

# VAPORMATE™

Manual for fumigation.

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# Important notice.

## This manual for fumigation is intended for training purposes only

The purpose of this manual is to support the application of VAPORMATE™. This information is provided for guidance only. It is not intended to replace the registered product label. Compliance with the product label is a legal requirement and failure to comply so can result in prosecution. We make no warranties expressed or implied and assume no liability in connection with the use of this information. Users are responsible for ensuring full compliance with the applicable registered product label as this is a legally binding document. For further support please contact your local Linde supplier. Fumigant registration is country-specific. In the US, it is a violation of federal law to use this product in any manner inconsistent with its labelling. Read entire label before using this product. If the terms and conditions are unacceptable, return unopened container at once. Please refer to your local Linde representative for information on the registration status in your region.

For use by certified applicators using Linde-approved dispensing equipment. VAPORMATE dispensing equipment is designed for use with VAPORMATE fumigant only.

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In case of emergency, call the customer service number on your local label.

# 1. Introduction.

VAPORMATE has been developed by Linde as a post-harvest fumigant for use by certified applicators. VAPORMATE is a non-ozone depleting fumigant with a favourable toxicological profile for use on general horticulture as well as commodities impacted by stored product pests. VAPORMATE has flammability properties which meet classification criteria as a flammable gas.

# 2. Product stewardship.

Linde is committed to Responsible Care® during the manufacture, distribution, handling, use and disposal of its products. This commitment includes auditing customers to ensure that they are set up to use the product safely and comply with the relevant regulatory requirements and standards. Supply of this product is subject to customer screening checks. Contact your local Linde representative for further details.

## 3. Background.

### 3.1 Ethyl formate

Ethyl formate is an ester formed when ethanol (an alcohol) reacts with formic acid (a carboxylic acid). Ethyl formate has the characteristic smell of rum and is also partially responsible for the flavour in many foods. Ethyl formate occurs naturally in soil, water, vegetation and a range of raw and processed foods.

USFDA considers ethyl formate to be Generally Recognized As Safe (GRAS) under 21 CFR 184.1295 when used as a flavouring agent and adjuvant as defined in 21 CFR 170.3(o). Maximum allowable levels in foods, as served, are 0.05% (500 ppm) in baked goods, 0.04% (400 ppm) in chewing gum, hard candy and soft candy, 0.02% (200 ppm) in frozen dairy desserts, 0.03% (300 ppm) in gelatin puddings and 0.01% (100 ppm) in all other food categories. In Europe, the Joint FAO/WHO Committee on Food Additives concludes that ethyl formate does not present a safety concern at current levels of intake (0–3 mg/kg per day) when used as a flavouring agent. Ethyl formate also meets the specifications of the “Food Chemicals Codex”. From the inhalation exposure perspective, the Occupational Safety and Health Administration (OSHA) has established a PEL-TWA for ethyl formate of 100 ppm (300 mg/m<sup>3</sup>).

Common food products containing endogenous ethyl formate include raspberries (2.0–2.3 ppm), cabbage (0.1–0.9 ppm) and butter (approximately 1 ppm).

Ethyl formate has an ADI of 3 mg/kg body weight/day, set by an expert panel of the World Health Organisation (WHO) during its periodic reviews of food additives (JEFCA 1997). This means that a 60 kg person can safely consume 180 mg ethyl formate per day over a lifetime without any adverse effects.

Ethyl formate is a fast acting, flammable liquid that has been traditionally used for fumigation of dried fruit since the 1920s (Simmons and Fisher, 1945) and for controlling major stored product insects in Australia (Hilton and Banks, 1997).

### 3.2 VAPORMATE

Linde has developed VAPORMATE, which contains ethyl formate as the active ingredient (16.7% by weight, 11% by volume) in liquid carbon dioxide. When dispensed, the liquid carbon dioxide reduces flammability and acts as a vehicle to deliver the gaseous ethyl formate to the target pests.

| Ingredient     | CAS No.  | Content (w/w) |
|----------------|----------|---------------|
| Ethyl formate  | 109-94-4 | 16.7%         |
| Carbon dioxide | 124-38-9 | 83.3%         |

VAPORMATE raises no long-term residual concerns for commodities as the ethyl formate is rapidly hydrolysed (broken down) into formic acid and alcohol. Ethyl formate is considered safe as a residue in food.

Residue trials were conducted on asparagus, cacao bean, navel orange pulp, navel orange rind, nectarine, pineapple pulp, pineapple rind and table grapes. The commodities were fumigated for 4 hours at a fumigation level of either 387 g/m<sup>3</sup> and at an exaggerated level of 774 g/m<sup>3</sup>. Samples were analysed for ethyl formate and its major degradant formic acid prior to fumigation (0 hour) and 24 and 48 hours following fumigation.

Background levels of formic acid were found in all commodities prior to fumigation. In general, formic acid levels seen 24 and 48 hours following fumigation at both concentrations were lower than those seen prior to fumigation. Ethyl formate was noted prior to fumigation in cacao bean, nectarine, pineapple pulp and table grapes. At 24 and 48 hours post fumigation, ethyl formate was seen in cacao bean and pineapple pulp and at levels comparable to or less than those seen prior to fumigation. Ethyl formate residue levels in other commodities were below the Limit of Detection (LOD=0.09 ppm).

These fumigation trials clearly show that ethyl formate residues will not be of concern in fumigated commodities. Even in the few commodities in which ethyl formate was found, the levels were comparable to background ethyl formate levels in those crops.

