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A REVIEW OF THE TOXIC PROPERTIES OF SOME VAPORIZING LIQUID FIRE EXTINGUISHING AGENTS

by

P. F. THORNE

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SUMMARY

The toxic properties of six well-known vaporizing liquids have been compared with those of carbon dioxide and nitrogen, having regard to their relative extinguishing properties. Criteria for the choice of vaporizing liquids have been suggested.

DEPARTMENT OF THE ENVIRONMENT AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

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Introduction

The toxicity of vaporizing liquid extinguishing agents is an important factor governing their use and this note is an attempt to present all the available information, and to suggest criteria by which selection of vaporizing liquids can be made.

Vaporizing liquids are the halogenated derivatives of simple hydrocarbons, usually the lower paraffins, the halogens involved being fluorine, chlorine and bromine. The physical properties of the six best-known agents are given in Table 1, together with comparable values for carbon dioxide and nitrogen.

Nature of the toxic hazards of vaporizing liquids

There are three main toxic hazards associated with vaporizing liquids:

(1) A chronic exposure hazard arising from long term exposure to low concentrations of undecomposed agents.

(2) An acute exposure hazard resulting from short exposures to medium or high concentrations of undecomposed agents.

(3) An acute exposure hazard due to exposure to the agent which may have partially decomposed in a fire situation.

Hazard (1) refers to a situation in which personnel may be exposed over a period of time, for example to small amounts of agent arising from leaks in equipment or from continual handling of the substance. This would not be a serious hazard if the "Maximum Permissible Concentration" (M.P.C.) for long term exposure is above the odour threshold value. Table 2 lists the values of "M.P.C." for vaporizing liquids together with those values of odour threshold which are available. Where there are comparative values, it may be seen that the odour threshold value is higher than the "M.P.C.", and consequently the hazard could be serious unless regular monitoring were carried out.

Two situations need to be distinguished for hazard (2). The first is a situation in which the concentration is high enough to cause unconsciousness or death after an exposure of, say, 15 minutes. The second is a situation in which the concentration is not high enough to produce unconsciousness but may be high enough to produce symptoms of narcosis, e.g. depression of the respiratory system and loss of co-ordination. These symptoms are temporarily incapacitating and although they are not normally considered to be dangerous, they may, in a fire situation, place personnel in hazard due to the possible synergistic effect of heat, smoke, products of combustion and physical exertion.

Hazard (3) will occur when vaporizing liquids are discharged onto a fire. Hazard (2) will also exist in this situation but will be enhanced by the presence of pyrolysis products produced when the vaporizing liquid comes in contact with flame or hot surfaces. The pyrolysis products will consist mainly of the acid gases, hydrogen chloride, hydrogen bromide and hydrogen fluoride, according to the composition of the agent. In addition, carbon tetrachloride can produce phosgene (carbonyl chloride). The nature and quantity of the pyrolysis products will depend upon:

1) The agent used,
2) The rate of application,
3) The time taken to extinguish the fire or, if the fire is not controlled, the discharge time,
4) The size of the fire and the volume of the enclosure containing it,
5) The amount of ventilation in the enclosure,
6) The presence of hot metal surfaces.

It is difficult to predict in advance, the composition and concentration of pyrolysis products in any given fire situation.

Physiological action of vaporizing liquids.

The halogenated hydrocarbons are narcotics (anaesthetics) and as such can produce the following physical effects:

(1) Slight disturbance of judgement.

(2) "Drunkeness" associated with bewilderment and lack of control,

(3) Excitement and loss of control,

(4) Surgical anaesthesia (unconsciousness),

(5) Cessation of activity of the respiratory centre followed by death.

Some agents, particularly carbon tetrachloride, may produce systemic affects due to organic damage mainly to the visceral organs. Methyl bromide is also a nerve poison resulting in loss of vision, tremors, limb pains, muscular weakness, amnesia and psychological disturbances. It can also produce congestion and edema of the lung. Appendix I includes a summary of the mode of action of the agents.

