In-transit cargo fumigation Safety considerations for ships' crews and terminal operators

Javier Quintero Saavedra, MSc, CMIOSH, FNI

1. A recent vessel's call to discharge


Panamax bulker
66,000 tonnes maize
ex Brazil
Cargo fumigated in transit

Load port docs

Fumigation Notice

The fumigant to be used is ALUMINIUM PHOSPHIDE (IN TABLETS).
The product generates "phosphine" gas (PH_3) at 1 g/cubic meter.

After 12 days of exposure goods must be ventilated during 12 hours.

Fumigation procedures will be done in accordance with the IMO "RECOMMENDATIONS ON THE SAFE USE OF PESTICIDES IN SHIPS - APPLICABLE TO THE FUMIGATION ON CARGO HOLDS" MSC.1/CIRC.1264- 27 MAY 2008

Load port docs (2)

To
Master of
At the SANTOS HARBOR

Fumigant Management Plan

CONTENTS

Load port docs (3)

Fumigant Management Plan

Physicochemical properties

Phosphine chemical formula: PH_3

Aluminum Phosphide chemical formula: **Al P**

Chemical reaction: $AlP + 3H_2O \longrightarrow Al(OH)_3 + PH_3$

Molecular weight: **34,04**

Inflammability: **27,2 g/m^3**

Boiling point: **- 87ºC**

Solubility in water: **228 ml gas Phosphine/L at 17ºC**

Aspect: **inflammable and colorless gas, garlic or carbide smells.**

No info as regards relative density

Load port docs (4)

Fumigant Management Plan

During the trip gas concentrations safety checks in the engine rooms should be carried out each 8 hours in the first two days. After that one check per day will be sufficient. If the concentrations attain 0.3 ppm, ventilation should be turned to the maximum. If it is still growing, the hold ventilation openings near the engine room should be opened until gas concentration gets under 0.3 ppm.

Somewhat hidden info in respect of occupational exposure limit values

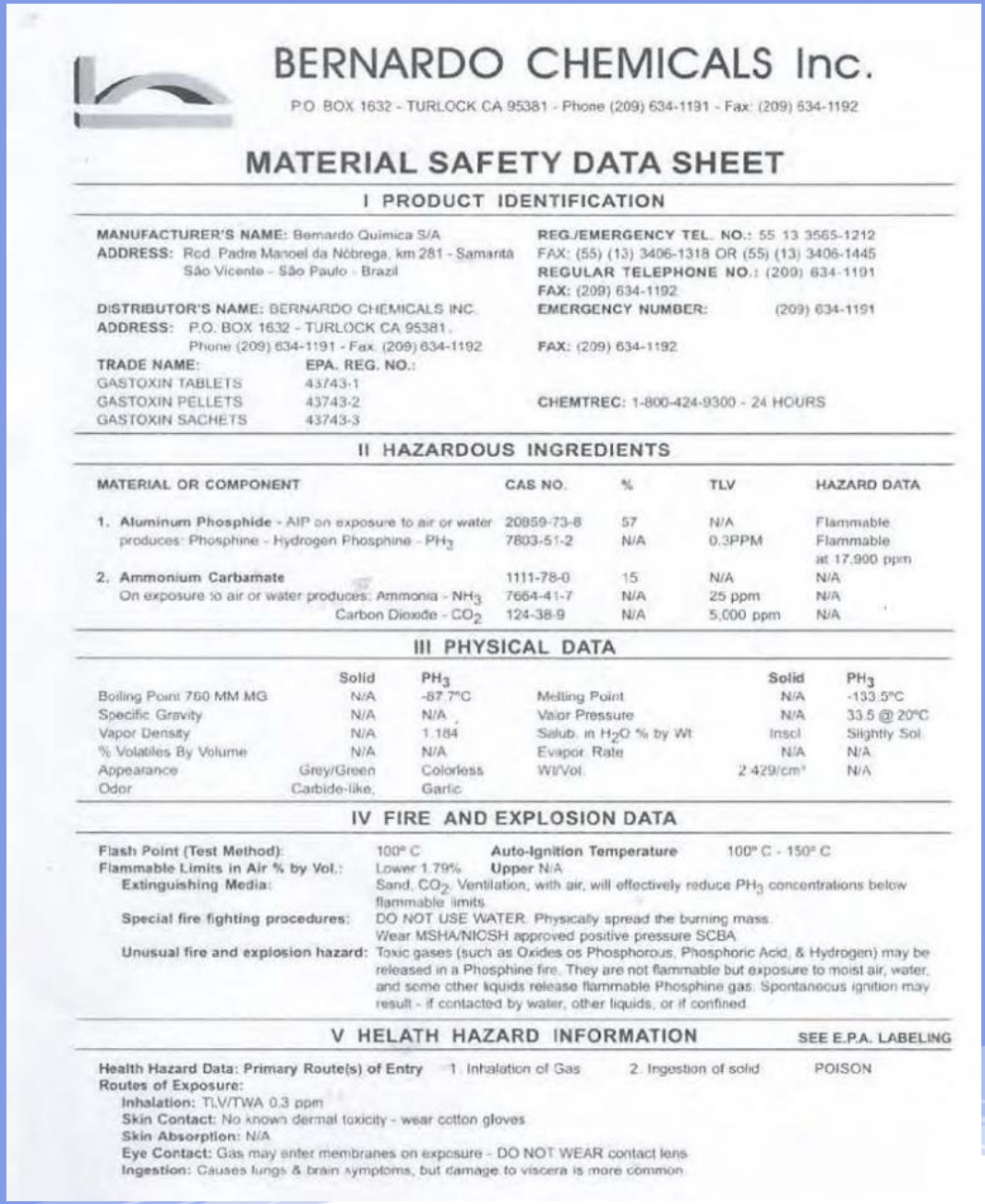
The fumigator just advises to check Engine Room spaces and to arrange for max ventilation if gas readings found to be 0.3 ppm or higher

