Donahaye, E.J., Navarro, S., Bell, C., Jayas, D., Noyes, R., Phillips, T.W. [Eds.] (2007) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Stored Products, Gold-Coast Australia. 8-13th August 2004. FTIC Ltd. Publishing, Israel. pp. 179-184

ETHYLENE OXIDE: NEW RECOMMENDED QUARANTINE FUMIGATION DOSAGE

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ABSTRACT

The Australian Quarantine and Inspection Service (AQIS) recommend Ethylene Oxide [EtO] because its unique penetrative properties make it the ideal fumigant to overcome barriers such as paints and lacquers. EtO will permeate through plastic materials and the treatment is conducted in a vacuum chamber to allow pre- and post- inert gas purging and containment of the high EtO concentrations.

The extremely flammable EtO quoted Higher Explosive Limit (HEL) of 100% does not allow any oxygen to be present. As a HEL of 100% is not possible for combustion, it is a statement of the ability of EtO to decompose.

The US Bureau of Mines reports 100% EtO burning with a less luminous "decomposition flame" which is propagated at high speed. The decomposition temperature of ethylene oxide in the gas phase at atmosphere pressure is reported to be 571ºC. The reaction is highly exothermic with the temperature rising from 571ºC to 1200ºC in 2 milliseconds. While HELs less than 100% are quoted for sub-atmospheric pressures, the fumigation pressure at the AQIS concentration is too high to achieve a non-flammable/non-decomposable atmosphere.

This paper suggests a minor change to the AQIS recommended EtO dosage from 1500g/m^3 for 4 hours to 1200g/m^3 for 5 hours exposure time (i.e. no change to the current Ct product). At 1200g/m^3 the absolute pressure of EtO is ~550mm Hg and the HEL is ~98% which ensures a safe atmosphere using a carbon dioxide initial purge.

ETO FUMIGANT

Ethylene Oxide gaseous fumigant:

Ethylene Oxide [$(CH_2)_2O$] is a highly flammable (LEL=3.0%), colourless liquid which boils at 10.7ºC. The EtO gas has a specific gravity (air = 1) of 1.52 and 1 g/m^3 is equivalent to 555 ppm by volume (ie 1.5kg/m^3 = 83.25% EtO). While EtO can be formulated into non-flammable products these do not contain concentrations required in quarantine fumigations.

Quarantine: While existing fumigation schedules are well established to protect Australia against the importation of all quarantine pests there are some situation that needs a special approach. In particular the treatment of timber and other commodities that may have physical barriers such as paint and lacquers. EtO has the ability to penetrate painted wood or plastic coated commodities and to ensure successful treatment is conducted in a vacuum chamber which allows for pre- & post-inert gas purging and attainment of the high EtO concentrations recommended.

EtO Flammability

EtO Limits in Air*:* Coward & Jones (1952) studies of EtO flammability limits in air showed:

"In a closed tube, 5cm in diameter with hot-wire, all mixtures containing more than 3.6% EtO propagate flame upwards. Above 68% the flame is blue. At 100% a 'decomposition flame', still less luminous, is propagated with higher speed. The effects of pressure on the flammability of EtO in air at reduced pressure are shown in Figure 1"

TABLE 1
Coward & Jones (1952): EtO flammability limits in air

Gas/vapour	Limits in air***	
	LEL	HEL
EtO	**3.0* – 3.6****	**80* - 100****
*	Upward propagation in large vessels, open at lower ends	
**	Closed or small vessels	
***	No values given for limits in O2, or for minimum O2 % for flammability	

EtO Limits in Air/CO_2: Coward & Jones (1952) studies of EtO flammability limits in air and CO_2 are shown in Figure 2. The graph in Figure 2 is a traditional 'nose curve' (6%EtO, 42.5%CO_2). From this data it can be shown that, to render all possible mixtures of EtO and air non-flammable at ordinary temperatures & pressures, at least 7.15 volumes of CO_2 are required per unit volume of EtO.'(ie 12.3% EtO in CO_2). The decomposition of rich mixtures masks a virtual HEL of about 35%.