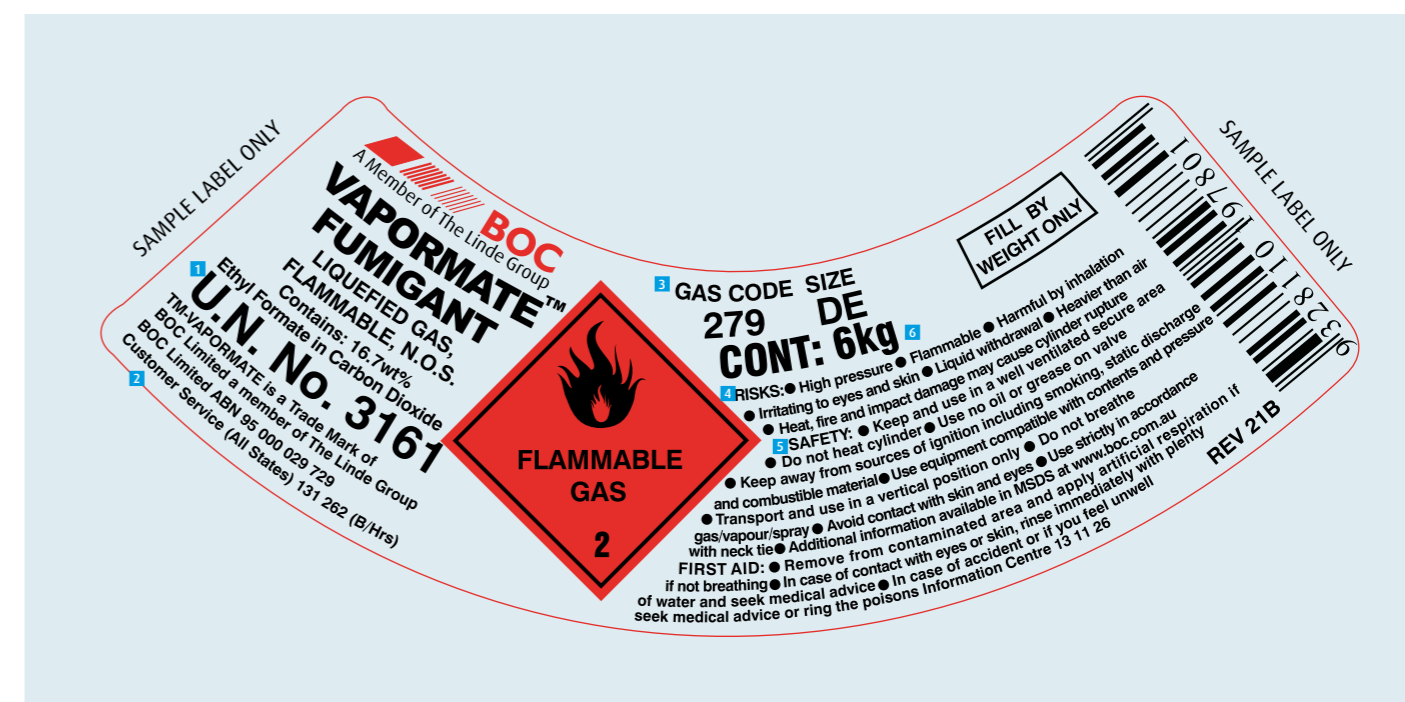
## 4. Physical and chemical properties.

### VAPORMATE has the following chemical properties:

|  |   |
|--|---|
| Appearance                                 | Colourless gas  |
| Odour                                      | Fruity rum-like odour   |
| Volatiles                                  | 100%  |
| Vapour density (air=1)                     | Carbon dioxide 1.52; ethyl formate 2.6  |
| Melting point                              | -78.5°C/-109.3°F (carbon dioxide sublimation point)   |
| Boiling point                              | -78°C/-108.4°F (carbon dioxide); 54°C/129.2°F (ethyl formate)   |
| Flammability                               | VAPORMATE is classified as an extremely flammable gas due to ethyl formate, which is a flammable liquid, and carbon dioxide, which is a liquefied gas |
| Liquid mixture in cylinder                 | Withdrawn as a liquid and vaporised before application  |
| Solubility (in water)                      | 0.759 cm <sup>3</sup> /cm <sup>3</sup> (carbon dioxide)   |
| Chemical structure                         | Ethyl formate: <chem>HCOOC2H5</chem><br>Carbon dioxide: <chem>O=C=O</chem>  |
| Chemical formula                           | Ethyl formate: <chem>C3H6O2</chem><br>Carbon dioxide: <chem>CO2</chem>  |
| Cylinder pressure (when full at 25°C/77°F) | 6,300 kPa (CO <sub>2</sub> vapour pressure)   |
| Cylinder valve outlet                      | AS 2473 type 40 side outlet   |
| Hazchem code                               | 2YE   |
| Dangerous goods                            | 2.1   |
| UN number                                  | 3161  |

See below for a typical VAPORMATE label. Please refer to your local label for the details specific to your region.

1 U.N. No. poison identification number 2 Customer service number 3 BOC gas code 4 Risks 5 Safety instructions 6 Product weight



VAPORMATE neck label (sample).

## 5. Safety.

VAPORMATE is for use by certified applicators using Linde-approved vaporising blending equipment and people under their direct supervision.

### General

- Carefully read the container label and product specimen label and follow instructions explicitly.
- Never work alone when applying fumigant from within the storage structure (if re-entry is required) or aerating commodities after the fumigation is over.
- Never allow untrained personnel to handle VAPORMATE.
- The use of respiratory protection is required if ethyl formate concentration exceeds 100 ppm and carbon dioxide exceeds 5,000 ppm.
- Post VAPORMATE placards at fumigated areas, including all entrances and exits. Ensure that no personnel are inside any of the structures to be fumigated prior to initiating fumigation.
- Notify appropriate owners, employees, and/or operators at the facility each time prior to initiating fumigation and provide relevant safety, health and environmental information to local fire and rescue officials annually for use in the event of an emergency.
- Do not connect containers to dispensing equipment until all fumigation notice placards have been posted and the space to be fumigated is clear and secured.
- Wear personal protective equipment as described in this fumigation manual.

Applicators must comply with the relevant regulations for fumigation when using VAPORMATE.

General safety guidelines are provided in the VAPORMATE manual for fumigation. The following paragraphs identify the main hazards that should be taken into consideration when working with VAPORMATE. A proper risk assessment and fumigation management plan should be carried out in relation to both the specific conditions where the operations are performed and the possible emergency situations which may occur.

### 5.1 Toxicity

Exposure standards for the components of VAPORMATE – carbon dioxide and ethyl formate – are outlined below:

#### Carbon dioxide

ES-TWA: 5,000 ppm (ACGIH: NOHSC)  
ES-STEL: 30,000 ppm (ACGIH: NIOSH;NOHSC)

#### Ethyl formate

ES-TWA: 100 ppm

#### TWA: Time Weighted Average

The average airborne concentration of a particular substance when calculated over a normal eight hour work day for a five hour working week.

The maximum allowable exposure level for carbon dioxide in the working atmosphere (8 hour shift, 40 hour week) is 0.5% (5,000 ppm by volume) and 0.01% (100 ppm for ethyl formate).