Load port docs (5)

Fumigant Management Plan

Non GHS compliant SDS found in the Manual

Noted as odd since Brazil has already implemented it



BERNARDO CHEMICALS Inc.

P.O. BOX 1632 - TURLOCK CA 95381 - Phone (209) 634-1191 - Fax: (209) 634-1192

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME: Bernardo Quimica S/A
ADDRESS: Rod. Padre Manoel da Nóbrega, km 281 - Samaritá
São Vicente - São Paulo - Brazil

REG./EMERGENCY TEL. NO.: 55 13 3565-1212
FAX: (55) (13) 3406-1318 OR (55) (13) 3406-1445
REGULAR TELEPHONE NO.: (209) 634-1191
FAX: (209) 634-1192

DISTRIBUTOR'S NAME: BERNARDO CHEMICALS INC.
ADDRESS: P.O. BOX 1632 - TURLOCK CA 95381,
Phone (209) 634-1191 - Fax: (209) 634-1192

EMERGENCY NUMBER: (209) 634-1191
FAX: (209) 634-1192

TRADE NAME:	EPA. REG. NO.:
GASTOXIN TABLETS	43743-1
GASTOXIN PELLETS	43743-2
GASTOXIN SACHETS	43743-3

CHEMTREC: 1-800-424-9300 - 24 HOURS

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	CAS NO.	%	TLV	HAZARD DATA
1. **Aluminum Phosphide** - AlP on exposure to air or water	20859-73-8	57	N/A	Flammable
produces: Phosphine - Hydrogen Phosphine - PH_3	7803-51-2	N/A	0.3PPM	Flammable at 17,900 ppm
2. **Ammonium Carbamate**	1111-78-0	15	N/A	N/A
On exposure to air or water produces: Ammonia - NH_3	7664-41-7	N/A	25 ppm	N/A
Carbon Dioxide - CO_2	124-38-9	N/A	5,000 ppm	N/A