Non Flammable EtO Atmospheres:

Pre-Purge*:* Purging is done to avoid explosive mixtures within the chamber. The pre purge, with evacuation, reduces the oxygen content of the chamber to less than that required to combust a rich mixture.

This maximum safe oxygen content can be calculated from the HEL. Thus -

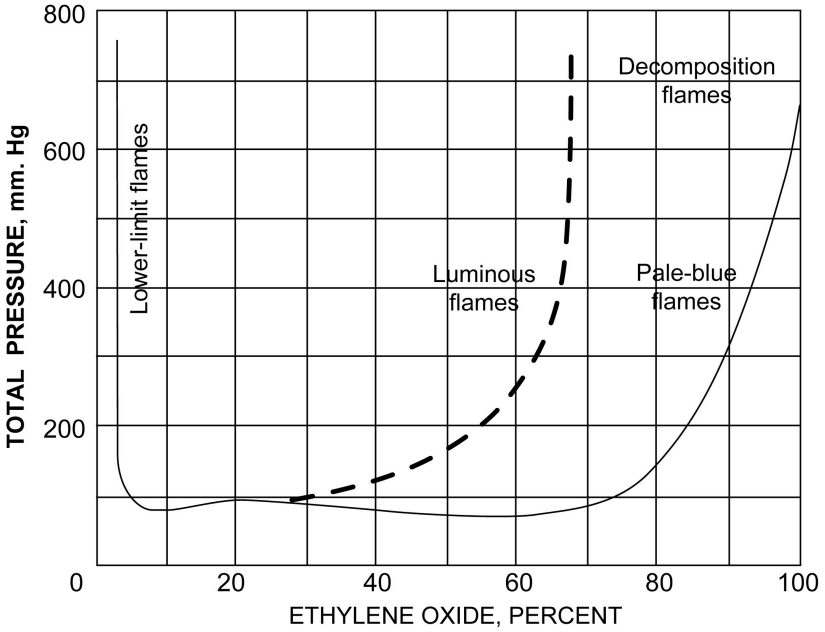
$$\text{Air content} = 100 - \text{HEL}$$

$$\text{Max.}O_2 \text{ content} = 0.21(100\text{-HEL})$$

Unfortunately, the oft-quoted HEL for ETO of 100% does not allow any oxygen to be present, a HEL of 100% is not possible for combustion, and is a statement of the ability of ETO to decompose. Fortunately, at reduced pressures it is possible to measure an HEL at less than 100% - leading to the possibility of a purge to reduce the oxygen content to a safe level. See Figure 1 where the right-hand line is the HEL at varying sub-atmospheric pressures.

Table 2 is constructed from Figure 1. It shows that a modest purge of about 1/10th of the chamber volume (with 2 evacuations) will reduce the oxygen content sufficiently. Because the aim is simply to reduce oxygen content, either nitrogen or CO_2 can be used.

Fig.1 - FLAMMABILITY of ETHYLENE OXIDE-AIR MIXTURES at REDUCED PRESSURES



Coward & Jones - Figure 51.

TABLE 2
Pre-purge requirements

Absolute pressure (mm Hg)	**HEL (%ETO) ex Fig 51**	**MAX O_2 (%)**	**O_2 ex residual air (%)**	**Purge Press (air+CO2) (mm Hg)**	**ETO concentration @ 25°C (g/m^3)**
[1]50.7			21.00		0.00
70	60	8.4	15.21	91.80	[2]46.14
85	70	6.3	12.53	100.80	82.00
100	73	5.67	10.65	95.20	117.86
140	80	4.2	7.61	91.80	[3]213.48
200	84	3.36	5.32	80.33	356.91
300	89	2.31	3.55	77.89	595.97
310	90	2.1	3.43	82.92	619.88
400	94	1.26	2.66	107.10	835.03
500	96	0.84	2.13	128.52	1074.09
600	99	0.21	1.77	[4]428.42	1313.15
686.8	100	0	1.55	infinity	[5]1500.00