Assessment of toxicity data

The toxicity data that is available is based mainly upon experiments using laboratory animals, although there is some data on carbon dioxide for humans.

Animal experiments[3] usually consist of the exposure of test animals to various concentrations of the gas or vapour under investigation for a period of 15 minutes, the concentration being increased in successive experiments by predetermined amounts. The animals are observed for mortality during exposure and for a period of up to 14 days after. On the basis of these results the "Approximate Lethal Concentration" (A.L.C.) is assessed, this being the concentration which will just cause no mortalities during and after the exposure. More elaborate experiments[4] can be performed in which the time of exposure can also be varied. Concentration is plotted against time on a log/log basis and the resulting curves are known as Lethal Concentration Time (LCT) curves. Three criteria are often used:

(1) The LCT (100) curve representing conditions under which all the test animals die.

(2) The LCT (50) curve representing conditions under which half the test animals can be expected to die.

(3) The LCT (0) curve representing conditions under which no test animals die. This is similar to the "A.L.C.".

The third condition is the most relevant for present purposes but is necessarily the sole one. As outlined above, conditions can exist where concentrations less than the "A.L.C." or "L.C.T. (0)" value for a given exposure time can be dangerous due to the early stages of narcosis. Some experiments have included observations of the conditions producing surgical anaesthesia in the test animals. Values of "A.L.C.", "L.C.T. (0)" for 15 minutes exposures and narcosis times are given in Table 3.

Dangerous Concentrations have been listed in Table 4 on the basis of data given in Table 3. For C.T.C., M.B., C.B., B.C.F. and 1.1.1.Trichloroethane, the Dangerous Concentration has been taken as the lowest value of "A.L.C." or "L.C.T. (0)". As indicated in footnote (b) of Table 3, a Dangerous Concentration of 50% has been taken for B.T.M. as at this level of dilution, the oxygen concentration is 10% (the dangerous concentration for humans). A similar figure has been taken for nitrogen. Although animals can survive high concentrations of carbon dioxide, it has been found that 10% carbon dioxide can be dangerous for humans after 10 minutes even when oxygen is added.

Table 4 also lists values of "peak concentrations" as determined in the standard "limits of flammability" apparatus. This is the concentration of extinguishing agent which will prevent propagation of flame in all mixtures of n-hexane vapour and air. Table 4 gives an "Order of Merit" figure for the agents, defined by Krop[2] as the ratio 'R' of the "peak" extinguishing concentration to the dangerous concentration. On the assumption that results of animal experiments are a good indication of the dangerous concentrations expected for humans, then values of 'R' greater than about unity indicate that the agent ought not to be used for total flooding systems in which humans are likely to be involved in the event of accidental discharge. On this basis, only B.C.F., B.T.M., and Nitrogen can be considered safe. Table 4 also gives values of 'K' for the different agents, where 'K' is the ratio of the extinguishing concentration relative by weight to that of carbon dioxide, to the dangerous concentration relative by weight to that of carbon dioxide. 'K' thus provides a measure of comparison of the hazard of the different agents with the hazard of carbon dioxide, values of 'K' above unity indicating a greater hazard, and below unity a lesser hazard than that presented by carbon dioxide.

The agents have been rated in order of increasing toxicity based on a consideration of 'K'. Orders of increasing toxicity based on dangerous concentrations above both on a volume and a weight basis run broadly parallel, with the first agent and the last three agents in the same position, but with some change of positions in between.

The above assessment does not take into account the production of pyrolysis products when the agents are used in a fire situation. The experiments performed to assess this hazard have been of the following types:

(1) The exposure of laboratory animals to pyrolysis products after the vaporised agent has been passed through an iron tube heated to 800°C. The "A.L.C." of the mixture of pyrolysis products and undecomposed agent is determined[3].

(2) Determination of extent of decomposition on passing vapour of the agent through a stainless steel tube at various temperatures[4].

