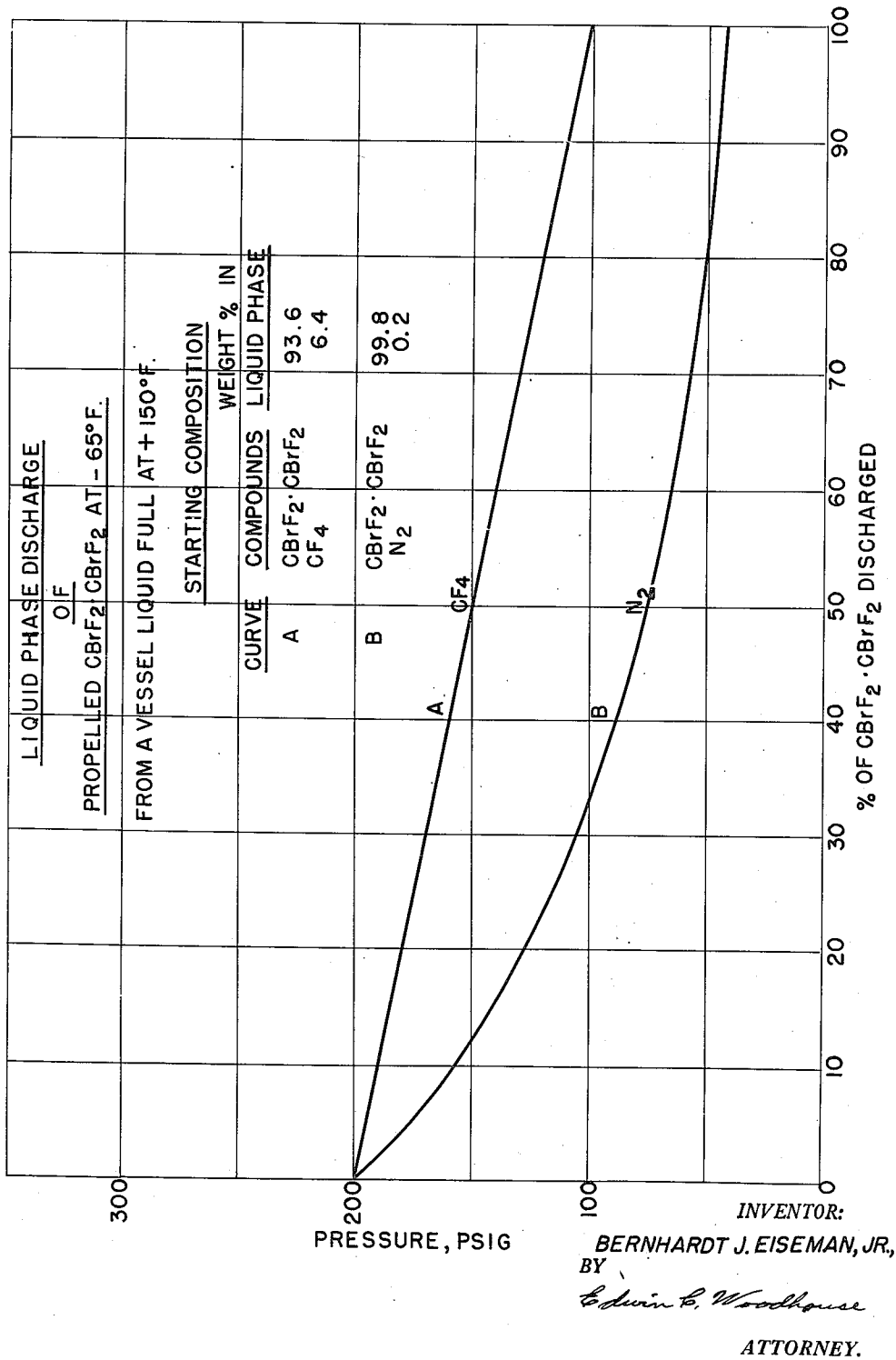


Sept. 22, 1953

B. J. EISEMAN, JR
FIRE EXTINGUISHING COMPOSITION OF CBrF_2 OR CF_2
BY CF_2 BY CONTAINING CF_4 AS A PROPELLANT
2,653,130
Filed May 17, 1951



UNITED STATES PATENT OFFICE

2,653,130

FIRE EXTINGUISHING COMPOSITION OF
CBr₂F₂ OR CF₂BrCF₂Br CONTAINING CF₄
AS A PROPELLANT

Bernhardt J. Eiseman, Jr., Wilmington, Del., as-
signor to E. I. du Pont de Nemours & Com-
pany, Wilmington, Del., a corporation of Dela-
ware

Application May 17, 1951, Serial No. 226,921

7 Claims. (Cl. 252-8)

1

This invention relates to self-propelling liquid compositions, and particularly to compositions of such character which are adapted for use as fire extinguishants having exceptionally desirable properties for use at varying ambient temperatures.