[1] first evacuation (to 28" Hg); [2] based on vap. press = $2600 g/m^3$@ 1087.6 mmHg; [3] tobacco etc = $160 g/m^3$; [4]still only 0.56 of atm. - CO2 is only 0.5 atm; [5] AQIS concentration

Because the concentration (and pressure) of ETO for AQIS fumigation is so high, Figure 1 does not confer any benefit (HEL = 100%). However, note that at 1313 g/m^3, a half volume purge would provide a safe atmosphere. At constant Ct (concentration x time), the fumigation time would be extended by only 14%.

If the AQIS concentration is inviolate, safety can only be achieved by either avoiding sources of ignition within the chamber, or by safely venting any ignition.

The apparent ignition-free operation of the Granville Tobacco chambers for years without purging suggests that sources of ignition are rarely present. The safety of pre-purging requires that there is no ingress of air into the chamber during fumigation. The rich ETO mixture will be flammable with the increase of the oxygen content from in-leaks. Purge gas can be used to pad the chamber to near-atmospheric pressure to minimise leaks. Alternatively, operator monitoring of the chamber absolute pressure will detect leaks.

Post-Purge: The Post-Purge function is to reduce the atmosphere to below the LEL to avoid ignitions.

Assuming the atmosphere during fumigation is 100% (accurate for AQIS fumigation); evacuation to 28"Hg and breaking the vacuum to atmospheric pressure with an inert gas will give an EtO concentration of 2/30 or 6.7% (67000 ppm).

This is above the LEL, but Ref.1, including Figure 2, indicates a maximum ETO content in CO_2 for non-flammability of 9 - 12%. So a single CO_2 purge will produce a non-flammable atmosphere.

The same data is not available for nitrogen [N_2]. A conservative estimate suggests that an EtO-N_2 mixture is flammable above 4.8% ie two N_2 purges would be necessary.

Further air purges will reduce the EtO concentration to below the TLV (1ppm) and provide enough oxygen -

TABLE 3

Air Purge No.	EtO (ppm)	N_2 (%)	O_2 (%)
0	67000	100	0
1	4467	80.4	19.6
2	298	79.1	20.9
3	20	79.0	21.0
4	1.3	79	21
5	0.08	79	21

Note: The purge calculations ignore desorption of EtO from the product.

Purge gas requirements for a full purge of a typical (??m^3) chamber are - Nitrogen = 48m^3; CO_2 = 88kg