(3) Determination of the extent of decomposition when the vapour of the agent is introduced into the air feeding a small diffusion flame[8, 13].

(4) Determination of the extent of decomposition when the agents are applied to fires contained in enclosures[8, 11, 12, 13].

Table 5 shows results for the type (1) experiments above. The "A.L.C." of the mixture of pyrolysis products and undecomposed agent is compared with the "A.L.C." of the completely undecomposed agent. This comparison shows that the "A.L.C." of the decomposed mixture is substantially lower than that for the original agent except for methyl bromide, which appears to be less hazardous when decomposed, and carbon dioxide which is unchanged.

Table 6 lists the available values of "A.L.C." and "M.P.C. for individual decomposition products and also gives an indication of concentrations likely to cause discomfort.

Table 7 shows the extent of decomposition which occurred in type (2) experiments for C.B., B.C.F. and B.T.M. at temperatures up to 750°C. B.T.M. appears to be the most stable agent in this range.

B.C.F. decomposed less than C.B. up to 650°C, but above this temperature its decomposition was much more marked than that of C.B.

Table 8 shows some results obtained using technique (3). In all cases, dangerous concentrations of free halogens and halogen acid gases were produced, C.T.C. being markedly worse than the other agents investigated.

Table 9 shows results for experiments of type (4) on practical fires. It can be seen that in all cases, the concentrations of acid gases produced would have caused discomfort, and in a few cases would have been harmful. Carbon Tetrachloride in general produced the most dangerous conditions. It is interesting to note that under exceptional circumstances, i.e. a fire in a very small enclosure or a fire not extinguished, agents containing a large proportion of fluorine are capable of producing dangerous concentrations of hydrogen fluoride.

Comparison of Tables 8 and 9 would indicate that the laboratory experiments using gas flames were more severe than the practical fire tests. This is also likely to be true of the experiments involving heated tubes.

The use of vaporizing liquids should be considered in relation to other conditions which are likely to exist in a fire situation. It has been found[14] that except when a fire is very well ventilated, dangerously toxic concentrations of carbon monoxide are always produced. Other toxic products may be present depending on the nature of the combustible, and the hazards can be increased due to the presence of heat, smoke, high humidity, and reduction in oxygen concentration. Any addition, therefore, to the hazards already present is undesirable. A recent development with B.C.F. has been aimed at removing the acid gases produced on decomposition by introducing into the B.C.F. on discharge, a quantity of anhydrous ammonia, the quantity in itself being insufficient to increase the hazard due to accidental discharge[15,16]. The ammonia is designed to neutralise the acid gases, and although no measurements are available, demonstrations have indicated that this does in fact happen, although there is some loss of visibility due to the production of fumes of ammonium halides.

Conclusions

The foregoing review suggests that, of the vaporizing liquids considered, only B.C.F. and B.T.M. would present no toxic hazard in total flooding systems in which the agent was accidentally discharged in the presence of personnel.

When such systems are discharged onto a fire, all agents will produce halogen acide gases by pyrolysis. The evidence available indicates that the incorporation of calculated amounts of ammonia into the system will reduce the hazard due to these products without substantially increasing the toxic hazard on accidental discharge.

Carbon dioxide is generally accepted for use in hand extinguishers in enclosed spaces. It is reasonable to propose that no agent for use in hand extinguishers should present a greater toxic hazard than carbon dioxide. On this basis, methyl bromide, carbon tetrachloride and 1.1.1. trichloroethane would not be acceptable.