#### STEL: Short-Term Exposure Limit

Expressed as airborne concentrations of substances, averaged over a period of 15 minutes. Workers should not be exposed at the STEL concentration continuously for longer than 15 minutes, or for more than four such periods per working day. A minimum of 60 minutes should elapse between successive exposures at the STEL concentration.

The STEL for carbon dioxide is 3.0% or 30,000 ppm. There is no STEL value listed for ethyl formate.

The toxicity data presented is based on ethyl formate as it has greater toxicity than carbon dioxide.

#### Ethyl formate

| Test animal | Route      | Lethal dose or concentration                     |
|-------------|------------|--|
| Rat         | Inhalation | LC <sub>83</sub> 24 g/m <sup>3</sup> for 4 hours |
| Guinea pig  | Oral       | LD <sub>50</sub> 1110 mg/kg                      |
| Rat         | Oral       | LD <sub>50</sub> 4290 mg/kg                      |

#### 5.1.1 Short term (acute) exposure

##### Inhalation

Ethyl formate has a characteristic fruity rum-like odour that can be easily detected by smell. The odour threshold is 18–20 ppm which is well below the 100 ppm TLV.

Ethyl formate can form vapour concentrations at room temperature that may pose an inhalation hazard. At relatively low airborne concentrations (330 ppm), the vapour can irritate the nose and throat.

High concentrations can cause damage to the central nervous system (CNS). Symptoms may include loss of coordination, fatigue, nausea and headaches, or even the accumulation of fluid in the lungs (pulmonary oedema). Typically, the symptoms of pulmonary oedema, such as shortness of breath, may not appear until a few hours after exposure. Concentrations of 10,000 ppm or higher (near lethal concentrations) in animals have caused narcosis. Rats have survived short term exposures to 4000 ppm.

##### Skin contact

Ethyl formate is slightly absorbed through the skin, although this route of exposure is not expected to produce significant toxic effects or irritation. The dermal LD<sub>50</sub> in rats is greater than 5000 mg/kg body weight.

##### Eye contact

Liquid ethyl formate caused mild eye irritation in laboratory animal studies. In workers, vapour concentrations of 330 ppm caused slight irritation of the eyes with rapidly increasing nasal irritation with the effects likely to subside after several hours.

#### 5.1.2 Long term (chronic) exposure

Ethyl formate or its metabolites are not known to accumulate in the body. It reacts with moisture to form formic acid and ethanol, which are readily exhaled or excreted or metabolised and then excreted.

#### 5.1.3 First aid

In the unlikely event of an individual being unconscious or not responding, ensure that you are safe before attempting a rescue. The appropriate personal protective equipment should be used (coveralls, goggles, respirator with a type A organic vapour cartridge, self-contained breathing apparatus (SCBA) or an air-line respirator).

##### Inhalation

If an individual is suffering from breathing difficulties, remove them from the source of contamination or into fresh air. Oxygen may be beneficial, but it should only be administered by a trained individual. If irritation persists, obtain medical attention immediately.

If breathing has stopped, contact the emergency services (ambulance), with trained personnel administering emergency first aid while waiting for the ambulance crew to arrive.

##### Eye contact

Continuously flush eyes with clean water should irritation occur. Continue for 15 minutes as a minimum and keep the patient calm. Seek medical attention immediately.

##### Skin contact

Avoid contact with skin. If product gets on skin or clothing, remove contaminated clothing and wash affected areas with soap and water. Launder contaminated clothing before reuse. Wash thoroughly after handling and before eating, drinking, chewing gum, or using tobacco. If irritation persists, obtain medical attention immediately.

##### Ingestion

The primary route of exposure for VAPORMATE is inhalation. Ingestion is highly unlikely as VAPORMATE is applied as a gas.

### 5.2 Flammability

VAPORMATE is flammable and will ignite in the presence of a spark or open flame or other ignition sources. Do not use or store near heat or an open flame. Do not puncture or incinerate the container. Store tightly sealed containers in a cool dry area.

Ethyl formate is a flammable liquid and the flammability range in air of its vapours is 2.6 vol% (LEL)–18.2 vol% (UEL).

#### As a consequence, VAPORMATE has the following flammable properties:

|                                      |                                  |
|--------------------------------------|----------------------------------|
| Lower Explosion Limit (LEL)          | 31 vol% (3.3 vol% ethyl formate) |
| Upper Explosion Limit (UEL)          | 47 vol% (5.0 vol% ethyl formate) |
| Minimum Ignition Energy (MIE)        | 490 mJ *                         |
| Maximum explosion pressure           | 680 mbar                         |
| Maximum explosion pressure rise rate | 8.5 bar/s                        |
| Deflagration index (Kg)              | 2.3 bar·m/s                      |
| Linear burning speed                 | 23 cm/s                          |
| Burning velocity                     | 6.7 cm/s                         |

##### Notes:

\* There is a strong possibility of VAPORMATE fractionation under certain conditions; the minimum ignition energy may be lower than 490 mJ

The table shows the flammable properties of VAPORMATE compared with the properties of some of the most common flammable substances:

|                                      | Unit    | VAPORMATE  | Ethylene | Ammonia | Phosphine                 | Flour, cake | Grain dust | Rice   |
|--------------------------------------|---------|------------|----------|---------|---------------------------|-------------|------------|--------|
| Lower Explosion Limit (LEL)          | vol%    | 31 (3.3) * | 2.4      | 115     | Auto-ignites in moist air |             |            |        |
| Upper Explosion Limit (UEL)          | vol%    | 47 (5) **  | 32.6     | 30      | Auto-ignites in moist air |             |            |        |
| Minimum Ignition Energy (MIE)        | mJ      | 490        | 0.07     | 680     | Auto-ignites in moist air | 25-80       | 30         | 40-120 |
| Maximum explosion pressure           | mbar    | 680        |          | 4200    |                           |             |            |        |
| Maximum explosion pressure rise rate | bar/s   | 8.5        |          | 10-12   |                           |             |            |        |
| Deflagration index (Kg)              | bar·m/s | 2.3        | ~200     |         |                           |             |            |        |
| Linear burning speed                 | cm/s    | 23         |          |         |                           |             |            |        |
| Burning velocity                     | cm/s    | 6.7        |          | 7.2     |                           |             |            |        |

\* relevant ethyl formate concentration 3.3 vol%

\*\* relevant ethyl formate concentration 5.0 vol%

A general assumption is that ignition of a flammable gas/air mixture requires an ignition source with an energy <1 mJ. The energy needed to ignite a mixture should be compared to the possible energy generated by some common sources such as:

- Operating electrical contactor, not ex-proof many J
- Particles at grinding some J
- Electrostatically charged person 10-100 mJ
- Dropped mobile phone 10-20 mJ

Flammability may be managed by a range of measures:

- The use of flameproof equipment (e.g. fans)
- The addition of 285g of carbon dioxide per 1kg of VAPORMATE used prior to the fumigation, creating a non-flammable environment allowing standard equipment to be used
- Potential ignition sources (e.g. fans) to be introduced only if the ethyl formate level is 25% of the LEL (<0.85 vol%.)

