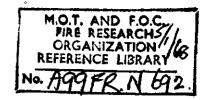# Fire Research Note
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THE TOXIC AND EXTINCTION PROPERTIES OF
MIXTURES OF VAPORIZING LIQUIDS

by

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# FIRE
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## SUMMARY

Methods for calculating the toxicity and peak concentration of mixtures of vaporizing liquid extinguishing agents are discussed.

The results for a proprietary mixture have been assessed, and compared with those of its constituents, and other agents.

MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE

JOINT FIRE RESEARCH ORGANIZATION

# THE TOXIC AND EXTINCTION PROPERTIES OF MIXTURES OF VAPORIZING LIQUIDS

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## INTRODUCTION

The toxic properties of individual vaporizing liquids have been reviewed[1], but some extinguishers contain mixtures of different vaporizing liquids, for example 1.1.1. trichloroethane and chlorobromomethane. This note outlines a method for calculating the dangerous concentration of such mixtures. In order to assess the relative toxic hazard presented by mixtures of vaporizing liquid extinguishing agents, the 'peak concentration' for extinction is also required. Experimental values of this quantity are not always available for mixtures and methods of estimation are therefore discussed.

The toxic hazard of a proprietary liquid mixture of 80 per cent $^V/v$ 1.1.1. trichloroethane and 20 per cent $^V/v$ chlorobromomethane, for which an experimental value of peak concentration is available, has been assessed and related to those of other vaporizing liquids according to the criteria suggested in the above-mentioned review.

## THE TOXIC PROPERTIES OF A MIXTURE OF VAPORIZING LIQUIDS

A mixture of vapours having very similar toxic properties is considered below and it is assumed that the effects of components are additive. Possible synergistic effects have been ignored.

Let $\gamma_T$ = dangerous concentration of the mixture in air
(per cent by volume)

$\gamma_i$ = dangerous concentration of an individual component i in air
(per cent by volume)

$C_i$ = concentration of component i in a dangerous mixture in air
(per cent by volume)

$x_i$ = volume fraction of the dangerous mixture occupied by component i.

$$\therefore \quad C_i = x_i \gamma_T \tag{1}$$

and

$$\frac{C_i}{\gamma_T} = x_i \tag{2}$$

For a dangerous concentration of a mixture to occur

$$\frac{c_i}{\gamma_i} \geqslant 1 \tag{3}$$

Combining (1) and (3)

$$\sum \left(\frac{x_i \gamma_T}{\gamma_i}\right) = 1$$

or

$$\gamma_T = 1 / \sum \left(\frac{x_i}{\gamma_i}\right) \tag{4}$$

If the vapour mixture is formed by partial evaporation from a liquid surface, then the composition of the vapour mixture formed under these circumstances will be richer in the more volatile component/s and consequently will have a toxicity different from that resulting from complete evaporation of the mixture.

Let $f_i$ = mole fraction of component  i  in the liquid mixture

$p_i$ = vapour pressure of component  i  above the liquid mixture

$p_i^o$ = vapour pressure of pure component  i

Paoult's law states

$$p_i = f_i . p_i^o \tag{5}$$

also we have

$$c_i = k\, p_i \tag{6}$$

where  k  is a constant.

Therefore re-writing (2) and (3)

$$\sum \frac{c_i}{\gamma_T} = \sum \frac{c_i}{\gamma_i} = 1 \tag{7}$$

Combining  with (5) and (6)

$$\gamma_T = \frac{\sum f_i p_i^o}{\sum \dfrac{f_i p_i}{\gamma_i}} \tag{8}$$

APPLICATION OF THE METHOD TO A PROPRIETARY LIQUID MIXTURE OF 80 PER CENT BY
VOLUME 1.1.1. TRICHLOROETHANE AND 20 PER CENT BY VOLUME CHLOROBROMOMETHANE

(1) Complete vaporization of a liquid mixture

Liquid density of 1.1.1. trichloroethane = 1.33 gm/m

"          "     of chlorobromomethane      = 1.95 gm/ml

The mixture therefore contains $\dfrac{80 \times 1.33 \times 100}{(80 \times 1.33) + (20 \times 1.95)}$ per cent by weight

