5, characterised in that the pressurising gas

is nitrogen.

7. An agent or method according to any one of claims 2,4 and 5, characterised in that the pressurising gas is selected from the group comprising nitrogen, argon, helium, and carbon dioxide.

8. An agent or method according to any preceding claim, characterised in that the atomised discharge has a droplet size distribution in the range 20-200 micrometres.

9. An agent or method according to any preceding claim, characterised in that the non-flammable partially or fully fluorinated hydrocarbon comprises perfluorohexane.

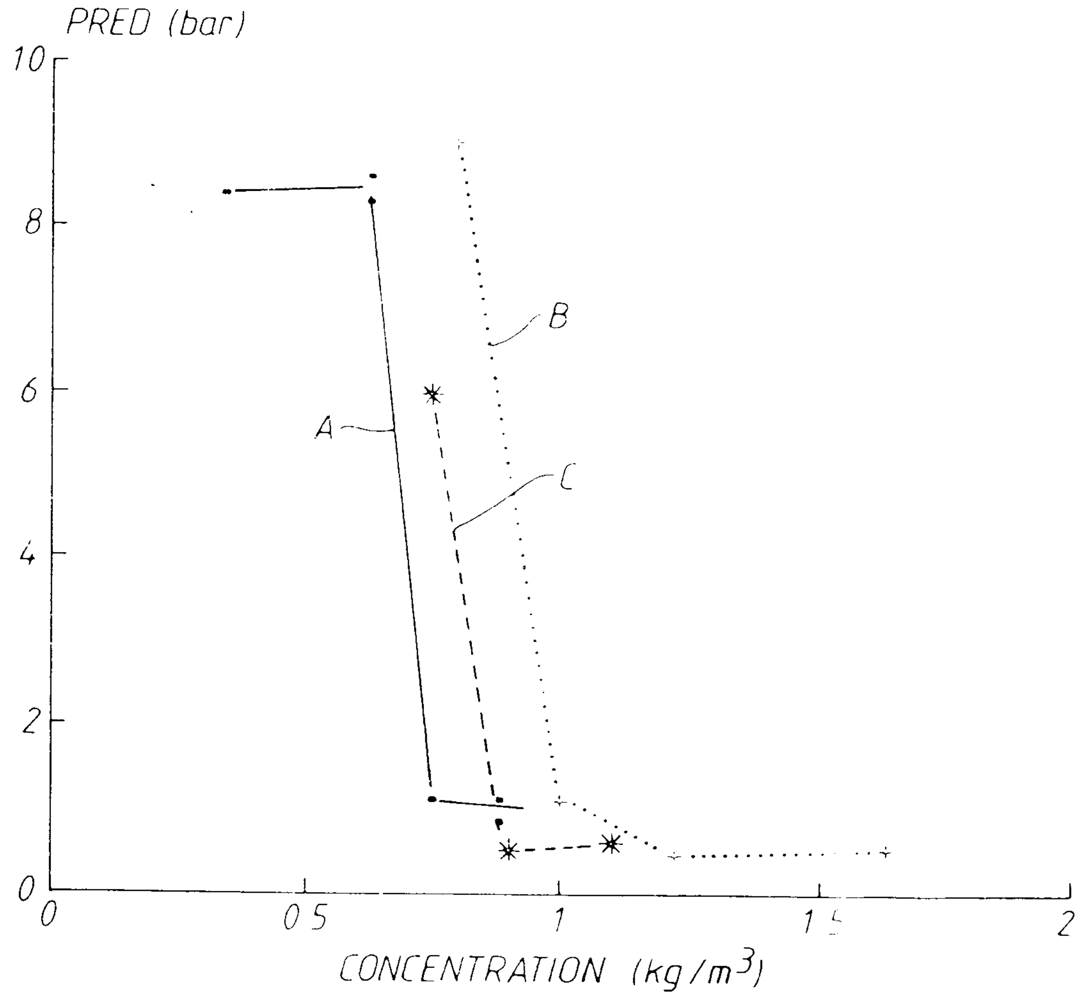
10. An agent or method according to any one of claims 1 to 8, characterised in that the non-flammable partially or fully fluorinated hydrocarbon comprises one or more of the following: perfluoropentane, perfluorohexane; perfluoroheptane; perfluoroctane; and perfluorononane.

11. A fire suppression agent, characterised by a mixture of a liquid component and a gaseous component, the liquid component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point above OC, and the gaseous component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point below OC.

12. An agent according to claim 11, characterised in that the liquid component comprises perfluorohexane and the gaseous component comprises trifluoromethane.

13. An agent according to claim 12, characterised in that the mole ratio of the perfluorohexane and the trifluoromethane in the mixture is approximately 2:1.

14. An agent according to claim 11, characterised in that the liquid component comprises perfluorohexane and the gaseous component comprises heptafluoropropane.


PRED (bar)
10
8
6
4
2
0
A
B
C
0
0 5
1
2
CONCENTRATION (kg/m3)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 2037

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.5)
X	EP-A-0 460 991 (ATOCHEM) * the whole document * ---	1-14	A62D1/00
X	US-A-5 084 190 (R.I.FERNANDEZ) * column 3, line 26 * * column 5, line 14 * * claims * ---	1-8,11	
X	WO-A-9 104 766 (E.I. DU PONT ET NEMOURS AND COMPANY) * claims * ---	1-8,11	
A	WO-A-9 201 491 (GREAT LAKES CHEMICAL CORPORATION) ---		
A	CHEMICAL ABSTRACTS, vol. 85, no. 8, 1976, Columbus, Ohio, US; abstract no. 48936s, 'Mixed fire extinguisher' page 135 ; * abstract * & JP-A-51 034 595 (DAIKIN KOGYO CO.) -----	1-14	TECHNICAL FIELDS SEARCHED (Int. Cl.5) A62D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04 JUNE 1993	DALKAFOUKI A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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