III PHYSICAL DATA

	Solid	PH_3		Solid	PH_3
Boiling Point 760 MM MG	N/A	-87.7°C	Melting Point	N/A	-133.5°C
Specific Gravity	N/A	N/A	Vapor Pressure	N/A	33.5 @ 20°C
Vapor Density	N/A	1.184	Solub. in H_2O % by Wt	Insol	Slightly Sol.
% Volatiles By Volume	N/A	N/A	Evapor. Rate	N/A	N/A
Appearance	Grey/Green	Colorless	Wt/Vol.	2.429/cm³	N/A
Odor	Carbide-like,	Garlic			

IV FIRE AND EXPLOSION DATA

Flash Point (Test Method): 100° C **Auto-Ignition Temperature** 100° C - 150° C
Flammable Limits in Air % by Vol.: Lower 1.79% **Upper** N/A
Extinguishing Media: Sand, CO_2. Ventilation, with air, will effectively reduce PH_3 concentrations below flammable limits.
Special fire fighting procedures: DO NOT USE WATER. Physically spread the burning mass. Wear MSHA/NICSH approved positive pressure SCBA
Unusual fire and explosion hazard: Toxic gases (such as Oxides os Phosphorus, Phosphoric Acid, & Hydrogen) may be released in a Phosphine fire. They are not flammable but exposure to moist air, water, and some other liquids release flammable Phosphine gas. Spontaneous ignition may result - if contacted by water, other liquids, or if confined.

V HELATH HAZARD INFORMATION

SEE E.P.A. LABELING

Health Hazard Data: Primary Route(s) of Entry 1. Inhalation of Gas 2. Ingestion of solid POISON
Routes of Exposure:
Inhalation: TLV/TWA 0.3 ppm
Skin Contact: No known dermal toxicity - wear cotton gloves
Skin Absorption: N/A
Eye Contact: Gas may enter membranes on exposure - DO NOT WEAR contact lens
Ingestion: Causes lungs & brain symptoms, but damage to viscera is more common

ISP 78 Fumigation

Current GHS compliant SDS found via internet search

BEQUISA
SAFETY DATA SHEET

1. PRODUCT AND COMPANY IDENTIFICATION

Product Identity:	**Gastoxin® Sachets**	EPA Reg. No. 43743-3
	Gastoxin® Tablets	EPA Reg. No. 43743-1
	Gastoxin® Pellets	EPA Reg. No. 43743-2

Recommended use of the chemical and restrictions on use: For use against insects which infest stored commodities. RESTRICTED USE PESTICIDE. Read and understand the entire label before using. Use only according to label directions. It is a violation of Federal law to use this product in a manner inconsistent to label directions.

Manufacturer:	Bequisa Avenida Antonio Bernado, 3950 Parque Industrial Imigrantes- CEP 11349-380 Sao Vicente- Sao Paulo- Brazil	**Supplier:**	Bernardo Chemicals, Inc. P.O. Box 1632 Turlock, CA 95381
Telephone:	+55-13-3565-1212	**Telephone:**	(209) 634-1191
Emergency Phone:	55 13 3565-1212	**Emergency Phone:**	(209) 634-1191 1-800-424-9300 (CHEMTREC- 24 hrs)

SDS Date of Preparation: 6/17/15

2. HAZARDS IDENTIFICATION

GHS Classification:

Physical	Health
Substances and mixtures which, in contact with water, emit flammable gases Category 1	Acute Inhalation Toxicity Category 1 Acute Oral Toxicity Category 2 Acute Dermal Toxicity Category 3 Eye Damage Category 1

GHS Label Elements:
Danger!

Hazard Statements

In contact with water releases flammable gases, which may ignite spontaneously.
Fatal if swallowed.
Toxic in contact with skin.
Causes serious eye damage.
Fatal if inhaled.

Precautionary Statements

Do not allow contact with water.
Handle and store contents under inert gas and protect from moisture.
Do not breathe dust or gas.
Wash thoroughly after handling.
Do not eat, drink or smoke when using this product.
Use only outdoors or in a well-ventilated area.
Wear protective gloves, protective clothing, eye protection and face protection.

