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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

THE FLAMMABILITY OF MIXTURES OF ETHYLENE OXIDE AND METHYL BROMIDE

by
E. H. Coleman and G. H. J. Elkins

Summary

It is proposed to use a mixture of ethylene oxide and methyl bromide as a fumigant. The flammable limits of such mixtures have been determined in a standard tube.

It is concluded that vapour mixtures of ethylene oxide and methyl bromide in the proportions of 1 : 2 parts by volume will not form flammable mixtures with air.

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Fire Research Station,
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Herts.

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INTRODUCTION

For some years ethylene oxide has been used as a fumigant especially for the protection of stored dried fruit against attack by insects[1], [2]. In recent years however methyl bromide has been introduced as a fumigant and because of its great penetrative power and toxicity to insects it has superseded some older fumigants[4].

It is proposed to use a mixture of ethylene oxide and methyl bromide vapours as a fumigant and at the request of the Pest Infestation Laboratory Department of Scientific and Industrial Research the flammable limits of such mixtures have been investigated.

Method of fumigation

The usual method of fumigation[2] is to subject the fruit to an atmosphere of carbon dioxide (added in the solid form), and then ethylene oxide, pressurized with 10 per cent of carbon dioxide to facilitate its dispersal, is added from cylinders. The initial carbon dioxide treatment is used to reduce the resistance of the insects to the fumigant. This method of fumigation allows carbon dioxide to diffuse and its concentration to be reduced before admitting ethylene oxide.
When fruit is fumigated, the boxes of fruit are stacked in piles and some time elapses between the admission of the gases and their complete diffusion through the fruit. Thus, at one stage in the process there is a high concentration of ethylene oxide in the spaces between the boxes. By the method recommended,[2] the concentrations of vapours 30 minutes after application should be 1 per cent ethylene oxide and 5 per cent carbon dioxide, but the initial concentration of ethylene oxide may be as high as 12 per cent. Although carbon dioxide reduces the fire hazard, Burgoyne and Williams - Leir (3) showed that under the recommended conditions it is still possible for hazardous atmospheres to be produced.

Previous work

The flammable limits of ethylene oxide and of mixtures of ethylene oxide and carbon dioxide, have been determined by several workers (5, 6, 7), limits of 3·0 and 80 per cent for ethylene oxide in air are quoted by Coward and Jones (5). The upper limit is probably too low because of the difficulty of observing the flames produced. The present authors have found the lower limit of ethylene oxide in air to be 3·75 per cent by volume which agrees with the value of 3·78 per cent found by Burgoyne and Neale (6) and 3·5 per cent found by Smith (7). The peak value of mixtures of carbon dioxide and ethylene oxide was approximately 6 per cent ethylene oxide and 44 per cent carbon dioxide and thus vapour mixtures containing 12 per cent ethylene oxide and 88 per cent carbon dioxide are not flammable whatever their concentration in air.

When using the method of fumigation quoted above the ratio of ethylene oxide to carbon dioxide is just within the flammable range, and the initial ratio is almost certainly well within it. Furthermore, although the concentration of gases after 30 minutes is below the flammable limit, local pockets of higher concentration could exist. The initial concentration is well within the flammable range.

It appears therefore that there is a real hazard arising from the use of mixtures of ethylene oxide and carbon dioxide.

EXPERIMENTAL

Present work

The flammable limits of mixtures of ethylene oxide and methyl bromide were determined at the Joint Fire Research Organization in a standard flammable limits tube (5) at 12°C-14°C. The properties of the two constituents are given in Table 1, and the flammable limits curve obtained is shown in Figure 1.

TABLE 1

The physical properties of ethylene oxide and methyl bromide

Compound	Molecular weight	Density g/ml	Boiling point °C	Flash point °F	Flammable limits in air (per cent by volume)		Vapour pressure (0 °C) mm Hg
					Upper	Lower	
Ethylene oxide C_2H_4O	44·05	1·965	10·7	Below 0	3·75	100	493
Methyl bromide CH_3Br	94·95	1·732	3·56	-	-	-	620

The flammability curve undulates and there are peaks at 6·3, 8·5 and 16 per cent of ethylene oxide corresponding to 10·3, 9·1 and 8·2 per cent of methyl bromide. When the tangent AB drawn to the curve from the origin (air = 100 per cent), it can be shown that mixtures of vapour containing 1 part of ethylene oxide to 2 parts of methyl bromide will not be flammable. The tangent CD drawn from the point ethylene oxide = 100 per cent shows that mixtures of methyl bromide and air containing more than 11 per cent of methyl bromide will not be flammable whatever quantity of ethylene oxide is added.

The experiments were carried out with laboratory grade ethylene oxide, but in practice cylinders of ethylene oxide containing 10 per cent of carbon dioxide would be used. The carbon dioxide would not reduce any fire hazard by a significant degree since the work of previous authors shows that carbon dioxide has little effect on the lower limit.

No investigation was made of the reason for the successive peaks shown in the curve. It is possible that they are related to the observations of other workers that ethylene oxide may burn with a combustion flame, a cool flame, or a decomposition flame.

Conclusions

Mixtures of ethylene oxide and methyl bromide vapours in the proportions 1 : 2 by volume may be safely used in air as a fumigant, provided that the gases are introduced in such a way that the ethylene oxide cannot accumulate in separate pockets.

