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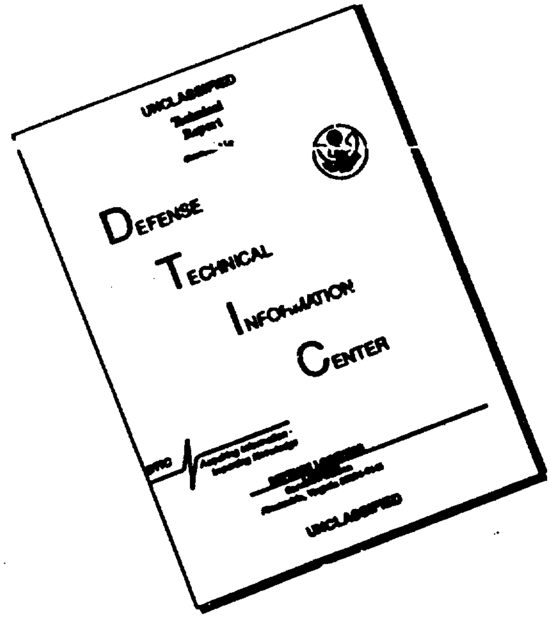

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STUDIES ON FUMIGANT "ETHYLENE OXIDE" (IV)

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Studies on the Fungicidal and Insecticidal Properties of Various Mixtures of Ethylene Oxide and Methyl Bromide

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Introduction

Experiments on the fungicidal and insecticidal properties of ethylene oxide are conducted and reported in paper No 2[1] and No 3[2], confirming its high effectiveness. In paper No 1[3], it was pointed out that the practical utility of ethylene oxide is limited due to its wide range of explosion, and in order to reduce its explosive property, methyl bromide is mixed as an inert gas and investigated for the properties of a fumigant in a mixture system. In this paper, the experimental results on the fungicidal and insecticidal properties of this mixture system and its explosive nature of concentration ranges are reported together with the observations on their practical utility.

I. Experimental Method

1) Fungicidal and insecticidal effect and gas dispersion.

The effects of fungicide and insecticide are measured according to the same method as in paper No 2. The temperature of the fumigant is adjusted to 29°. The measurements on the dispersion of methyl bromide gas are conducted according to the method of Stenger, Shrader and Beshgeton[4]. Namely, the fungi are taken out from the arranged location by means of glass capillary. 50 ml. aliquots are taken out with a hypodermic syringe and absorbed in 1 N KOH in methanol.

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After the absorbed solution is hydrolyzed at 60-65° in a sealed system, a constant amount of N/10 $AgNO_3$ standard solution is added as an acidic HNO_3. These are quantitatively analyzed by adding N/10 KCNS dropwise and using an indicator.

$$CH_3Br + KOH = KBr + CH_3OH$$

$$KBr + AgNO_3 = AgBr + KNO_3$$

$$AgNO_3 + KCNS = AgCNS + KNO_3$$

2) The measurements and investigations on the explosion limit of three components system, ethylene oxide, methyl bromide and air.

In paper No 1, the measurements on the explosion limit are conducted by a flow method. However, as pointed out in III a) and b) of paper No 1, the explosion limit is narrowed sometimes and the experimental errors tend to be large. Therefore, authors have conducted the measurements according to an electric spark method and a metal disconnection method.

a) Electric spark method[5]

As shown in Figure 1, the explosion container is made from glass tube of 345 ml capacity (diameter 66 mm x height 100 mm x thickness 10 mm). A bakelite plate of 12 mm thickness is installed on the bottom part and fixed to the glass tube with an epoxy adhesive. Both the electrodes (Cu line) and gas insertion tube (glass capillary of inner diameter 1 mm) are fixed to the bakelite plate at the bottom part. Electricity is sparked between the 2 mm space of both electrodes using a neon trans as a spark source (first side 100 V; second side 12000 V). The cover at the top is made from a bakelite plate of 12 mm thickness and 120 mm square. Vaseline is used on the contacting part of the cover with glass tube. First, the pressure inside the container is reduced with a vacuum pump until it is lower than that of the gas insertion tube, and then ethylene oxide and methyl bromide gases are injected into the container separately with a hypodermic syringe. Then, the air is injected into the container until the pressure inside becomes normal. In the experiment under an insufficient supply of air, ethylene oxide or methyl bromide gas is first placed in the container and then the amount of air corresponding to the gas needed is taken out (this amount is known by mercury pressure). The constant amount of gas is then injected into the container with a hypodermic syringe to achieve a desired ratio of the mixture. By pushing the switch at a distant place, electricity is sparked and the presence of an explosion is determined.