Current GHS compliant SDS (2)

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure Guidelines:

Aluminum Phosphide (as aluminum, metal and insoluble compounds)	1 mg/m3 TWA ACGIH TLV (Respirable) 5 mg/m3 (respirable fraction), 15 mg/m3 (total dust) TWA OSHA PEL
Non-Hazardous Components	None Established
Ammonium Carbamate (as ammonia)	17 mg/m3 TWA, 24 mg/m3 STEL ACGIH TLV 35 mg/m3 TWA OSHA PEL

Exposure limits in respect of phosphine as the active ingredient noted as missing.

It is mentioned under section V in the dated MSDS attached to the fumigant management plan but not expressly related to phosphine

2. Analysis of the relevant IMO Circular

IMO MSC.1/Circ.1264 27 May 2008

Recommendations on the safe use of pesticides in ships applicable to the fumigation of cargo holds

IMO MSC.1/Circ.1264 27 May 2008

3.3.2.7 The ship should carry:

.1 gas-detection equipment…, together with instructions for its use and the occupational exposure limit values set by the flag State regulations for safe working conditions

IMO MSC.1/Circ.1264 27 May 2008 (2)

Appendix 1. Fumigants suitable for shipboard use

3.2 Phosphine

3.2.3. Prior to discharge, ventilation must be done, forced if necessary, to reduce the gaseous residues below the occupational exposure limit values set by the flag State regulations in the free spaces

IMO MSC.1/Circ.1264 27 May 2008 (3)

‘adequate respiratory protective equipment’
(Main text para. 3.3.2.7.3)

The SDS for GASTOXIN reads ‘of approved type’ which is also a way to skip on stating the actual equipment to wear

IMO MSC.1/Circ.1264 27 May 2008 (4)

No express mention to the availability of electronic gas-monitoring equipment, just to gas-detection equipment

Might the above explain why most ships receive and blindly accept colorimetric tubes that are no match against electronic gas monitors?

Purchasing cost in Spain, approx. EUR 330
Calibration every 6 months @ approx. EUR 100

IMO MSC.1/Circ.1264 27 May 2008 (5)

Main text

3.3.2.18

‘when the presence of personnel in cargo holds is necessary for the handling and operation of unloading equipment, continuous monitoring of the fumigated spaces should be carried out…’

IMO MSC.1/Circ.1264 27 May 2008 (6)

3.3.2.19

During the final stages of the discharge, when it becomes necessary for personnel to enter the cargo holds, such entry should only be permitted subsequent to verification that such cargo holds are gas free

IMO MSC.1/Circ.1264 27 May 2008 (7)

Do shipmasters and discharge ports actually enforce above 3.2.18 and 3.2.19 provisions?

A gas-free certificate upon arrival, prior commencement of the discharge, is not contemplated in the Circular but all too usual

3. Is there a need to fumigate?

Radiograph showing internal stages of insects within wheat kernels

Source: Principles of (phosphine) fumigation by Professor Bhadriraju Subramanyam, Kansas State University. IAOM 4th Annual SE Asia District Conference. October 2013. Ho Chi Minh, Vietnam

4. Phosphine (PH_3)

PH_3

Widely used fumigant to control insects in stored grain and other agricultural commodities replacing the ozone layer depleting, methyl bromide

PH_3 (2)

Relative vapour density (air = 1) 1.17

Explosive @ concentrations above 1.6% in air

Odourless and colourless in pure form

PH_3 (3)

Technical grade PH_3 prepared by hydrolysis of aluminium phosphide (AlP) or magnesium phosphide (Mg_3P_2) has a garlic-like odour due to impurities

Odour threshold in the region of 0.5 ppm (0.7 mg/m³) with some sources stating 2 ppm

PH_3 (4)

TLV – OEL – WEL – PEL - OES

8 hour TWA (time-weighted average), 40-41 hr working week

EU, PRC

0.1 ppm (0.14 mg/m³)

ACGIH, USA, Australia, Japan (JSOSH)

0.3 ppm (0.4 mg/m³)

PH_3 (5)
Really that dangerous?

