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THE FLAMMABILITY OF MIXTURES OF ETHYLENE DICHLORIDE AND CARBON TETRACHLORIDE USED AS FUMIGANTS.

by

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

Summary

It is proposed to use ethylene dichloride/carbon tetrachloride mixtures to fumigate tobacco in South America. The flammable limits of such mixtures have been determined using a standard tube.

They show that there is little risk of fire or explosion if the mixture contains more than 25 per cent by volume of carbon tetrachloride.

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Introduction

Ethylene dichloride is used commercially as a fumigant for stored grain and it is usually diluted with carbon tetrachloride to reduce the fire hazard. The most commonly used mixture contains 1 part by volume carbon tetrachloride and 3 parts by volume ethylene dichloride but more recently mixtures of the proportions 1:1 and 1·3 carbon tetrachloride to ethylene dichloride have been used. The method of application is to pour the liquid mixture into silos, or over piles of sacks, which are then sheeted over and left for some days. The vapour from the 1:3 mixture of carbon tetrachloride and ethylene dichloride is usually regarded as a negligable fire risk (1). It is proposed to use this mixture to fumigate tobacco in South America, and the present investigation was made to determine the likely fire hazard.

Previous Work

Coward and Jones (2) quote a Russian source (3) that 4·5 per cent of carbon tetrachloride vapour prevents combustion in all mixtures of ethylene dichloride and air. Popov and Beezub (4) examined the flammable limits of mixtures of carbon tetrachloride and ethylene dichloride, at 50°C and at 21-23°C, in a small vessel (75mm long x 45mm diameter), and concluded that below 8°-9°C ethylene dichloride could be used undiluted. At temperatures below 50°C the vapour from a liquid mixture of ethylene dichloride and carbon tetrachloride in the proportions of 3:1 by volume was not flammable. Below 25°C and with less than 4·8 per cent ethylene dichloride vapour in the air, mixtures with a vapour ratio of 86 per cent ethylene dichloride and 14 per cent carbon tetrachloride would be safe. This corresponds to a liquid mixture containing 98·5 per cent ethylene dichloride by volume.

Present Work

The flammable limits of carbon tetrachloride/ethylene dichloride mixtures in air have been measured at the Joint Fire Research Organization in a standard flammable limits tube(5) at 28- 30°C. The properties of the two constituents are given in Table 1, and the flammable limits curve obtained is shown in Figure 1. together with the curve obtained by Popov and Beezub.

TABLE 1.

THE PHYSICAL PROPERTIES OF ETHYLENE DICHLORIDE AND CARBON TETRACHLORIDE

Compound	Mol. Wt.	Liquid Density g/ml.	Boiling Point °C	Flash Point (Closed) °C	°F	Flammable Limits per cent		Vap. Press. mm. Hg. 0°C	10°C	20°C	30°C
						Lower	Upper				
Ethylene Dichloride $C_2H_4Cl_2$	99	1·26	83·7	13·3	56	6·2	15·9*	20	38	66	110
Carbon Tetrachloride CCl_4	154	1·58	76·8	—	—			32	56	91	140

* Upper limit measured at 100°C

The peak value from the curve obtained with the present work, occurs with a mixture of 10·2 per cent ethylene dichloride and 3·5 per cent carbon tetrachloride vapours in air. This corresponds to a liquid mixture of carbon tetrachloride and ethylene dichloride containing 85·5 per cent ethylene dichloride by volume. These figures are somewhat lower tha n those of Popov and Beezub, and the difference may be accounted for by the effect of diffusion with the very small vessel used by those authors. From the graph it seems certain that vapour mixtures containing more than 27 per cent of carbon tetrachloride in ethylene dichloride are not flammable. The Russian curve gives a rather lower figure of 25 per cent.

Application to fumigating conditions

There are two vapour mixtures possible from a liquid mixture containing carbon tetrachloride and ethylene dichloride. When all the liquid evaporates from a mixture in the proportion of 1:3 by volume the ratio of carbon tetrachloride vapour to ethylene dichloride vapour is constant at 1:3·65, and the percentage of ethylene dichloride vapour in the atmosphere depends on the amount evaporated into a given volume of air. If the temperature is too low to permit complete evaporation of both liquids, the vapour concentration will be different and can be calculated from Raoult's law. At 20°C the concentration above the surface of a 1:3 liquid mixture of carbon tetrachloride and ethylene dichloride will be:-

Carbon tetrachloride	2·5	per cent by volume
Ethylene dichloride	6·5	" " " "
Air	91·0	" " " "

The ratio of carbon tetrachloride to ethylene dichloride in this atmosphere is 1:2·6.