### 5.2.1 Fire prevention

The dosing equipment must be suited to a potentially explosive atmosphere according to the relevant regulation.

The fumigation chamber must be equipped with explosion-proofed devices where these are needed in the chamber, e.g. lighting, fan, heater, etc. according to the relevant regulation. If this is not possible, additional measures should be considered such as pre-inerting with carbon dioxide. An extra 285 g of carbon dioxide should be added per 1 kg of VAPORMATE used.

Any potential ignition sources not needed during or after the fumigation processes must be eliminated/removed.

All equipment is to be earthed (grounded) as a precaution against build-up of static electricity (ignition source). Feed lines/pipes must be regularly cleaned and maintained.

### 5.2.2 Fire fighting

Extreme temperatures caused by a fire may cause cylinders to rupture. The fire service should be notified when cylinders have been involved in a fire. Cylinders can be cooled by applying water from a protected location. Do not approach any cylinders suspected of being exposed to high temperatures.

### 5.3 Asphyxiation

Any substantial release of carbon dioxide is potentially hazardous, especially inside a poorly ventilated space. The health effects of inhaling carbon dioxide include headache, dizziness, restlessness, breathing difficulty, sweating, malaise (vague feeling of discomfort), increased heart rate, cardiac output and blood pressure, coma, asphyxia, convulsions and unconsciousness. In low concentrations, the health effects of carbon dioxide are physiologically reversible, but in high concentrations carbon dioxide can cause unconsciousness and be fatal.

| CO <sub>2</sub> (vol%) | Likely health effects  |
|------------------------|--|
| 1-1.5                  | Slight effect on chemical metabolism after exposure of several hours   |
| 3                      | The gas is weakly narcotic at this level, giving rise to deeper breathing and reduced hearing ability coupled with a headache and an increase in blood pressure and pulse rate   |
| 4-5                    | Stimulation of the respiratory centre occurs, resulting in deeper and more rapid breathing. Signs of intoxication will become evident after 30 minutes' exposure   |
| 5-10                   | Breathing becomes more laborious with headache and loss of judgement   |
| 10-100                 | When the carbon dioxide concentration increases above 10 vol%, unconsciousness will occur in under one minute and unless prompt action is taken, further exposure to these high levels will eventually result in death |

**Important note:** The effects of carbon dioxide are independent of the effects of oxygen deficiency. The oxygen content in the atmosphere is therefore not an effective indication of the danger. It is possible to have a low oxygen content of 18 vol% and a high carbon dioxide content of 14 vol%, which is very dangerous. Therefore monitoring the oxygen content in areas where carbon dioxide is released will not provide adequate protection or warning against an increase of carbon dioxide.

### 5.4 Low temperatures

The snow produced from leaks of liquid carbon dioxide is extremely cold (-78.5°C/-109.3°F) and may cause frostbite on contact with skin. If carbon dioxide snow comes into contact with the eyes, it may cause severe eye injury. Also, rapid evaporation of the liquid can cause frostbite and cold burn.

### 5.5 Safety equipment

Protective clothing should be worn during the fumigation process to ensure worker safety. Where the TLV is exceeded, for either ethyl formate (100 ppm) or carbon dioxide (5000 ppm) respiratory protection must be worn. A full-face respirator (with an appropriate organic vapour filter) must be worn where the ethyl formate TLV is exceeded while self-contained breathing apparatus (SCBA) must be worn where the carbon dioxide or both TLVs are exceeded. Gloves, goggles, steel capped safety boots and earplugs are also recommended by Linde.

Linde can supply a wide range of safety equipment.

#### 5.5.1 Full-face respirator

Linde recommends the use of a type AX (organic filter) respirator filter cartridge where ethyl formate levels are found above 100 ppm. Individuals should comply with the recommendations of the filter manufacturer regarding best practice for cartridge use and maintenance.

Note: This type of breathing protection does not protect against the asphyxiation risks of carbon dioxide. Where high concentrations of carbon dioxide are found in the atmosphere, SCBA should be used.

#### 5.5.2 Self-contained breathing apparatus (SCBA)

Self-contained breathing apparatus is recommended where there is a risk of oxygen depletion. Carbon dioxide is the propellant for VAPORMATE, and dose rates above 10 g/m<sup>3</sup> create an atmosphere within the fumigation chamber where carbon dioxide exceeds the TLV level. SCBA should be used to enter the fumigation chamber until appropriate ventilation has taken place.

Ensure that the SCBA manufacturer's instructions are followed when using SCBA.

#### 5.5.3 Gas detection systems

Personal exposure monitoring must be conducted by using a gas detection monitor or detection tubes. These devices must be able to detect ethyl formate in the range of 0-100 ppm and carbon dioxide in the range of 0-30,000 ppm.

The CO<sub>2</sub> alarm level in an occupied room must be set at 0.5 vol%.

To prevent an explosive mixture with air, the gas detection monitor must be able to detect ethyl formate in the range of 0-28 vol%. See section 5.2 for how to manage a potentially explosive environment.

**Important note:** monitoring the oxygen content in areas where CO<sub>2</sub> is released will not provide adequate protection or warning against an increase of carbon dioxide.

### 5.6 Material compatibility

When using VAPORMATE, care must be taken to ensure that compatible materials are used in both the fumigation chamber and the application equipment. Therefore Linde recommends using a Linde approved portable electric vaporiser (PEV), which is manufactured using compatible materials and has all the necessary control systems required to ensure safe and effective delivery.

Linde uses high specification carbon dioxide with general moisture levels around 50 ppm (max. 100 ppm). Carbon dioxide can be corrosive in the presence of moisture and, as a precaution, acid-resistant materials such as stainless steel should be used when applying VAPORMATE.

Ethyl formate decomposes to form ethanol and formic acid. It will react adversely in the presence of oxidising agents, nitrates and strong acids, and so these should be avoided.