References

1. W. BURNS BROWN — Application of fumigants to ships and warehouses J. Soc. Chem. Ind. April, 1937. Vol. LVI. pp. 116-122.

2. W. BURNS BROWN and A.E.R. HIGGINS — The control of insects infesting dried fruits. H.M.S.O. 1942.

3. J.H. BURGOYNE and G. WILLIAMS-LEIR — The prevention of ethylene oxide explosions in fumigation chambers Home Office R. & E. Department.F.Division. Imperial College Report No. 95.

4. W. BURNS BROWN — Fumigation with Methyl bromide under gas proof sheets Pest. Inf. Res. Bulletin No.1. H.M.S.O. 1954.

5. H.F. COWARD and G.W. JONES — Limits of flammability of gases and vapours. U.S. Bureau of Mines Bulletin 503. Washington 1952.

6. J.H. BURGOYNE and R.F. NEALE — Limits of inflammability and spontaneous ignition of some organic combustibles in air. Fuel Vol. XXXII No. 1. Jan., 1953.

7. I.E. SMITH — Progress report of work carried out at Imp. Coll. Sci. & Tech., Dept. Chem. Eng. & App. Chem. Dec., 1952.

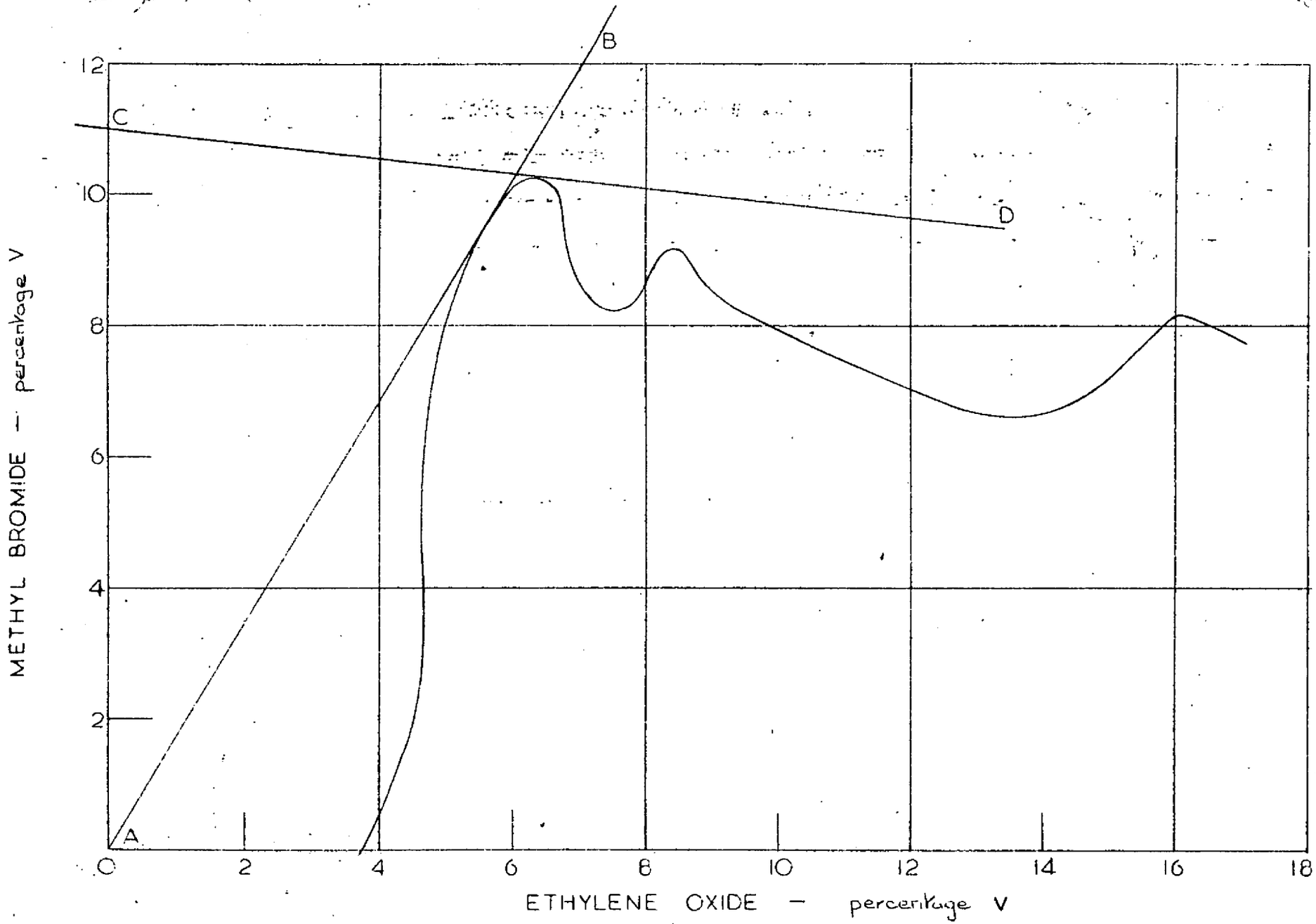

FIG. 1. THE EFFECT OF METHYL BROMIDE ON THE LOWER FLAMMABILITY LIMIT OF ETHYLENE OXIDE IN AIR.