When the system is in the region of explosion, the cover at the top flies off with a severe sound. Otherwise, the system just sparks without any effect.

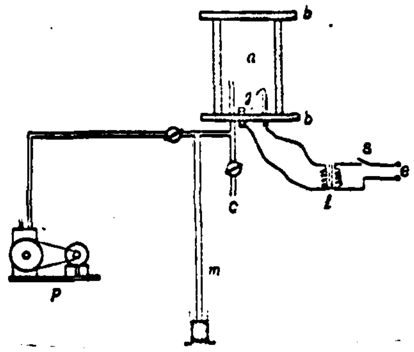

Figure 1

Apparatus for Measuring the Limit of Explosion by an Electric Spark Method

a.	Glass tube	p.	Vacuum pump
b.	Bakelite plate	m.	Manometer
c.	Gas insertion mouth	l.	Neon-trans
g.	Electric discharge space	s.	Push button
		e.	Electric source

b) Metallic line disconnection method

As shown in Figure 2, a rubber line is installed in a 2 liters or 1 liter, wide mouth bottle. Both electrodes (Cu line), glass capillary and a manually operated square stick are fixed. The electrodes are connected with a manganese line (0.1 mm x 5 mm). Gas is inserted in a similar manner as in a). The gas in the bottle is distributed uniformly by means of a manually operated square stick, and then the rubber line is loosened. At the distant place, the electric current of 100 V is passed and the manganese line is disconnected. If the system is in the region of explosion, the rubber line flies apart with a severe sound of explosion. If the system is not in the region of explosion, the manganese line is just cut off.

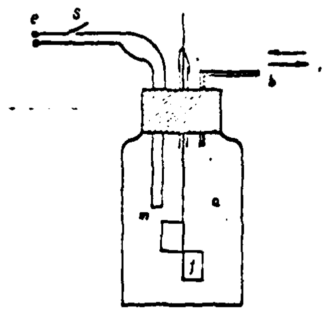

Figure 2

Apparatus for Measurement by Metallic Line Disconnection Method

a. Wide mouth bottle
b. Gas insertion mouth
e. Electric source
f. Manually operated square stick
s. Push button
m. Manganese line

c) Investigations of the method of measurements.

The limit of explosion on two components system, methyl bromide and air, is investigated by the electric spark method and metal disconnection method. The results are shown in Table 1 together with the literature values.

TABLE 1

Limit of Explosion on Two Components System, Methyl Bromide and Air

	Method of Measurement	Limit of Explosion
Experimental values	Electric Spark Method	14~17%
	Metal Disconnection Method	13~16.5%
Literature value (6)	(Electric Spark Method)	13.5~14.5%
Literature value (7)	Metal Disconnection Method	10.0~15.4%

(Total pressure 9.8 Kg/cm^2 5~30%)

From Table 1, it is seen that the values obtained from the electric spark method agree closely with those obtained from the metal disconnection method. Also, if the experimental values are compared with the literature values, the experimental values have a wider range in the electric spark method and a narrow range in the metal disconnection method.

However, the errors are not significant and within ±2%. Thus, the method of these measurements are considered accurate and reliable.

II. Experimental Results and Observations

1) The effects of fungicide and insecticide and gas dispersion.

a) The effects of fungicide

The effects of fungicide are examined for ethylene oxide 25%, methyl bromide 75% and 50% mixture of ethylene oxide and methyl bromide. Also, the effects of ethylene oxide alone are taken from Table 4 of paper No 2 and listed in Table 2 below.