Table 1

Some physical properties of vaporizing liquid extinguishing agents with nitrogen and carbon dioxide for comparison

Agent	Chemical formula	Molecular weight	Boiling point (°C)	Freezing point (°C)	Vapour density (air = 1)	Liquid density gm/cm^3 (20°C)	Concn. in saturated air (25°C) p.p.m.	Vapour density of saturated air
Carbon tetrachloride	CCl_4	154	76.8	- 22.8	5.3	1.59	152,000	1.65
Methyl bromide	CH_3Br	95	4.5	- 93.0	3.27	1.73	-	-
Chlorobromomethane	$CH_2Cl\,Br$	129.4	67.0	- 88.9	4.4	1.95	194,000	1.67
Bromochlorodifluoromethane	$CF_2Cl\,Br$	165.4	- 4.0	- 160.5	5.7	1.83	-	-
1.1.1. trichloroethane	$CH_3C\,Cl_3$	133.4	74.1	- 30.6	4.6	1.33	167,000	1.6
Bromotrifluoromethane	$CF_3\,Br$	149	- 58.7	- 166.0	5.2	1.81	-	-
Nitrogen	N_2	28	- 196	- 210	0.97	-	-	-
Carbon dioxide	CO_2	44	- 78.5	- 56.6 at 2 atm.	1.5	-	-	-

Table 2

"M.P.C." and odour threshold values for vaporizing liquids

Agent	"M.P.C." value(6)		Odour threshold value (p.p.m.)
	p.p.m.(a)	mg/m^3	
Carbon Tetrachloride	10	65	79
Methyl bromide	10	35	"High"
Chlorobromomethane	200	1050	400
Bromochlorodifluoromethane	Not yet established(b)		-
1.1.1. trichloroethane	350	1900	"Not a strong odour" 500
Bromotrifluoromethane	1000	6100	-
Carbon dioxide	5000	9000	Odourless
Nitrogen	-(c)	-(c)	Odourless

(a) 1,000 p.p.m. = 0.1 per cent by volume

(b) Likely to be 500 p.p.m. to 1000 p.p.m.

(c) Not available, but likely to be less than 200,000 p.p.m. (equivalent to approximately 17 per cent oxygen)(7).

Table 3

Toxicity of undecomposed vaporizing liquids towards laboratory animals

Agent	A.L.C.(3) for rats per cent by volume	L.C.T.(6)15 min(4) per cent by volume		Narcosis time (min) at A.L.C. for rats(3)	Narcosis times for conc'ns less than A.L.C.(3)		Underwriters classification (see Appendix 2)
		Rats	Guinea pigs		Time (min)	Conc'n (%V/v)	
Carbon tetrachloride	2.9	1.2	2.0	5.0	8-10	1.1	2
Methyl bromide	0.6	–	–	10.0	15	Not stated	2
Chlorobromomethane	6.4	2.6	2.8	1.0	5	2.7	3
Bromochlorodifluoromethane	32.6	28.0	24.0	1.0	8 15	12.2 10.0	5
Bromotrifluoromethane	83.4(b)	83.0(b)	80.0(b)	1.0	15	32.2	6
1.1.1.Trichloroethane	–	2.2(1)	–	–	–	–	–
Carbon dioxide	65.6(a)	65.0(a)	40.0(a)	1.0	1.0	60	5
Nitrogen	–(c)	–(c)	–(c)	–	–	–	6

Notes

(a) Ref (5) shows that 10% can be dangerous for humans after 10 minutes exposure even when oxygen is added. This concentration of carbon dioxide would also reduce oxygen concentration to a dangerous level for humans (see note (b)).

(b) Corresponding oxygen concentration approximately 4%. Humans suffer asphyxiation if oxygen concentration falls below 10% for these exposure times; this corresponds to 50% of added diluent.

(c) Figure for humans will be 50% (see note (b)).