### 5.7 Public safety

When fumigating in or adjacent to a public area, applicators must be aware of the potential dangers and their (legal) responsibilities in this area.

When assessing a fumigation site, a fumigant management plan covering the safety of the technician, the customer and his staff and the general public should be carried out on the particular job, and procedures modified where necessary to reduce these risks to an acceptable level.

### 5.8 Personal safety

The risk of exposure to gases like ethyl formate and carbon dioxide which have defined occupational exposure limits and the risk of explosive atmosphere creation are the most obvious and important issues to manage. Good monitoring of the fumigation site and the enclosure is the best way to control this risk.

#### Working at heights and use of access equipment

When working above certain heights, health and safety legislation requires the applicator to work from a platform fitted with safety rails. If this platform is not available then safety harnesses and fixing points are used.

When fumigating large structures such as buildings, certified harnesses and ropes are used as well as safety helmets.

### 5.9 Confined spaces hazard

Access to and working in confined spaces is covered by legislation in many cases.

As a general rule, for any entry or work in a confined space, a particular risk assessment must be carried out and a permit to work used to ensure a safe working environment.

When fumigating, a technician may encounter various types of confined spaces:

- A chamber used for fumigation
- A silo
- A cavity, drain, sub floor area, roof void contained in or adjoining a fumigation area.

It is also very important when fumigating to be aware of:

- Low oxygen atmospheres (particularly when using controlled atmospheres) and the need for a complete aeration of the fumigation area post-treatment. A minimum of 19.5% oxygen is required in a workspace at all times and this needs to be confirmed by monitoring
- Working around ducts and drains when sealing a fumigation enclosure
- Working around power lines during sheet fumigation
- Working near potential heat sources.

### 5.10 Handling emergencies

Whilst no applicator wants to experience them, emergencies do happen!

An emergency is experienced when a normally controlled system for whatever reason breaks down. Surprise, danger and often confusion accompany this breakdown. To add to this, personal injury is also common.

A cool head is required when all this happens suddenly, and so the most important response to an emergency is rehearsed calmness together with immediate action.

Train for emergencies and draw up procedures based on a risk assessment of the type of jobs being done so that if an emergency happens, you know what to do and are in a position to make the right decisions.

### 5.11 Emergency procedures

Draw up emergency and operational procedures to cover any risk or hazard relating to a risk that you have identified. For example:

- A person affected by fumigant (the hazard) exposure
- A person injured by a fall (the hazard is the height)
- Pets injured during fumigation
- Property damage
- Handling the media

When planning to prevent a potential emergency, you may need to consider:

- What would the effect of the weather be?
- Are you near a main road or other public area? Traffic accident risk – exposure of drivers to fumigant.
- Will you need to use access equipment?
- Will you need to involve police/ambulance/emergency services?
- What are the risks of personal injury?
- What is the risk of property damage?
- What is the risk of damage to a valuable commodity?

Linde, in conjunction with numerous partners, has conducted a number of studies with VAPORMATE. This has enabled Linde to create comprehensive labels in a number of countries based on local conditions, commodities and pests of concern.

## 6. Legal requirements.

Pesticides legislation deems it an offence to use a pesticide in a way that is likely to cause injury to another person or harm a non-target plant or animal. It is a legal requirement to read and to follow the instructions on the label of a registered pesticide.

In addition to this, Occupational Health and Safety legislation requires that employers provide a safe work environment that includes adequate training, supervision, safe work practices and provision of appropriate personal protective equipment.

Safety Data Sheets (SDS) must be held for all registered pesticides (including VAPORMATE), and these should be made available to anyone who has been exposed. The MSDS must be readily available at all times as it contains vital information for use in emergencies.



## 7. Environment.

VAPORMATE is an effective replacement for methyl bromide on a range of fresh commodities and stored products. USFDA considers ethyl formate, the active ingredient in VAPORMATE, to be Generally Recognized As Safe (GRAS). It simply degrades to metabolites that occur naturally in the environment.

VAPORMATE is non-ozone depleting and has no known global warming potential. As such, it is more environmentally friendly than a number of conventional fumigants.

## 8. Cylinder safety.

VAPORMATE cylinders must be properly labelled with Linde product specimen labels. VAPORMATE is supplied in high pressure cylinders in a range of sizes to meet customer portability and volume requirements. Best practice guidelines for the transport, storage and handling of gas packages should be followed at all times to ensure the health and safety of all users/operators.

### 8.1 Cylinder storage

VAPORMATE should not be stored near combustible or incompatible materials. Cylinders should be stored below 45°C/113°F in a dry, well-ventilated area on a firm, level floor. All cylinders should be secured to prevent them from falling over.

If it is not possible to store cylinders in a well-ventilated area, then monitoring equipment should be used to record levels of ethyl formate and carbon dioxide in the atmosphere.

### 8.2 Cylinder transport

During transport, the following principles should be followed. Cylinders should:

- be transported upright
- be secured
- have their valves protected
- be separated from the driver
- have the appropriate placards displayed

Visit your local Linde website for more information.

### 8.3 Cylinder leaks

In the unlikely event of a cylinder leak, evacuate personnel within the area and contact your local Linde representative. Linde will then confirm the best action based on your individual situation. Refer to your local label for contact information.

## 9. VAPORMATE efficacy.

### 9.1 Mode of action

When the insects are exposed to VAPORMATE, ethyl formate binds with cytochrome a and inhibits cytochrome c oxidase in the insect cell. Inhibition of cytochrome c oxidase leads to depletion of molecular oxygen in the cells, subsequently resulting in the loss of cell function and cell death.