TABLE 2

Fungicidal Effect of Ethylene Oxide and Methyl Bromide Mixture and Ethylene Oxide By Itself

(1) クン蒸剤の種類および薬量	(3) 試料位置 / (2) 微生物	(4) 容量内	(5) (クン蒸時間：24時間の死滅率) (6) 小麦粉袋内		(7) 玄米袋内	
			外側 (a)	中心部 (b)	外側 (a)	中心部 (b)
(8) 臭化メチル200 g/1.5m³	(c) 細菌	89～90	78～80	70～72	80～82	60～62
(9) 酸化エチレン25%・臭化メチル75% 100 g/1.5m³	(c) 細菌	88.0	87.5	78.8	88.8	87.5
	(d) 糸状菌	100	100	*1	100	*1
(10) 酸化エチレン25%・臭化メチル75% 200 g/1.5m³	(c) 細菌	96	94.3	82.5	92.8	86.3
	(d) 糸状菌	100	100	100	100	100
(11) 酸化エチレン50%・臭化メチル50% 200 g/1.5m³	(c) 細菌	100	99.0	98.0	98.3	98.5
	(d) 糸状菌	100	100	100	100	100
*2 (12) 酸化エチレン 200 g/1.5m³	(c) 細菌	96	95.5	91	94	87
	(d) 糸状菌	100	100	100	100	100

(13) *1 *Pen. islandicum* の寄生した玄米粒は殺菌効果を認めたが，*Asp. chevalieri* 寄生の玄米区では完全な効果が得られなかった.

(14) *2 第2報，第4表より抜萃.

Key:
1. Kind and amount of fumigant
2. Micro-organism
3. Location of material
4. Content
5. Time of fuming : 24 hours death rate
6. Flour (a) out side
   (b) central part
7. Unpolished rice (a) outside
   (b) central part
8. Methyl bromide 200 g/1.5 m³ c. Bacterium

Key continued on following page

9.	Ethylene oxide 25% : methyl bromide 75% 100 g/1.5m3	c. Bacterium d. Fibroid bacillus
10.	Ethylene oxide 25% : Methyl bromide 75% 200 g/1.5m3	c. Bacterium d. Fibroid bacillus
11.	Ethylene oxide 50% : Methyl bromide 50% 200 g/1.5m3	c. Bacterium d. Fibroid bacillus
12.	Ethylene oxide 200 g/1.5m3	c. Bacterium d. Fibroid bacillus

13. *1 Insecticidal effects are observed in unpolished rice with a parasitic Pen. islandicum but no insecticidal effects are observed in unpolished rice with a parasitic Asp. chevalieri

14. *2 Taken from Table 4 of paper No 2

As is clear from Table 2, a complete effect of insecticide is obtained for the fibroid bacilli. An examination on the effect of insecticide for a bacterium, when the same amount (200 g/1.5m3) of reagent is used, indicates almost the same degree of activity between ethylene oxide alone and ethylene oxide 25%; methyl bromide 75% mixture. (Extinction rate 82.5% - 96%). When 50% of methyl bromide is added to ethylene oxide, the effectiveness of insecticide is even higher (extinction rate 98% - 100%). In comparing with these, methyl bromide alone has a very low insecticidal effect (extinction rate 60 - 96%). Thus, methyl bromide alone does not give a satisfactory result, but when added to ethylene oxide as an inert gas, the insecticidal effect is not lowered for the same amount as ethylene oxide alone required for fumigating. Thus, its purpose is served.

b) The effect of insecticide

The effects of insecticide during the fumigating time of 10-60 minutes are obtained for 100 g or 200 g/1.5m3 of the mixture of ethylene oxide 25% and methyl bromide 75% and 200 g/1.5m3 of 50% mixture of ethylene oxide and methyl bromide. Table 3 shows the effect of ethylene oxide 25 g/1.5m3 on Kokuzo imago.

When the speed of insecticide on Kokuzo imago from Table 3 is compared with ethylene oxide 25% and methyl bromide 75% mixture of 100 g/1.5m3 and ethylene oxide 25 g/1.5m3, the advantages of adding methyl bromide as an explosion inert gas for ethylene oxide are clearly seen, and 100% of insecticidal effect is obtained after 30 minutes of fumigating.

c) State of gas dispersion

When methyl bromide alone is used as a fumigant at the proportion of 200 g/1.5m3, the gas concentrations in the container, the center part of the unpolished rice bag, and outside and center part of flour

TABLE 3

Insecticidal Effect of Ethylene Oxide and Methyl Bromide Mixture (Numbers are the Extinction Rate)