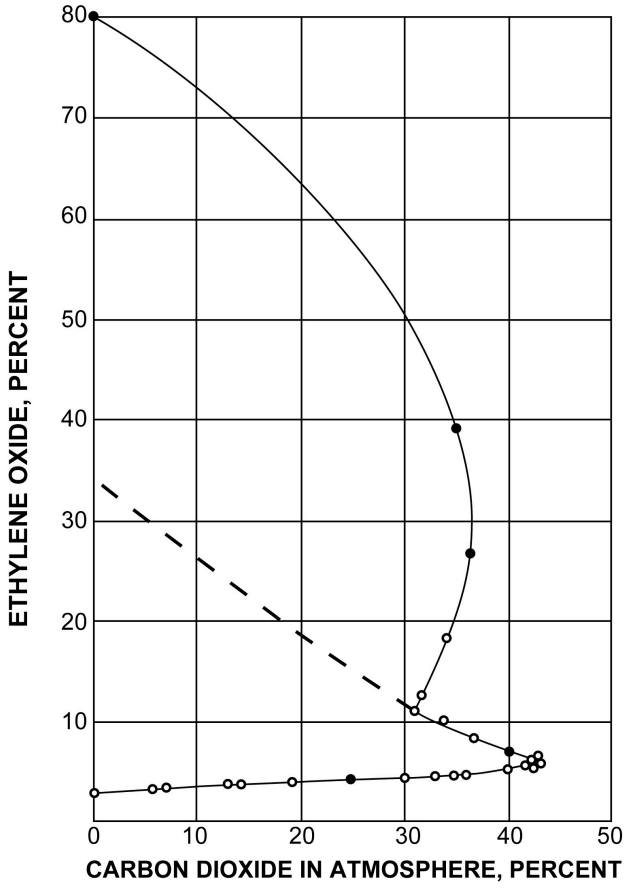
Safe & Effective Fumigation

Concentration x Time (Ct) Product: The critical issue with fumigation is the amount of gas acting on the insects over a certain period of time. While in the literature this is often expressed as mg.hr/l (milligram hours per litre), in practical fumigation g.hr/m^3 (gram hours/cubic metre) is more user friendly. To maintain a constant Ct requires continuous monitoring and constant additions of the fumigant to overcome leakage from the structure and sorption by the commodity. Another option is to measure the concentration and calculate a cumulative Ct and extend the exposure time until the Ct has been achieved (this may also require repeat additions of the fumigant).

EtO Efficacy: Most EtO documented fumigation quarantine schedules recommend a Ct less than 500 g.hr/m^3 however for snails in cargo the rate is increased a factor of 5 to ~2500g.hr/m3. The current AQIS recommended dosage is 1500g/m^3 for 4 hours i.e. a Ct of 6000 g.hr/m^3 and the suggested alternative of 1200g/m^3 for 5 hours maintains this high Ct of 6000 g.hr/m^3.

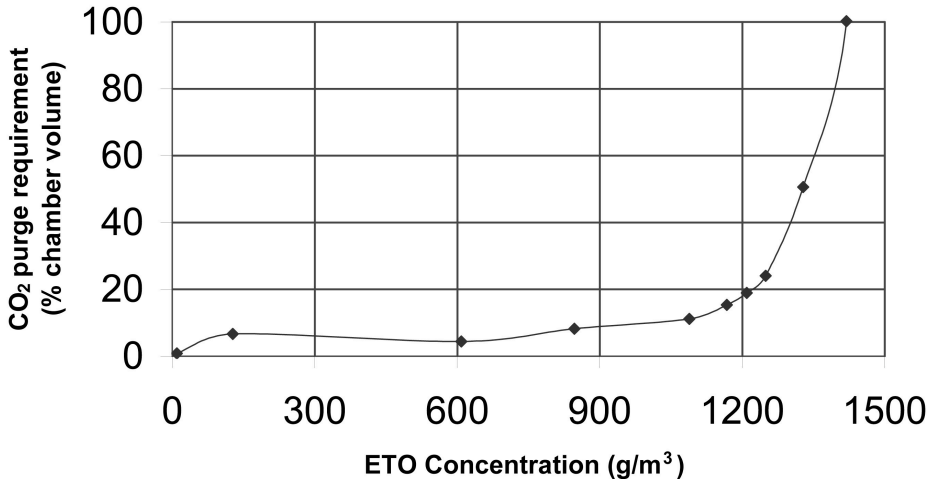
It is understood that the very high AQIS dose is required to ensure the effective fumigation of specially challenging commodities requiring fumigation especially coated (paint, resins, plastic) woods and other commodities. The additional sterilising properties of EtO are a bonus associated with using this sterilant/fumigant.

Fig.2 - LIMITS of FLAMMABILITY of ETHYLENE OXIDE in AIR and CARBON DIOXIDE



Coward & Jones - Figure 52.

Fig.3 - ETO PRE-PURGE



REFERENCES

Coward, H.F. and Jones, G.W (1952)"Limits of flammability of gases & vapors", US Bureau of Mines – Bulletin 503.

Jones, G.W. and Kennedy, R.E. "Extinction of EtO flames with CO_2", Industrial & engineering chemistry – Vol 22, No2,

Zabetakis, M.G. "Flammability characteristics of combustible gases & vapors", US Bureau of Mines – Bulletin 627.