### 9.2 Commodities that can be fumigated

Below is an indicative label – please ask your local representative for the most up-to-date label.

| Situation  | Insect  | Temperature | Application rate/<br>exposure time                                |
|--|---|-------------|---|
| Cereal grains and oilseeds in sealed storage (with moisture content ≤12%). Grain storage premises and equipment. | Complete control of all stages of: lesser grain borer ( <i>Rhyzopertha dominica</i> ), flour beetle ( <i>Tribolium castaneum</i> ), psocids ( <i>Liposcelis bostrychophila</i> , <i>L. entomophila</i> , <i>L. decolor</i> ), storage moths ( <i>Esphestia</i> spp., <i>Plodia</i> spp.), saw-toothed grain beetle ( <i>Oryzaephilus</i> spp.), flat grain beetle ( <i>Cryptolestes</i> spp.). Complete control of eggs, larvae and adults of: rice weevil ( <i>Sitophilus oryzae</i> ) | > 15°C/59°F | 660 g/m <sup>3</sup> (3 hours) or 420 g/m <sup>3</sup> (24 hours) |
| Lettuce (not bagged or similar)  | Aphid ( <i>Nasonovia ribisnigri</i> )   | > 15°C/59°F | 120 g/m <sup>3</sup> (1 hour)                                     |
| Onion  | Onion thrips ( <i>Thrips tabaci</i> ) (adults only)   | > 15°C/59°F | 160 g/m <sup>3</sup> (1 hour)                                     |
| Sweet pepper or capsicum   | Western flower thrips ( <i>Frankliniella occidentalis</i> )   | > 15°C/59°F | 70 g/m <sup>3</sup> (2 hours)                                     |
| Sweet potato and rhubarb   | Detritus moth ( <i>Opogona omoscopa</i> )   | > 15°C/59°F | 30 g/m <sup>3</sup> (2 hours)                                     |
| Banana   | Mites ( <i>Oligotetranychus</i> spp.), mealybugs ( <i>Dysmicoccus</i> spp.), scale ( <i>Aspidiotus</i> spp.)  | > 15°C/59°F | 420 g/m <sup>3</sup> (6 hours)                                    |
| Pineapple  | Mites ( <i>Dolichotetranychus floridanus</i> ), mealybugs ( <i>Dysmicoccus neobrevipes</i> ), scale ( <i>Diaspis bromiliae</i> )  | > 15°C/59°F | 420 g/m <sup>3</sup> (2 hours)                                    |
| Strawberry   | Western flower thrips ( <i>Frankliniella occidentalis</i> )   | > 15°C/59°F | 160 g/m <sup>3</sup> (1 hour)                                     |
| Kiwi (excluding golden kiwi)   | Oleander scale ( <i>Aspidiotus nerii</i> ), long-tailed mealybugs ( <i>Pseudococcus longispinus</i> )   | > 15°C/59°F | 140 g/m <sup>3</sup> (6 hours)                                    |
| Table grapes   | Light brown apple moth ( <i>Epiphyas postvittana</i> ), redback spiders ( <i>Latrodectus hasselti</i> ), two-spotted mite ( <i>Tetranychus urticae</i> ), long-tailed mealybug ( <i>Pseudococcus longispinus</i> ), western flower thrips ( <i>Frankliniella occidentalis</i> ), plague thrips ( <i>Thrips imagines</i> )   | > 10°C/50°F | 240 g/m <sup>3</sup> (4 hours)                                    |
| Citrus   | Long-tailed mealybug ( <i>Pseudococcus longispinus</i> (Targioni-Tozzetti), citrus mealybug ( <i>Planococcus citri</i> (Risso))   | > 10°C/50°F | 90 g/m <sup>3</sup> (1 hour)                                      |

### 9.3 Dose calculation

Dose rate is calculated by determining the volume of the empty fumigation area in cubic metres and then applying VAPORMATE by weight. The treatment chamber must remain completely sealed for the recommended exposure period to allow VAPORMATE to work.

An example is provided below for cereal grains fumigated in a 20 foot (6.1 m) container.

|                    |  |
|--------------------|--|
| Container volume   | = 33 m <sup>3</sup>                        |
| Recommended dosage | = 420 g/m <sup>3</sup> (24 hours exposure) |
| VAPORMATE required | = Dose X volume                            |
|                    | = 420 g/m <sup>3</sup> x 33 m <sup>3</sup> |
|                    | = 13.86 kg of VAPORMATE                    |
|                    | (to be applied by weight)                  |

Important note: It is not possible to pre-determine whether a specific dosage does or does not lead to the creation of a potentially flammable/explosive atmosphere inside the fumigation chamber. Independently from the dosage rate selected, it is always recommended to eliminate any ignition sources inside the fumigation area and to ensure the atmosphere is safe before entering.



## 10. Residues.

Fumigation with VAPORMATE presents no long-term residual concern. This is a result of ethyl formate rapidly hydrolysing (breaking down), with the residue (formic acid and ethanol) being indistinguishable from the natural levels found in foodstuffs. As an example, the Australian Pesticides and Veterinary Medicines Authority (APVMA) has listed ethyl formate in 'Table 5', a grouping of chemicals for which a maximum residue limit (MRL) is not required or for chemicals that are not expected to contaminate food. There is a current Food Standards (FSANZ) MRL of 1 mg/kg for ethyl formate applied to dried fruit (Australia) and 250 ppm for cereal grains and dried fruits (New Zealand only). Please look at your local label to understand the residue requirements there.

The lack of residues from VAPORMATE removes the need for a withholding period before the sale of commodities post-fumigation. This means that as soon as the levels of ethyl formate and carbon dioxide are safe in the fumigation chamber, the commodity is saleable at market for consumption.

## 11. Application technology.

Successful fumigation is reliant upon the applicator applying VAPORMATE using appropriate application technology as defined below.

### 11.1 Portable electric vaporiser (PEV)

VAPORMATE should be applied using a heated vaporiser to ensure that the ethyl formate is vaporised effectively. Linde-approved equipment must be used to apply VAPORMATE.



VAPORMATE should be applied to the chamber, via the vaporiser, using a leak-proof, flexible, kink-resistant tube which is durable and compatible with the product. Teflon, stainless steel and polytetrafluoroethylene (PTFE) are all compatible with VAPORMATE.

### 11.2 Fans

For small enclosures, an Envirosol nozzle system may be used to distribute the product for shorter fumigation periods. Flameproof fans may be used in large fumigation chambers to ensure that VAPORMATE is distributed evenly throughout the chamber. The fan is switched on 10–15 minutes before the gas is introduced and 30 minutes after application, or until an equilibrium is attained. For large structures like silos, recirculation fans can be installed as an integral part of a permanent fumigation facility. Fans must be flameproof if used during application.

### 11.3 Temperature control

To ensure VAPORMATE efficacy, the fumigation chamber must be maintained at a constant temperature above 10°C/50°F. In colder climates, a heater may be required to maintain the required temperature during fumigation. Heaters must be flameproof if used during application.

Temperature is an important factor for successful fumigation. Insects are cold-blooded, so increasing the temperature increases the metabolism of an insect. Increasing the metabolism means increased respiration of the insect. This is mainly due to the increased rate of activity and respiration of insects in response to the rise in temperature. Relatively large changes in temperature are not required. Achieved temperatures of 25 to 30°C (78 to 86°F), for example, can have a very positive effect on fumigation efficacy and efficiency. Conditions for successful fumigation improve as the temperature rises.