The ethylene dichloride/carbon tetrachloride mixtures are applied to grain at the rate of 1 gallon of mixture per 5 tons of grain. The usual mixture contains 1 part by volume carbon tetrachloride to 3 parts by volume of ethylene dichloride. The volume of air voids in grain was calculated from the following data, (Table 2) supplied by the Pest Infestation Laboratory.

TABLE 2

VOLUME OCCUPIED BY DIFFERENT GRAINS

Grain	Volume Occupied per Ton Cu Ft.	Air Voids per cent.
English wheat	48	Approximately 43 for all grains.
Mannitoba wheat	43	
Oats	72	
Barley	57	
Yellow maize	48	

Mannitoba wheat occupies the least space and at 20°C the void space is 92·45 cu.ft. (2618 l), and Oats occupies the most space and at 20°C the void space is 154·8 cu.ft, (4360 l). If total evaporation of the applied liquid took place the concentration of vapour in air present would be as in Table 3.

TABLE 3.

CONCENTRATION OF CARBON TETRACHLORIDE AND ETHYLENE DICHLORIDE VAPOURS ABOVE 5 TONS GRAIN IF TOTAL EVAPORATION OCCURS.

Grain	Carbon Tetrachloride per cent volume	Ethylene Dichloride per cent volume
Mannitoba wheat	8·1	40·0
Oats.	4·75	24·1

Because of its low vapour pressure, this concentration of ethylene dichloride could not be attained except at temperatures above 50°C and consequently over the usual range of atmospheric temperatures, liquid would still be present. The concentrations of the two vapours will then be different from those given in Table 3 and they will vary with the temperature. When the liquid mixture is poured over the grain, some will be absorbed by the grain as liquid and one constituent may be absorbed more than another. The composition of the liquid mixture will thus be affected and in turn the composition of the vapour will be affected. The relative liquid absorptions have not been measured and the calculations have been based on the assumption that the liquid is of the 1:3 composition at 20°C which is outside the flammable mixtures area of Figure 1. In Table 4, an estimation has been made of the amounts of ethylene dichloride and carbon tetrachloride evaporated, based on the calculations from Raoult's Law.

TABLE 4.

AMOUNTS OF CARBON TETRACHLORIDE AND ETHYLENE DICHLORIDE ACTUALLY EVAPORATED

Grain	Percentage Liquid Evaporated		Composition of Atmosphere per cent vol.		
	Carbon tetrachloride	Ethylene dichloride	Carbon tetrachloride	Ethylene dichloride	Air
Mannitoba wheat	31	18	2·5	6·5	91
Oats.	51	29	2·5	6·5	91

The composition of the liquid phase will thus be different from the original 1:3 mixture. If air movements remove the vapour, the composition of the atmosphere in the void spaces will be changed, and over a period of time there will be a tendancy towards an increase in the concentration of ethylene dichloride vapour. It is apparent that the present trend of increasing the carbon tetrachloride proportion of the mixtures is justified since it allows for the loss of a considerable proportion of the carbon tetrachloride in the mixture.

Conclusions.

From the results obtained there appears to be little likelihood of a flammable mixture being formed when liquid mixtures of carbon tetrachloride and ethylene dichloride containing at least 25 per cent of carbon tetrachloride by volume are used as fumigants. In all cases a considerable amount of the liquid fumigant added will be absorbed by the solids being fumigated; and this will mean a substantial reduction in the total vapour/air mixtures produced.

References.

(1) E.U. Crosby, H.A. Fiske, F.W. Forster National Fire Protection Association Handbook of Fire Protection 11th edn. P.120.
(2) H.F. Coward, G.W. Jones, U.S. Bureau of Mines Bulletin 503. page 103.
(3) P.V. Popov and K. Beezub. Trans. Inst. Fertil. and Insectofungicides (U.S.S.R. No.123, 1931-32 pp. 210-214).
(4) P.V. Popov and K. Beezub. Trans. Inst. Fertil and Insectofungicides Moscow, 1939, 2 (135) p. 98-102.
(5) H.F. Coward and G.W.Jones U.S. Bureau of Mines Bulletin 503.