1.1.1. trichloroethane = 73 per cent

∴ weight per cent of chlorobromomethane  = 27 per cent

vapour density 1.1.1. trichloroethane  = 0.372 lb/ft$^3$

"          "     chlorobromomethane       = 0.356 lb/ft$^3$

$x_1$ (1.1.1. trichloroethane) = 0.72

$x_2$ (chlorobromomethane)      = 0.28

From Ref.(1) Table 4

$\gamma_1$ = 2.2 per cent

$\gamma_2$ = 2.6 per cent

From equation (4)   $\gamma_T$ = 2.30 per cent (8.45 lb/1000 ft$^3$)

(2) Partial evaporation from quid surface

Molecular weight 1.1.1. trichloroethane  = 133.4

"          "     chlorobromomethane       = 129.4

$f_1$ = 0.72

$f_2$ = 0.28

$p_1^o$ = 127 mm Hg

$p_2^o$ = 157 mm Hg

From equation (8)

$\gamma_T$ = 2.32 per cent

It can be seen that in this particular case, the toxicity of the partially
evaporated mixture is little different from that of the completely vaporized
mixture. If, however, the volatiles and/or the dangerous concentrations of
the components are markedly different from each other, then greater differences
in the toxicities of the completely vaporized and partially vaporized mixtures
can be expected.

# EXTINCTION PROPERTIES OF MIXTURES OF VAPORIZING LIQUIDS

The method of Le Chatelier is recommended by Coward and Jones[4] for the calculation of peak (extinguishing) concentrations of mixtures of chemically inert gaseous inhibitors such as nitrogen, carbon dioxide, argon. The formula is similar to that used above for the calculation of dangerous concentrations of mixtures and can be written:

$$P = \frac{\sum y_i}{\sum \left(\frac{y_i}{P_i}\right)} \qquad (9)$$

where   $P$ = 'peak' concentration of the mixture

$y_i$ = concentration of component $i$

$P_i$ = 'peak' concentration of component $i$

This method can be used for calculating peak concentrations of mixtures of components, the peak concentrations of which all occur at the same fuel/air ratio. This is not necessarily the case for halogenated hydrocarbons.

Malcolm[2] suggested a method for estimating peak concentrations of pure halogenated hydrocarbons in which an 'atomic resistivity' was assigned to each halogen atom in the molecule. The values of 'atomic resistivity' were:

|  |  |
|---|---|
| Fluorine | 1 |
| Chlorine | 2 |
| Bromine | 10 |
| Iodine | 16 |

The peak concentration was calculated from the formula

$$\text{Peak concentration} = \frac{100}{\text{'atomic resistivities'}} \qquad (10)$$

Belles[3] modified this approach by including a value for any hydrogen in the molecule. His values were

|  |  |
|---|---|
| Fluorine | 1 |
| Chlorine | 1.9 |
| Bromine | 5.1 |
| Iodine | 13.4 |
| Hydrogen | 2.9 |

The peak concentration was then calculated in a similar way. This method could be used for mixtures if the peak concentrations of the components occurred at the same fuel/air ratio.

The peak concentration of the 1.1.1. trichloroethane/chlorobromomethane mixture has been determined experimentally at J.F.R.O. The limit curve showed that a peak value occurred with a mixture containing 9.2 per cent of the inhibiting mixture. There was, however, a small detached region at 10.75 per cent at which flame was propagated for a distance of 2 ft from the point of ignition. This was also a 'peak concentration' and was considered to be the accepted value.

For comparison, a 'peak concentration' for the mixture has been calculated for the mixture using the three methods outlined above. The results are given in Table 1 below.

Table 1

Comparison of experimental and calculated peak values for the mixture

| Agent | Experimental peak concentration | Calculated peak concentration | | |
|---|---|---|---|---|
| | | Coward & Jones | Malcolm | Belles |
| 1.1.1. Trichloroethane | 11.5 | – | 16.7 | 6.9 |
| Chlorobromomethane | 6.35 | – | 8.35 | 7.8 |
| Proprietary mixture | (10.75<br>( 9.2 | 9.65 | 13.7 | 7.1 |

It can be seen that the additive technique recommended by Coward and Jones predicts the peak concentration of the mixture satisfactorily considering the uncertainty in the experimental value. The methods of Malcolm and Belles are unreliable for 1.1.1. trichloroethane and chlorobromomethane and mixtures of the two.