Lethal Concentration (LC_{50})

Concentration in air, 4-hour exposure, lethal to at least 50% of test animals

Rats 15 ppm / Mice 30 ppm

US NIOSH IDLH Value

Immediately Dangerous to Life or Health

50 ppm

US NIOSH IDLH Values established

(1) to ensure that the worker can escape from a given contaminated environment in the event of failure of the respiratory protection equipment

(2) to indicate a maximum level above which only a highly reliable breathing apparatus, providing maximum worker protection, is permitted

Indian fumigation workers exposed to 0.17 - 2.11 ppm PH_3 for 20-30 mins symptoms of respiratory irritation, headache, giddiness, lethargy, irritability, nausea and epigastric pain immediately after exposure (Misra et al., 1988)

'Health risks in international container and bulk cargo transport due to volatile toxic compounds'

Table 5 Examples of reported incidents/intoxications with fumigants on bulk cargo ships

Date	Location	Fumigant	No. of subjects		Reference/source
			Affected	Fatalities	
September 1978	Bulk grain freighter, East coast Canada/USA	PH_3	31[1)]	2[1)]	[46] (PubMed)
1988-1996	Danish bulk carriers	PH_3	2	1[2)]	[45] (PubMed)
		Unknown pesticide	4	3[2)]	
October 2007	General cargo ship, Russia – UK	PH_3	1	1	MAIB Accident Flyer 1/2008
2010	General cargo ship, Latvia – Antwerp	PH_3	2	1	Gard News 204 Nov 2011/Jan 2012 http://www.gard.no/
2010	Bulk carrier US East coast	PH_3	16	0	
2009	General cargo ship, Lagos, Nigeria	PH_3	6[3)]	1[3)]	
2000	Bulk carrier US West coast	PH_3	12	0	
1997	Geared bulker Brazil – Ireland	PH_3	5	0	

[1)] 2 children.
[2)] 4 stowaways.
[3)] 6 stowaways.

Xaver Baur et al
Journal of Occupational Medicine and Toxicology (2015) 10:19
European Society for Environmental and Occupational Medicine (EOM)

5. Available PH_3 based fumigants

PH_3 based fumigants

- Liquefied pressurised gas mixtures containing PH_3

- Tablets, pellets, sachets, gas permeable bags or blister packs containing metal phosphides (AlP or Mg_3P_2) that in contact with water or ambient air moisture give rise to PH_3 gas

$$AlP + 3H_2O \longrightarrow PH_3 + Al(OH)_3$$

$$Mg_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Mg(OH)_2$$

PH_3 based fumigants (2)

Registered commercial PH_3 or PH_3 generating products contain inert ingredients to regulate the release of PH_3 and suppress or retard flammability

Those for application in gas state present the advantage that they are safer. No chemical reaction is involved and this allows for the instant/immediate start of the fumigation

PH_3 based fumigants (3)

Liquefied compressed gas mixture ECO_2FUME in cylinders for instance contains 2 % by weight PH_3 and 98% compressed CO_2 that acts as propellant and retards flammability

Liquefied pressurised gas mixture $VAPORPH_3OS$ Phosphine fumigant in cylinders is blended on site to less than 3% v/v with forced air to eliminate the flammability hazard

PH_3 based fumigants (4)

GASTOXIN tablets = 57% PH_3

DELICIA-GASTOXIN tablets = 68% PH_3

Percentages refer to technical grade PH3, i.e. upon the hydrolysis of AlP

They usually start to react 1 hour after application

Known potential risk:

Not reacting fully during the fumigation period and doing so in the course of the discharge on becoming exposed to moisture ex fresh air ambient

PH_3 based fumigants (5)

Inert ingredients of the above tablets
Basically ammonium carbamate which reacts into ammonia (NH_3) and CO_2

$$NH_2COONH_4 \longrightarrow 2NH_3 + CO_2$$

ACGIH TLV NH_3 25 ppm (17 mg/m^3)
EC SCOEL recommended OEL 20 ppm (14 mg/m^3)