## 12. Fumigation preparation.

VAPORMATE fumigation must be conducted by a certified applicator. Safe work procedures, protective equipment and first aid procedures must be in place before the first fumigation.

Prior to fumigation, all people, non-target animals, desirable growing plants and medicine must be removed from the fumigation area.

### Requirements for certified applicator to be present and responsible for all workers:

The responsible certified applicator must be physically present and maintain visual and/or voice contact with all fumigation workers during the application of the fumigant. Once the application is complete and the structure has been made secure, the certified applicator does not need to be physically present at the site.

The responsible certified applicator must be physically present and maintain visual and/or voice contact with all fumigation workers during the initial opening of the fumigation structure for aeration. Once the aeration process is secured and monitoring has established that aeration can be completed safely the certified licensed applicator does not need to be physically present and trained person(s) can complete the process and remove the placards.

Persons with documented training in the handling of VAPORMATE must be responsible for receiving, aerating and removal of placards from vehicles, transport containers and trailers that have been fumigated in transit.

Read all directions completely before use and follow all directions and precautions when using this product.

### 12.1 Risk assessment

A risk assessment should be conducted before the first fumigation to control any hazards that may adversely impact the applicator, nearby residents and/or the environment. Appropriate control measures such as working and emergency procedures, personal protective equipment, etc. should be put in place and included in the fumigation plan/documentation.

The risk assessment should consider the following hazards (as a minimum):

- Exposure to ethyl formate and carbon dioxide higher than the defined occupational exposure limits i.e. TLV-TWA, max. workplace concentration
- Fire/explosion
- Asphyxiation
- Pressure release
- Cold burns
- Electric shock
- Liquid trapped in pipes or equipment
- Hazards related to cylinder handling/storage

### 12.2 Fumigation chamber

Effective sealing of the fumigation chamber will reduce the need to apply additional fumigant as well as maintain a safe environment for those working in the general vicinity.

Leaks can be identified by carefully examining the fumigation chamber and associated application equipment. Particular attention should be paid to walls, roof, floor, door seals and pipework joints. Entry and exit points for fumigation and sample tubes should also be checked and sealed if necessary. Polyethylene sheeting, nonporous panels, fumigation tape, spray adhesives, foams and insulation materials can be used to help seal the fumigation structure.

If VAPORMATE is used in shipping containers, best practice is to pressure test before the product is applied. Pressure testing can be performed using a compressed air supply from a portable compressor or gas cylinder into the closed container up to 250 Pa. When the pressure reaches 250 Pa, turn off the compressed air supply and allow the pressure to decay to 200 Pa. Then start measuring the time from 200 Pa to 100 Pa. Record the pressure decay time. The pressure decay time should be 10 seconds or more. If the container does not pass the pressure tests, it must be enclosed under a gas-proof sheet before fumigation.

Sand or water snakes should be used for gas-proof sheet fumigation. A minimum of two rows of sand snakes (65–75% fill) or a single continuous row of water snake (75%–85% fill) must be used to create a continuous seal with the ground surface.

Do not introduce VAPORMATE mixtures into a vacuum chamber(s).

### 12.3 Leak testing

Personal protective equipment (respiratory protection) should be worn when leak testing. Leak testing procedures should be followed to verify the integrity of all components, lines and connections. Leak tests are conducted by passing an inert gas (nitrogen) through the system and spraying leak detection fluid (soap/water solution) on all joints and outlets. The appearance of fine bubbles indicates the presence of a leak.

A silo may be leak checked using a pressure drop test. The system is sealed and pressurised and then monitored over a period of time. A reduction in the pressure indicates that there are leaks in the system. A risk assessment should be completed and a set procedure followed to ensure that design limitations/maximum working pressures of the silo are not exceeded. Over-pressurisation of large vessels can lead to catastrophic failure.

### 12.4 Monitoring hoses

To monitor concentrations of VAPORMATE in the fumigation chamber during exposure and ventilation periods, gas sampling lines (3 mm) may be installed. For large volumes (above 20 m<sup>3</sup>), three sampling lines can be used (sample line 1: top rear headspace of the chamber/container, sample line 2: middle of the chamber/container, sample line 3: bottom/front of the chamber/container). Each sample line can be colour coded to avoid confusion while sampling.

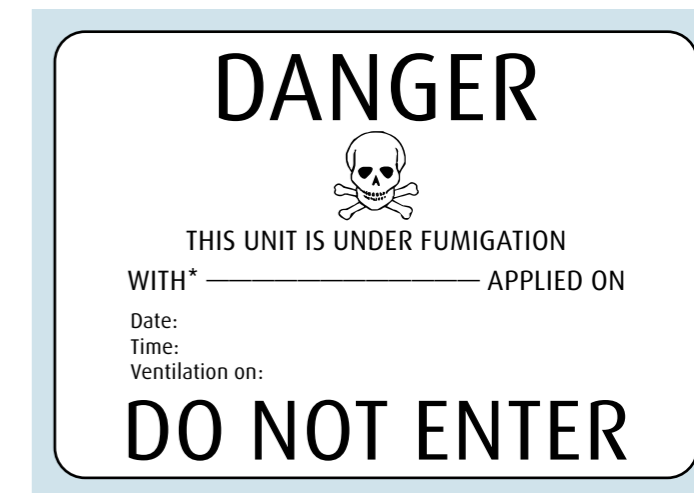
The VAPORMATE levels inside the container/chamber need to be checked for equilibrium 15 or 30 minutes after application. If the dose rate from the three sampling points is close to the recommended dose rate, the treatment period will begin (the variation from the three points of gas samples within the shipping container should be less than 15%). If it is above 15% then topping-up can be undertaken based on the dose required to compensate the loss.

### 12.5 Placarding and securing fumigated areas

A hazard zone must be identified and maintained in accordance with the relevant national standards. The zone should be marked with high visibility barriers/tape, and the area monitored to prevent unauthorised entry. Unauthorised/unprotected persons should be kept outside the hazard zone until the concentration of ethyl formate and carbon dioxide has reduced to safe levels:

Ethyl formate < 100 ppm  
Carbon dioxide < 5,000 ppm.

The following placards should be prominently displayed at all approaches to the hazardous area prior to fumigation:



Placards can be removed when fumigation and ventilation are complete and fumigant concentrations have reduced to safe levels. Above is an indicative sign – please refer to your local regulations.