Table 4

Comparison of toxicity and extinction properties of vaporizing liquids, carbon dioxide and nitrogen

Agent	Dangerous concentrations (DC)			Extinguishing concentration (EC)			$R = \frac{EC}{DC}$	$K = \frac{B}{A}$	Order of increasing toxicity	Order based on volume DC	Order based on weight DC
	% $^v/_v$	lb/1000 ft^3	Wt.rel. to CO$_2$ (A)	% $^v/_v$	lb/1000 ft^3	Wt.rel to CO$_2$ (B)					
C.T.C.	1.2	5.1	0.43	9.7(8)	41.4	1.24	8.1	2.9	7	7	7
M.B.	0.6	1.6	0.13	7.1(8)	19.0	0.57	11.8	4.4	8	8	8
C.B.	2.6	9.2	0.77	6.35(8)	22.0	0.66	2.4	0.86	4	5	5
B.C.F.	24.0	110.0	9.2	5.2(9)	24.0	0.72	0.22	0.08	2	3	2
B.T.M.	50.0(b)	210.0(b)	17.5	4.9(8)	20.4	0.61	0.098	0.035	1	1 =	1
1.1.1.Tri-chloroethane	2.2	7.7	0.64	11.5(1)	40.0	1.2	5.25	1.87	6	6	6
CO$_2$	10.0(a)	12.0(a)	1.0	28.0(8)	33.5	1.0	2.8	1.0	5	4	4
N$_2$	50.0(b)	39.0(b)	3.25	42.0(10)	32.8	0.98	0.84	0.3	3	1 =	3

(a) Figure known to be dangerous to humans(5)

(b) Figure corresponding to an oxygen concentration of 10%

Table 5

A.L.C. of pyrolysed agents against laboratory animals

Agent	"A.L.C." of pyrolysis products		Narcosis time at "A.L.C."(min)	"A.L.C." (dec) / "A.L.C." (undec)
	p.p.m.	mg/1		
C.T.C.	319	2.2	4.0	0.027
M.B.	16,400	63.0	5.0	2.74
C.B.	4,180	22.0	10.0	0.16
B.C.F.	7,650	52.0	8.0	0.033
B.T.M.	14,100	86.0	10.0	0.028
CO^2	687,000	1,235	0.25	1.0

Table 6

Dangerous concentrations of pyrolysis products (p.p.m.)

Product	"A.L.C."	Discomfort at:	"M.P.C."
HF	50	10	3.0
HCl	1000	35	5.0
HBr	-	-	3.0
F_2	-	-	0.1
Cl_2	40	-	1.0
Br_2	40	-	0.1
$COCl_2$	50	10	0.1

Table 7

Extent of decomposition of vaporizing agents at high temperatures (Mole %)(3)
contact time 2.2 seconds
stainless steel tube 0.21" I.D.

Temp. (°C)	Agent		
	CB	B.C.F.	B.T.M.
450	0	0	0
500	6	0	0
550	14	2	0
600	22	7	4
650	30	18	10
700	38	66	19
750	49	100	34

Table 8

Decomposition products of vaporizing liquids when contacted with coal gas flame(⌿)13

Agent	% Agent in mixture	Range of concentrations (p.p.m.)					% decomposition
		Cl_2	Br_2	H Cl	H Br	H.F.	
C.T.C.*	1.5 - 4.3	3,000 to 12,000	-	54,000 127,000	-	-	46 - 85
M.B.	1.0 - 1.9	-	1,000 to 2,000	-	8,000 to 16,000	-	83 - 100
C.B.	1.0 - 3.0	-	1,000 to 4,000	8,000 33,000	5,000 to 32,000	-	66 - 93 based on Cl_2 78 - 89 " " Br_2
B.T.M.	1.0 - 2.0	-	2,000 to 4,000	-	7,000 to 17,000	11,000 to 25,000	26 - 32 based on F_2 73 - 100 " " Br_2