It has been proposed to use propellants for fire extinguishants which are low in toxicity, are stable during storage and provide adequate pressure for discharge at temperatures near room temperature. However, such propellants are not operative at low temperatures because they do not provide sufficient pressures at such temperatures. By "low temperatures," as employed herein, I means temperatures equal to or below cold winter temperatures in the temperate zone, including, particularly, arctic temperatures and the low temperatures encountered at high altitudes by airplanes. A propellant, which is suitable for use at such low temperatures, must also be suitable for operation at high temperatures, such as the highest summer temperatures and the temperatures encountered in the desert and in the tropics, since the same extinguisher may be required to operate at both the low temperatures and the high temperatures as, for example, when employed in an airplane or the like.

Some fire extinguishants function mainly by smothering the flame, while others tend to suppress combustion even though oxygen is present. The latter type is the more effective, and probably functions by quenching free radical activity which is believed to be necessary for maintaining combustion even in the presence of oxygen. The bromo-fluoro alkanes, such as CBrF₃, CBr₂F₂ and CF₂BrCF₂Br, are examples of such latter type. If the propellant is of the former type, as is commonly the case, it should not be employed in such large proportions as to excessively dilute the more effective extinguishant.

A fire extinguishant composition, in order to be satisfactory for use under the varying temperature conditions hereinbefore referred to, must meet all of the following requirements:

1. Be low in toxicity;
2. Have high stability;
3. The propellant must provide adequate pressure at low temperatures, preferably at least 100 pounds per square inch gauge at -65° F., with-

2

out excessive dilution of the more effective propelled extinguishant;

4. Develop only moderate pressures at high temperatures;

5. The pressure must be well maintained during the entire discharge, i. e., until the last of the liquid has been expelled from the extinguisher; and

6. The propellant must be sufficient in volume so that a brief accidental discharge of gas phase, while the extinguisher is inverted, will not lead to an excessive loss of pressure.

Offhand, nitrogen would appear to be the obvious propellant for use at low temperatures, as it meets requirements 1 to 4 and also has the advantage of being low in cost. However, nitrogen does not meet requirements 5 and 6. This is because of the low solubility of nitrogen in the highly effective extinguishants which are suitable for use at low temperatures. Thus, there is little nitrogen present and, when a part of the nitrogen is expelled or lost, the pressure in the extinguisher drops rapidly. This latter result can be offset to some extent through the use of larger amounts of nitrogen, by employing higher pressures at the low temperatures or by employing a large gas space equivalent to an auxiliary tank above the liquid extinguishant, but these expedients are objectionable because the pressures become excessive at high temperatures and, in the case of a large gas space, requires large and bulky equipment.

It is an object of the present invention to provide new self-propelling liquid compositions having unusual properties. Another object is to provide a new self-propelling liquid composition which is particularly adapted for use as a fire extinguishant composition and which is operable and useful over a wide range of temperatures, and especially at low temperatures. A further object is to provide a method of applying such self-propelling liquid compositions. A still further object is to provide a package comprising a hermetically sealed container charged with such self-propelling liquid composition. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which

3

comprises a self-propelling liquid composition consisting essentially of a solution of carbon tetrafluoride (CF_4) in at least one of CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$, in which the CF_4 constitutes from about 2.5% to about 10% by weight of the liquid; the method of applying such composition to an object which comprises maintaining such liquid composition in a hermetically sealed container under the vapor pressure thereof and expelling such composition under such pressure through a discharge orifice and directing the expelled composition against such object; and a package which comprises a hermetically sealed container charged with such liquid composition under a pressure corresponding to the vapor pressure of such composition. In such compositions, the CF_4 acts as the propellant for expelling the liquid composition from the container. Such compositions are particularly adapted for use as self-propelling fire extinguishant compositions in which the CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$ act as the primary extinguishants and the CF_4 also acts as a fire extinguishant, functioning by smothering the flame, as well as the propellant.