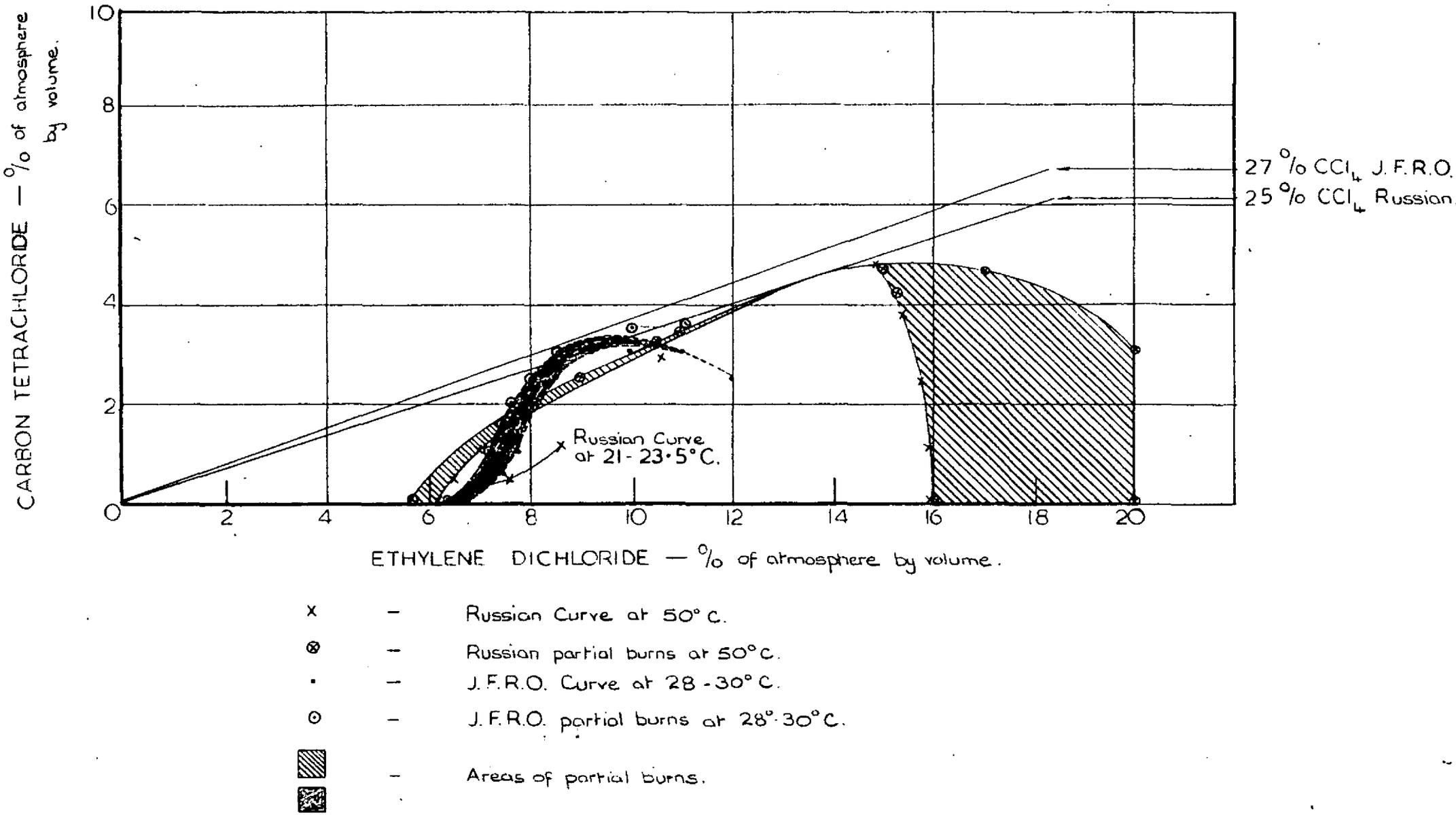

FIG.1. FLAMMABILITY LIMITS OF ETHYLENE DICHLORIDE IN CARBON TETRACHLORIDE

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