This means that inert components mitigate flammability risks but are dangerous to inhalation

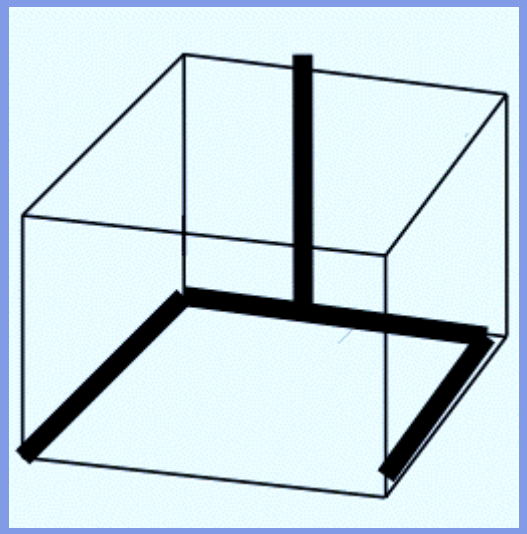
6. Fumigation methods and spaces

In-transit fumigation of vessel's holds

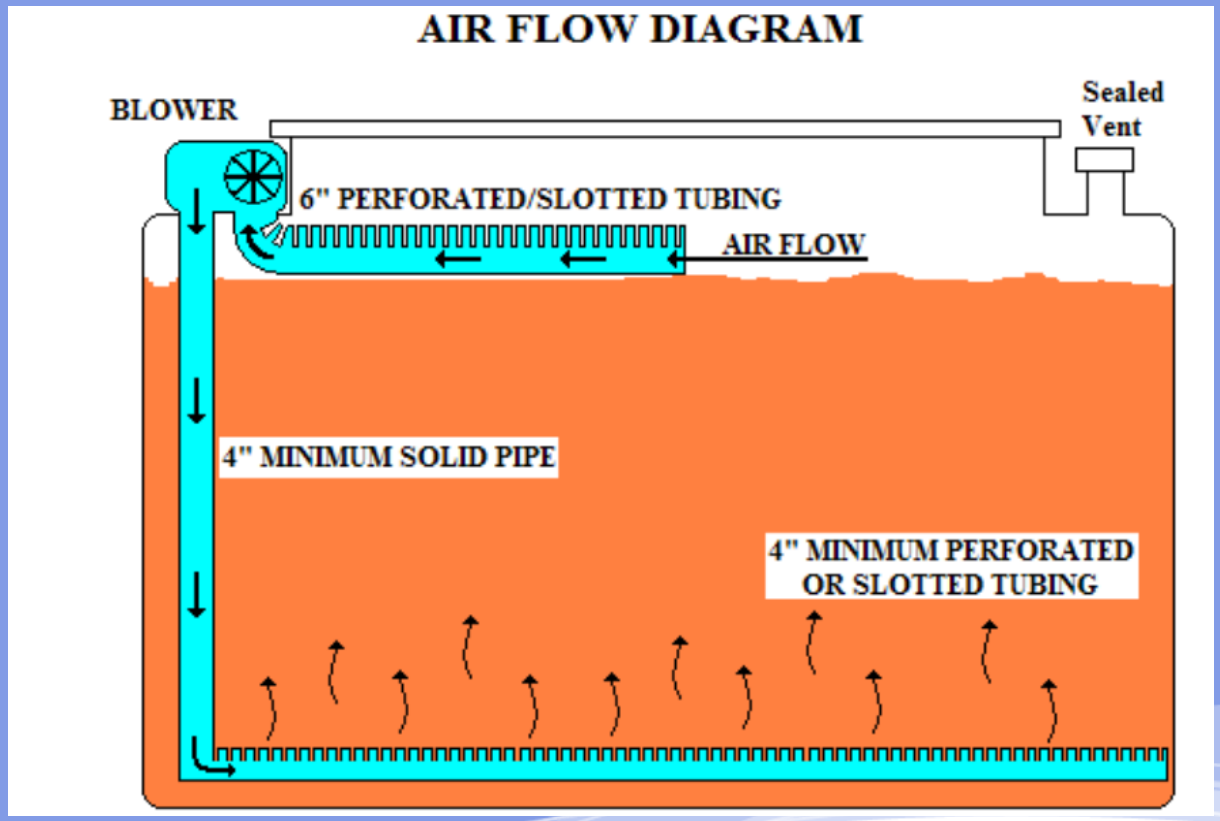
USDA FGIS acceptable application methods