(⌿) Agent introduced with the dried air feeding a small coal gas diffusion flame

* Carbonyl chloride not measured in decomposition products

Table 9

Decomposition products of vaporizing liquids used to extinguish fires

Fire detail	Agent	Max. acid conc'n. (p.p.m.)				Max. halogen conc'n (p.p.m.)			Amount of decomposition (%)	Remarks	Ref.
		H Cl	H Br	H.F.	Total	Cl_2	Br_2	Total			
27.5 cm dia. Hexane in 525 ft^3	C.T.C.				50				0.7	Agent directed onto fire	(13)
	C.B.				150				1.3	" " " "	
	M.B.				50				2.7	" " " "	
	B.T.M.				250				3.3	" " " "	
20 cm dia. Hexane in 525 ft^3	C.T.C.				480				1.7	Agent directed onto fire	(13)
	C.B.				80				0.6	" " " "	
	M.B.				70				1.6	" " " "	
	B.T.M.				130				0.7	" " " "	
27.5 cm dia. Hexane fire in 525 ft^3	C.T.C.				600				0.8	Agent directed into enclosure, not directly onto fire	(13)
	C.B.				90				0.2		
	B.T.M.				150				0.4		
1' x 1' methylated spirit in 75 ft^3	B.C.F.				29.2			6.8		Agent directed onto fire	(12)

Cont'd .....

Table 9 (cont'd)

Fire detail	Agent	Max. acid gas conc'n (p.p.m.)				Max. halogen conc'n (p.p.m.)			Phosgene conc'n. (p.p.m.)	Remarks	Ref.
		H Cl	H Br	H.F.	Total	Cl_2	Br_2	Total			
2' x 2' petrol in 3800 ft^3	C.B.	–	21	–	21	1	3	4.0	–	Agent directed onto fire	(12)
	B.C.F.	1	29	1	31	–	7	7.0	–	" " " "	(12)
1' x 1' petrol in 56 ft^3	B.C.F.	90	170	180	440	–	2	2	2	Agent directed onto fire	(11)
	C.B.	68	75	–	145	–	1	1	2	Fire extinguished	
	C.T.C.	375	–	–	375	–	–	–	48		
2' x 1' petrol in 850 ft^3	B.C.F.	13	11	30	54	2	–	2	1	Agent directed onto fire	(11)
	C.B.	13	16	–	29	2	–	2	2	Fire extinguished in	
	C.T.C.	1100	–	–	1100	–	19	19	37	3 – 4 seconds	
2' x 1' petrol in 850 ft^3	B.C.F.	250	92	180	522	–	6	6	3	Equal quantities of agent	
	C.B.	175	33	–	208	–	4	4	5	directed into fire.	
	C.T.C.	450	–	–	450	5	–	5	26	No extinction.	
	B.T.M.	–	22	66	88	–	1	1	2		

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Appendix I

Physiological action of vaporizing liquids

Carbon Tetrachloride	Narcosis plus severe damage to visceral organs which may be enhanced by consumption of alcohol, or by exercise.
Methyl Bromide	Narcosis. MB. is a nerve poison and will also cause lung damage.
Chlorobromomethane	Narcosis plus irritation of the lungs.
1.1.1. Trichloroethane	Narcosis - very little damage to viscera.
Bromochlorodifluoromethane	Narcosis.
Bromotrifluoromethane	Narcosis plus some lung damage. Low B.P. may cause freezing of skin and eyes on contact with liquid.
Carbon dioxide	Paralysis of respiratory centre.
Nitrogen	Simple asphyxiant.

Appendix 2

Underwriters' Laboratories classification of comparative life hazard of gases and vapours

Group	Definition	Classification of vaporizing liquids(2)
1	Gases or vapours which in concentrations of the order of ½ to 1 per cent for duration of exposure of the order of five minutes are lethal or produce serious injury.	
2	Gases or vapours which in concentrations of the order of ½ to 1 per cent for duration of exposure of the order of ½ hour are lethal or produce serious injury.	Methyl Bromide Carbon Tetrachloride
3	As above but 2 to 2½ per cent for 1 hour.	Chlorobromomethane
4	As above but 2 to 2½ per cent for 2 hours.	
5	Intermediate between groups 4 and 6	Carbon Dioxide* Bromochlorodifluoromethane
6	As for above but 20 per cent for 2 hours.	Bromotrifluoromethane

*Note that CO_2 produces anaesthetic effects in 10 minutes at 10 per cent concentration. Death can occur within minutes on exposure to 20 per cent-30 per cent.