CF_4 boils at -127.9°C ., CBr_2F_2 boils at 24.5°C . and $\text{CF}_2\text{BrCF}_2\text{Br}$ boils at 47.4°C . CF_4 is non-toxic and highly stable, even at quite high temperatures. I have found that solutions of CF_4 in each of CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$ have abnormally high vapor pressures at low temperatures, deviating widely from Raoult's law, which vapor pressures could not be predicted. Such deviation apparently decreases with increase in temperature. Also, CF_4 is quite soluble in each of CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$. Because of such properties of CF_4 and solutions thereof in CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$, about 2.5% of CF_4 by weight of the liquid will provide sufficient pressure at low temperatures (of the order of about 100 p. s. i. g. at -65°F .) to meet the requirements of a self-propelling fire extinguishant liquid, and will develop only moderate pressures at high temperatures. Also, such amount of CF_4 is sufficient to maintain the pressure to the degree required during the entire discharge, and so that a brief accidental discharge of the gas phase, while the container is inverted, does not lead to excessive loss of pressure. For most purposes and particularly for use as a fire extinguishant, the liquid will contain from about 2.5% to about 10% by weight of CF_4 and, preferably, from about 5% to about 10% by weight. For other purposes and particularly where the composition is to be used only at atmospheric temperatures or above, smaller proportions of CF_4 , down to about 1% by weight, may be used, 1% providing pressures of about 25 to 30 p. s. i. g. at -65°F . More than 10% by weight of CF_4 can be employed where the resulting higher pressures are desired.

When liquids are dissolved in each other, the expected result is that the vapor pressure exerted by each component ("partial pressure") will be approximately equal to the vapor pressure of the pure component multiplied by the mole fraction of that component present in the mixture (Raoult's law), and that the total pressure of the mixture will be the sum of the pressures of the individual components (the "partial pressures"). At -65°F ., CF_4 has a vapor pressure of 420 pounds per square inch absolute (p. s. i. a.). At this temperature, the vapor pressures of CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$ are a small fraction of one p. s. i. a. and are thus negligible, and the vapor pressure of CBrF_3 (B. P. -60°C .) is approximately 20 p. s. i. a. CBrF_3 represents the

4

expected case—only a small deviation from Raoult's law; while, with CBr_2F_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$, the actual pressure is 3 to 4 times that calculated by Raoult's law. This may be seen in the following Table I, where observed and calculated vapor pressures in p. s. i. a. are compared:

Table I

Compounds	Composition of the Liquid Phase		Vapor Pressure at -65°F . p. s. i. a.	
	Weight Percent	Mole Fraction	Calculated by Raoult's Law	Observed
$\text{CF}_2\text{BrCF}_2\text{Br}$	93.6	.833	70	215
CF_4	6.4	.167		
CBr_2F_2	95.0	.888		
CF_4	5.0	.112	47	215
CBr_2F_2	68.3	.56		
CF_4	31.7	.44		
CBrF_3	90.8	.853	79	81
CF_4	9.2	.147		

The disadvantages of the "normal" case, as represented by CBrF_3 , are the large proportion of the propellant required (above table) to give adequate discharge pressure at low temperature and the high pressure developed thereby at higher temperatures, as shown in the following Table II, wherein the pressures are given in pounds per square inch gauge (p. s. i. g.):

Table II

Compounds	Composition of the Liquid Phase, Weight Percent	Observed Vapor Pressure, p. s. i. g.	
		at -65°F .	at $+77^\circ\text{F}$.
$\text{CF}_2\text{BrCF}_2\text{Br}$	93.6	200	460
CF_4	6.4		
CBr_2F_2	95.0		
CF_4	5.0	200	430
CBr_2F_2	68.3		
CF_4	31.7		
CBrF_3	90.8	66	420
CF_4	9.2		

The disadvantage of nitrogen lies in its deficiency in gaseous volume as compared to CF_4 . This is shown by the number of vessel volumes of gaseous propellant at -65°F . and 100 p. s. i. g., i. e., the number of times the propellant present in the particular mixture would fill the vessel at -65°F . if the pressure were reduced to 100 p. s. i. g. The smaller the number of vessel volumes, the less effective is the propellant. The data are given in the following Tables III and IV for a vessel liquid full at 150°F ., the values in Table IV being for -65°F . except where indicated otherwise:

Table III

Compounds	Composition of the Liquid Phase, Weight Percent	Observed Vapor Pressure, p. s. i. g.		Number of Vessel Volumes of Gaseous Propellant at -65°F . and 100 p. s. i. g.
		at -65°F .	at $+150^\circ\text{F}$.	
$\text{CF}_2\text{BrCF}_2\text{Br}$	93.6	200	605	3.6
CF_4	6.4			
$\text{CF}_2\text{BrCF}_2\text{Br}$	99.6	400	605	1.2
Nitrogen.....	0.4			
CBr_2F_2	95.0	200	520	3.0
CF_4	5.0			
CBr_2F_2	99.7	300	520	1.0
Nitrogen.....	0.3			

Table IV

Compounds	Composition of the liquid phase		Volume of Vessel (cc.) ¹	Volume liquid (cc.)	Volume gas (cc.)	Weight in gas phase (grams)
	Wt. Percent	Grams				
CF ₂ BrCF ₂ Br	93.6	259.9	143	122	21	0
CF ₄	6.4	17.8				1.5
CF ₂ BrCF ₂ Br	99.6	259.9	136	113	23	0
N ₂	0.4	1.0				1.0
CBr ₂ F ₂	95.0	209.8	108	86	22	0
CF ₄	5.0	11.0				1.6
CBr ₂ F ₂	99.7	209.8	103	82	21	0
N ₂	0.3	0.6				0.7

¹ Vessel liquid full at 150° F.