(1) クン蒸剤の種類および薬量	(2) 供試害虫		(3) クン蒸時間（分） 5	10	15	25	30	35	45	50	60
(4) 酸化エチレン25%・臭化メチル75% 100g/1.5m³	(9)(a) コクゾウ	成虫	—	40	74	86	100	100	100	100	100
		幼虫	—	0	100	100	100	100	100	100	100
		サナギ	—	0	100	100	100	100	100	100	100
		卵	—	100	100	100	100	100	100	100	100
	(b) コクヌストモドキ	成虫	—	100	100	100	100	100	100	100	100
		幼虫	—	100	95	100	100	100	100	100	100
		サナギ	—	—	35	20	20	25	30	50	20
	(c) ナガシンクイ	成虫	—	100	100	100	100	100	100	100	100
(5) 酸化エチレン25%・臭化メチル75% 200g/1.5m³	(9)(a) コクゾウ	成虫	—	82	—	100	98	—	100	100	100
		幼虫	—	0	—	60	80	—	100	100	100
		サナギ	—	40	—	80	40	—	100	100	100
		卵	—	100	—	100	100	—	100	100	100
	(b) コクヌストモドキ	成虫	—	15	—	100	100	—	100	100	100
		幼虫	—	75	—	100	100	—	100	100	100
		サナギ	—	55	—	35	45	—	100	100	100
	(c) ナガシンクイ	成虫	—	65	—	100	100	—	100	100	100
(6) 酸化エチレン50%・臭化メチル50% 200g/1.5m³	(9)(a) コクゾウ	成虫	24	—	—	100	—	—	—	—	—
		幼虫	0	—	—	100	—	—	—	—	—
		サナギ	0	—	—	100	—	—	—	—	—
		卵	100	—	—	100	—	—	—	—	—
	(b) コクヌストモドキ	成虫	10	—	—	100	—	—	—	—	—
		幼虫	35	—	—	70	—	—	—	—	—
		サナギ	20	—	—	50	—	—	—	—	—
	(c) ナガシンクイ	成虫	65	—	—	100	—	—	—	—	—
(7) * 酸化エチレン25g/1.5m³	コクゾウ	成虫	—	—	18	—	66	—	34	—	84

(8) * 第2報第3表抜萃，90分で死滅率100%.

Key:
1. Kind and amount of fumigant
2. Insect
3. Time of fumigation
4. Ethylene oxide 25% : Methyl bromide 75% 100 g/1.5m³
5. Ethylene oxide 25% : Methyl bromide 75% 200 g/1.5m³
6. Ethylene oxide 50% : Methyl bromide 50% 200 g/1.5m³
7. Ethylene oxide 25 g/1.5m³
8. *Taken from Table 3 of paper No 2. Extinction rate 100% at 90 minutes.
9. (a) Kokuzo { imago, larva, chrysalis } (b) Kokunusto modoki { imago, larva, chrysalis }
   (c) Nagashinkui imago

at each time interval are shown in Table 4. From Table 4 it can be seen that the penetration speed of methyl bromide into unpolished rice bag and flour is extremely fast and after 2.5 hours of fumigation, the penetration is complete. On the other hand, the penetration speed of ethylene oxide into flour whose bulk density is high, is slow. (According to Table 5 of paper No 2 the gas concentration in the center part of flour bag at 7 hours of fumigation is only 43% of 23 hours fumigation)

Therefore, both components of the mixture of methyl bromide and ethylene oxide penetrates almost at the same time to the center part of the material whose bulk density is low (for example, unpolished rice), but as the bulk density of the material becomes higher, the penetration of ethylene oxide becomes slower compared with methyl bromide.

TABLE 4

State of Gas Dispersion After Methyl Bromide Is Put In

Amount put in : 200 $g/1.5m^3$

(1) ガス採取位置 (2) 時間	(3) 投薬後の経過時間				
	1	2.5	4	6.5	23.30
(4) 容器内	193.2	199.8	207.3	207.3	196.5
(5) 玄米袋の中心部	162.0	192.0	204.9	220.2	188.7
(6) 小麦粉袋内の外側	172.5	196.5	208.8	204.9	189.0
(7) 小麦粉袋内の中心部	121.5	184.8	186.3	189.0	192.6

(8) 数字はガス濃度を $g/1.5m^3$ に換算したもの

Key:
1. Location of gas taken
2. Time
3. Time past after the reagent is put in
4. In the container
5. Center part of unpolished rice bag
6. Outer part of flour bag
7. Center part of flour bag
8. The numbers express gas concentrations in $9/1.5m^3$

2) Limit of explosion on three components system, methyl bromide, ethylene oxide and air.