Placard “Signal Word” may vary by country contingent on the governmental agency regulation (for example: “warning, this product is toxic”, etc.).

## 13. Monitoring equipment.

The safe application of VAPORMATE requires the monitoring of both ethyl formate and carbon dioxide for both fumigation as well as safety during the ventilation period. In summary, concentration must be monitored during fumigation to ensure a successful treatment and the surrounding areas must be monitored to ensure the TLV is not exceeded for either ethyl formate or carbon dioxide.

Use an appropriate detection device (ethyl formate, carbon dioxide) or detection tube (ethyl formate) where deemed appropriate.

### 13.1 Multi-gas detectors

Multi-gas detectors can accommodate up to four sensors, allowing the monitoring of four different types of gas including ethyl formate and carbon dioxide. The detection limits are generally 0.01% to 5% (by volume) for ethyl formate and 0.01% to 25% (by volume) for carbon dioxide. Accuracy is usually  $\pm 0.1\%$ . Standard monitors have a powerful diaphragm pump which can draw the gas samples from the container, allowing multiple areas of the fumigation chamber to be monitored. Contact your local Linde representative for details on availability of multi-gas detectors.

For example, VAPORMATE can be monitored using a GFG Microtector II G450 multi-gas detector.

## 14. Monitoring frequency.

VAPORMATE concentration in the fumigation enclosure should be monitored on at least two occasions during the fumigation exposure period, i.e. at the start and at the end of the fumigation exposure period. The applicator should make sure that equilibrium is attained at the start of the fumigation.

## 15. Fumigation.

VAPORMATE is delivered under pressure into the fumigation structure. Effective results depend on the required concentration of VAPORMATE being maintained for the time specified in the directions for use. This requires the fumigation enclosure to be gas-tight.

Mechanical mixing by flameproof recirculation fans will ensure that the VAPORMATE reaches equilibrium within the fumigation chamber as quickly as possible.

The exposure time for fumigation should not start until equilibrium has been achieved. To ensure compliance with relevant bio-security standards, records of times, concentrations, dates, exposure times and dosage should be maintained.

The fumigation area should be secure at all times, preventing unauthorised access. If the area cannot be physically secured, a watchman should be stationed to keep intruders out of the hazardous area in accordance with local standards.

Complete control of listed pests may not always be achieved. Factors contributing to less than 100% control include gas leakage, poor gas distribution, unfavourable exposure conditions, etc. Improperly sealed areas may allow escape to non-fumigated areas. In addition, some insects are less susceptible to VAPORMATE than others. To maximise control, extreme care must be observed in sealing, correct dosages must be used, VAPORMATE levels should be measured within the chamber and if necessary topped up to ensure the correct concentration over time is maintained, proper application procedures must be followed, and temperature and humidity must be favourable.

The VAPORMATE application temperature will vary depending on the commodity fumigated. This is attributed to crop safety and product efficacy. Please consult your Linde representative for optimal temperature recommendations for the commodity being treated.

## 16. Preparing for ventilation.

The chamber must be thoroughly ventilated of ethyl formate vapour (less than 100 ppm) and carbon dioxide (less than 5,000 ppm) as determined by a detection monitor or detection tubes before out-loading or re-entry. VAPORMATE can be vented to atmosphere under local standards.

Prior to ventilation, all unauthorised persons should be cleared from the hazard zone. Persons remaining within the hazard zone must be equipped with personal protective equipment including appropriate respiratory protection.

Ventilation may be performed passively by allowing VAPORMATE fumigant to escape from opened vents in the fumigation enclosure or by forced air movement using flameproof fans.

Ventilation is complete when the concentrations within the fumigation enclosure are less than 100 ppm for ethyl formate and less than 5,000 ppm for carbon dioxide. This should be checked using the VAPORMATE detection device. Once the safe level has been reached, the hazard signs can be removed.

# 17. Troubleshooting.

The information given here is of a generic nature and should be used as a guide only. For more information, contact your local Linde representative and/or refer to the VAPORMATE MSDS.

## 17.1 Valves

VAPORMATE cylinders are fitted with specialised valves that may be damaged if excess force is used to open or close the valve. Valves should be fully opened and then backed off by a ¼ turn. This helps to prevent the valve sticking open during use. Valves should be closed by hand – no special tooling should be used in the opening or closing process as this may damage the valve.

### Stuck valve

Never use excessive force to open a valve as this will damage the valve. If a valve will not open or close using the maximum allowed torque, tag the valve appropriately and return the cylinder to Linde as faulty.

### Leaking valve

Linde has strict quality control procedures for all cylinder packages. Despite this, a cylinder leak should be considered as part of the fumigation risk assessment. The MSDS should be referred to where human exposure takes place and the defective cylinder should be isolated in a safe area. Call your local Linde representative if assistance is required.

**In case of emergency, call the customer service number on your local label.**

## 17.2 Cylinder condition

If the cylinder looks to have suffered some damage, care must be taken before continuing to use the cylinder. Call your local Linde representative if assistance is required.

## 17.3 Failure to control the target pests

VAPORMATE efficacy data has been documented over many years, with much of the data appearing in peer-reviewed journals. This data is then reviewed by the regulatory authorities which have approved the VAPORMATE claims. Where 100% mortality has not been achieved, one of the following factors may apply:

- The dosage recommended on the product label has not been followed
- The volume to be fumigated has not been calculated properly, leading to under-dosing
- Fumigation has not been maintained for the required length of time
- Failure of, poorly calibrated or inaccurate monitoring devices
- Loss of fumigant through leaks and poor sealing and confinement of fumigant
- Fumigation has taken place below the required temperature (10°C/50°F)
- The dosage requirements vary for different pests

Linde is keen to work with customers to ensure successful fumigation. Where issues occur, contact your account manager.

## 17.4 Non-target organisms

After fumigation, there may be signs of non-target organism activity. This does not mean that the fumigation has failed, but may be a result of:

- Organisms may require higher dosage compared with the target organisms
- Organisms may have received a toxic dosage and will eventually die
- The non-target organisms may have entered during the aeration period

# Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde offers more. We create added value, clearly discernible competitive advantages and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardised as well as customised solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimisation and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

Linde – ideas become solutions.

For more information about our fumigation solutions and details of current or pending regulatory tests and approvals, visit [www.linde-gas.com/fumigants](http://www.linde-gas.com/fumigants)

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