ASSESSMENT OF PROPRIETARY LIQUID MIXTURE CONTAINING 80 PER CENT BY VOLUME BY VOLUME 1.1.1. TRICHLOROETHANE AND 20 PER CENT BY VOLUME CHLOROBROMOMETHANE

1) Acute exposure hazard

The dangerous concentration of the vapour mixture has been calculated to be 2.3 per cent and the 'peak concentration' has been determined to be 10.75 per cent (or 9.2 per cent).

Table 2

| Agent | Dangerous concentration (DC) | | | Extinguishing concentration (EC) | | | $R = \dfrac{EC}{DC}$ | $K = \dfrac{B}{A}$ |
|---|---|---|---|---|---|---|---|---|
| | Per cent v/v | lb/1000 ft$^3$ | Wt. rel to $CO_2$ (A) | Per cent v/v | lb/1000 ft$^3$ | Wt. rel to $CO_2$ (B) | | |
| Chlorobromomethane | 2.6 | 9.2 | 0.77 | 6.35 | 22.0 | 0.66 | 2.4 | 0.86 |
| 1.1.1. Trichloroethane | 2.2 | 7.7 | 0.64 | 11.5 | 38.0 | 1.14 | 5.75 | 1.78 |
| Mixture of 80 per cent 1.1.1 Trichloroethane) 20 per cent Chlorobromomethane ) | 2.3 | 8.45 | 0.70 | (10.75 ( 9.2 | 39.5 33.8 | 1.18 1.0 | 4.65 4.0 | 1.69 1.43 |
| Carbon dioxide | 10.0 | 12.0 | 1.0 | 28.0 | 33.5 | 1.0 | 2.8 | 1.0 |
| Carbon tetrachloride | 1.2 | 5.1 | 0.43 | 9.7 | 41.4 | 1.24 | 8.1 | 2.9 |

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These values are tabulated in Table 2, together with corresponding figures for the pure components, carbon dioxide and carbon tetrachloride taken from reference (1) for comparison. The quantity 'R' in column 8 is the number of dangerous concentrations of the inhibiting vapour required to protect a flammable gas/air mixture at peak concentration level. It is considered[1] that any agent with a value of R greater than unity should not be used in total flooding systems in which humans are likely to be involved in the event of accidental discharge. The quantity K in column 9 provides a measure of comparison of the hazard of the different agents with the hazard of carbon dioxide. Values of K above unity indicate a greater hazard and below unity a lesser hazard than that of carbon dioxide.

It can be seen that the mixture is more toxic than chlorobromomethane but safer than pure 1.1.1. trichloroethane. The mixture presents a greater hazard than carbon dioxide but is about half as toxic as carbon tetrachloride.

2) Chronic exposure hazard

The 'M.P.C.' (maximum permissible concentration) for the mixture, calculated using equation (8) is given in Table 3 together with selected values for comparison.

<u>Table 3</u>

| Agent | 'M.P.C.' (P.P.M.) |
|---|---|
| Chlorobromomethane | 200 |
| 1.1.1. Trichloroethane | 350 |
| 20/80 mixture of above | 280 |
| Carbon dioxide | 5000 |
| Carbon tetrachloride | 10 |

Although the mixture is more toxic than chlorobromomethane for acute exposure to high concentrations, when the hazard is chronic, i.e. due to continual exposure to low concentrations such as can occur with leakage or during handling, then the mixture is about 40 per cent less toxic than chlorobromomethane. It is also almost thirty times less toxic on this basis than carbon tetrachloride.

## CONCLUSIONS

A method for calculating the toxicity of mixtures of vaporizing liquids has been given. The toxicity of mixtures which are liquid at ambient temperatures depends on whether total or partial vaporization occurs. Methods for calculating peak concentrations of these mixtures have been discussed.

It has been calculated that the proprietary liquid mixture containing 80 per cent by volume 1.1.1. trichloroethane and 20 per cent by volume chlorobromomethane is half as toxic as carbon tetrachloride for acute exposure to high concentrations and almost thirty times less toxic than carbon tetrachloride for chronic exposure to very low concentrations. The 'peak extinguishing concentration' of the mixture is about the same as for carbon tetrachloride.

## REFERENCES

(1)  THORNE, P. F.  A review of the toxic properties of some vaporizing liquid fire extinguishing agents.  Fire Research Note No. 659 (1967).

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