The results of measurements by the metal disconnection method and the electric spark method are shown in Figure 3. The results of Figure 3 show almost the same tendency as the results of Figure 2 in paper No 1 which was obtained by a flow method. Alos, from Figure 3, the limits of explosion on ethylene oxide, methyl bromide and ethylene oxide 25% : methyl bromide 75% are obtained and shown in Table 5.

TABLE 5

Limit of Explosion on Methyl Bromide, Ethylene Oxide, and Methyl Bromide 75% : Ethylene Oxide 25%

Component	Limit of Explosion
Ethylene oxide	3 ~ 100%
Methyl bromide	13 ~ 17%
Methyl bromide 75% : Ethylene oxide 25%	8 ~ 22%

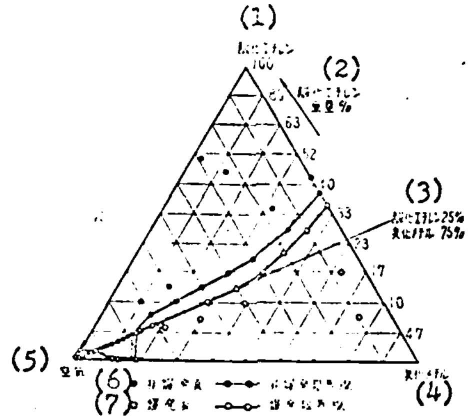

Figure 3

Limit of Explosion on Three Components System, Ethylene Oxide Methyl Bromide and Air

Key:
1. Ethylene oxide
2. Ethylene oxide weight percent
3. Ethylene oxide 25% : methyl bromide 75%
4. Methyl bromide
5. Air
6. • Non-explosion point -•-•- Non-explosion limit line
7. o Explosion point -o-o- Explosion limit line

From Table 5, it can be seen that ethylene oxide has an explosion region of 3-100%, whereas the gas mixture of ethylene oxide 25% and methyl bromide 75% has the explosion region of only 8-22%. Addition of methyl bromide has an extremely beneficial effect on the safety of ethylene oxide.

Next, when the flammability of fumigant containing ethylene oxide, ethylene oxide 75% : methyl bromide 25%, 50% mixture of ethylene oxide and methyl bromide, and ethylene oxide 25% : methyl bromide 75% is examined near a flame, ethylene oxide continues to burn until the liquid is exhausted, but ethylene oxide 75% extinguishes the flame by itself on the way. Ethylene oxide, 50% has the shorter burning period and 25% of the ethylene oxide burns when a flame is contacted, but extinguishes when the flame is separated. Thus, addition of 75% methyl bromide eliminates the flammability.

If the explosion ranges 8-22% of ethylene oxide 25% : methyl bromide 75% are expressed in the fumigation unit of $g/1.5m^3$, this corresponds to 440 g-1.22 $Kg/1.5m^3$ and the amount of ethylene oxide is 110-303 g. Therefore, if the effective amount of fungicide shown in Table 2 is considered along with the low limit value of explosion 440 $g/1.5m^3$ on ethylene oxide 25% and methyl bromide 75%, then the complete fungicidal effects are expected even below this amount. Thus, when these compositions are used as fumigant, it will be safe from explosion or fire hazard.

III. Summary

1. When methyl bromide is added to ethylene oxide, the fungicidal effect is the same as or better than ethylene oxide alone. The effect is slightly lower in the case of methyl bromide alone. Thus, the addition of methyl bromide not only prevents the explosion of ethylene oxide, but also reduces the amount of ethylene oxide required for eliminating fungi. On the other hand, the fibroid bacilli are completely eliminated with fumigant 200 $g/1.5m^3$.

2. Insecticidal speed of ethylene oxide is significantly increased by the addition of methyl bromide.

3. Fungicidal power of methyl bromide is less than ethylene oxide, but the speed of penetration into the fumigating material is higher.

4. Explosion limit of ethylene oxide 25% : methyl bromide 75% is 8-22% and corresponds to 440 g-1.22 $Kg/1.5m^3$. On the one hand, since the effective fungicidal amount is far below the lower limit of explosion, an explosion and fire hazard are considered practically nonexistent.

Studies on fumigant "ethylene oxide" II, (Journal of Hygienic Society 4, 212). Concerning the fungicidal and insecticidal effect in Table 6, the following error is corrected. Extinction rate 99.7 for center part of unpolished rice bag and center part of flour bag should be 97.

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