From the experimentally determined vapor pressure relationships and other data above given, the variation in pressure during discharge of representative solutions were calculated, and the calculated results of the solutions of CF₄ and nitrogen, respectively, in CF₂BrCF₂Br were employed to produce the graph shown in the accompanying drawing.

The corresponding curves for corresponding solutions of CF₄ and nitrogen, respectively, in CBr₂F₂ would apparently be nearly identical with those shown in the drawings. This is based on three calculated values for each solution, shown in the following Table V:

Table V

Compounds	Composition of liquid phase, Weight percent	Percent Liquid Discharged	P. s. i. g.
CBr ₂ F ₂	95.0	0	200
CF ₄	5.0	50	151
		100	103.5
CBr ₂ F ₂	99.7	0	200
Nitrogen	0.3	50	79
		100	42

From such graph and calculations, it is apparent that the pressure during the discharge is much better maintained by CF₄ than by nitrogen at low temperatures, when the discharge is slow so that there is equilibrium between the liquid and the gas during the discharge. The amount of CF₄ in the system is much greater than the amount of nitrogen and, therefore, after a certain percentage of the solution has been expelled, there will be a much larger amount of propellant remaining in the container when the propellant is CF₄ than when the propellant is nitrogen. Usually, in practice, the orifice of the container is opened wide fairly quickly, resulting in a sudden rapid discharge so that the propellant equilibrium between the liquid and the vapor cannot be maintained and, for a given amount of liquid discharged, the proportion of propellant expelled will be higher and the fall in pressure will be more rapid than shown by the graph. In such latter case, the advantage of CF₄ over nitrogen would be even greater than that shown in the graph, because of the larger amount of the CF₄ propellant available.

As is usual in the case of self-propelling compositions, the compositions of my invention will be maintained under pressure in a hermetically sealed container, such as a fire extinguisher, which is provided with a discharge orifice and a valve for controlling the flow of material through the orifice. The valve is normally closed to prevent passage of either gas or liquid through the orifice and is opened for expelling the liquid

through the orifice and directing it against an object to which it is to be applied. Such containers are well known and conventional and any of them, that will withstand the pressures involved, may be used.

It will be understood that the specific solutions disclosed in the tables are given for illustrative purposes solely and that the proportions of CF₄ dissolved therein may be varied as indicated in the general description. It is also apparent that mixtures of CBr₂F₂ and CF₂BrCF₂Br, in any desired proportions, may be used and the CF₄ can be dissolved therein in the same proportions as in the individual compounds.

From the preceding disclosure, it will be apparent that I have provided novel self-propelling liquid compositions having unusual properties and which are suitable for use over a very wide range of temperature conditions. Such compositions have exceptional and particularly desirable properties for use at low temperatures. Therefore, it will be apparent that my invention constitutes a very valuable contribution to and advance in the art.

40 I claim:

1. A self-propelling liquid composition consisting essentially of a solution of CF₄ in a member of the group consisting of CBr₂F₂ and CF₂BrCF₂Br, in which the CF₄ constitutes from about 2.5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

2. A self-propelling liquid composition consisting essentially of a solution of CF₄ in a member of the group consisting of CBr₂F₂ and CF₂BrCF₂Br, in which the CF₄ constitutes from about 5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

3. A self-propelling liquid composition consisting essentially of a solution of CF₄ in a member of the group consisting of CBr₂F₂ and CF₂BrCF₂Br, in which the CF₄ constitutes from about 5% to about 6.4% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

4. A self-propelling liquid composition consisting essentially of a solution of CF₄ in CBr₂F₂, in which the CF₄ constitutes from about 2.5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

5. A self-propelling liquid composition consisting essentially of a solution of CF₄ in CBr₂F₂, in which the CF₄ constitutes from about 5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

6. A self-propelling liquid composition consist-

ing essentially of a solution of CF_4 in $\text{CF}_2\text{BrCF}_2\text{Br}$, in which the CF_4 constitutes from about 2.5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

7. A self-propelling liquid composition consisting essentially of a solution of CF_4 in $\text{CF}_2\text{BrCF}_2\text{Br}$, in which the CF_4 constitutes from about 5% to about 10% by weight of the liquid, said composition being maintained in a confined space under a pressure corresponding to its vapor pressure.

BERNHARDT J. EISEMAN, Jr.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,926,396	Midgley et al. _____	Sept. 12, 1933
2,021,981	Bichowsky _____	Nov. 26, 1935
2,529,092	Lodes _____	Nov. 7, 1950