- **Surface treatment**
- **Sub-surface treatment (trench-in): Shallow trench approx. 0.3 m (1 foot) deep**
- **Recirculation system**

In-transit fumigation (2)



Recirculation system



In-transit fumigation (3)
Other methods
(used in non US ports)

Short probe

tubes of polyethylene approx.1.5 m long are inserted into the grain to a depth of 2/3 of their length; then filled with pellets or tablets to at least ½ of the length and then removed from the grain

In-transit fumigation (4)
Other methods

Long probe

tubes of polyethylene are inserted into the grain to a depth of at least 4 meters. Pellets or tablets are poured into the probe, and the probe is slowly extracted from the grain

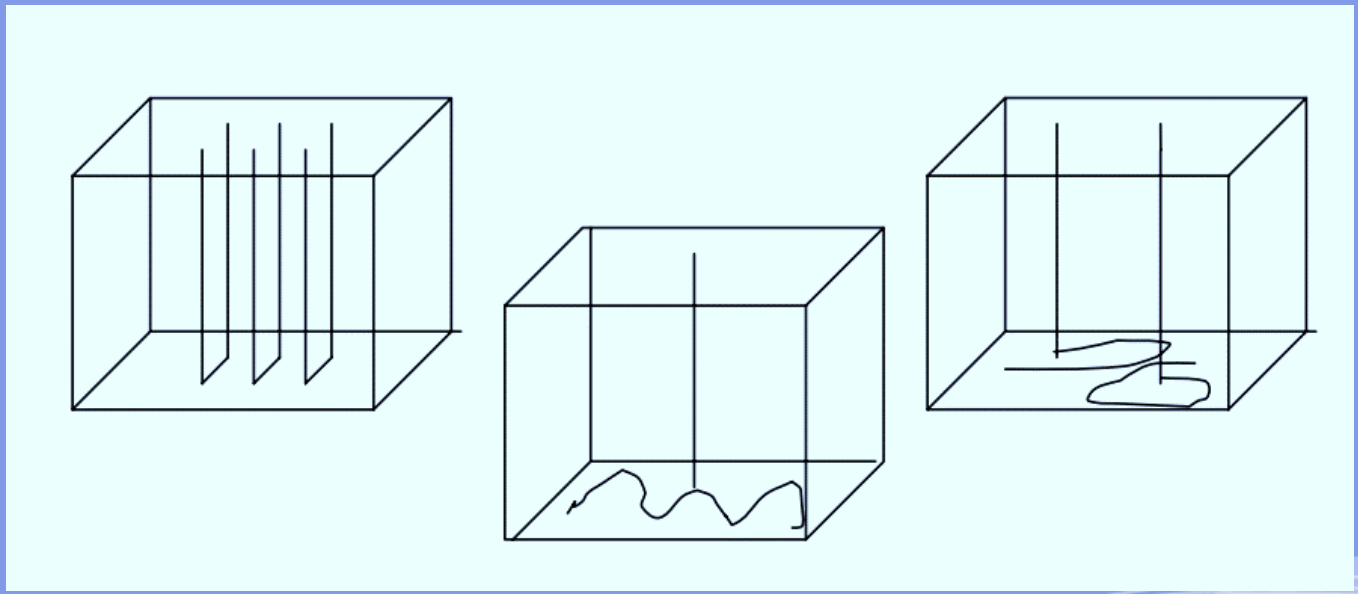
In-transit fumigation (5)
Other methods

Long probe/short probe combination

At least one long probe in each corner of the hold, applying the remaining dose using the short probe method

In-transit fumigation (6)
Other methods

Tubing system

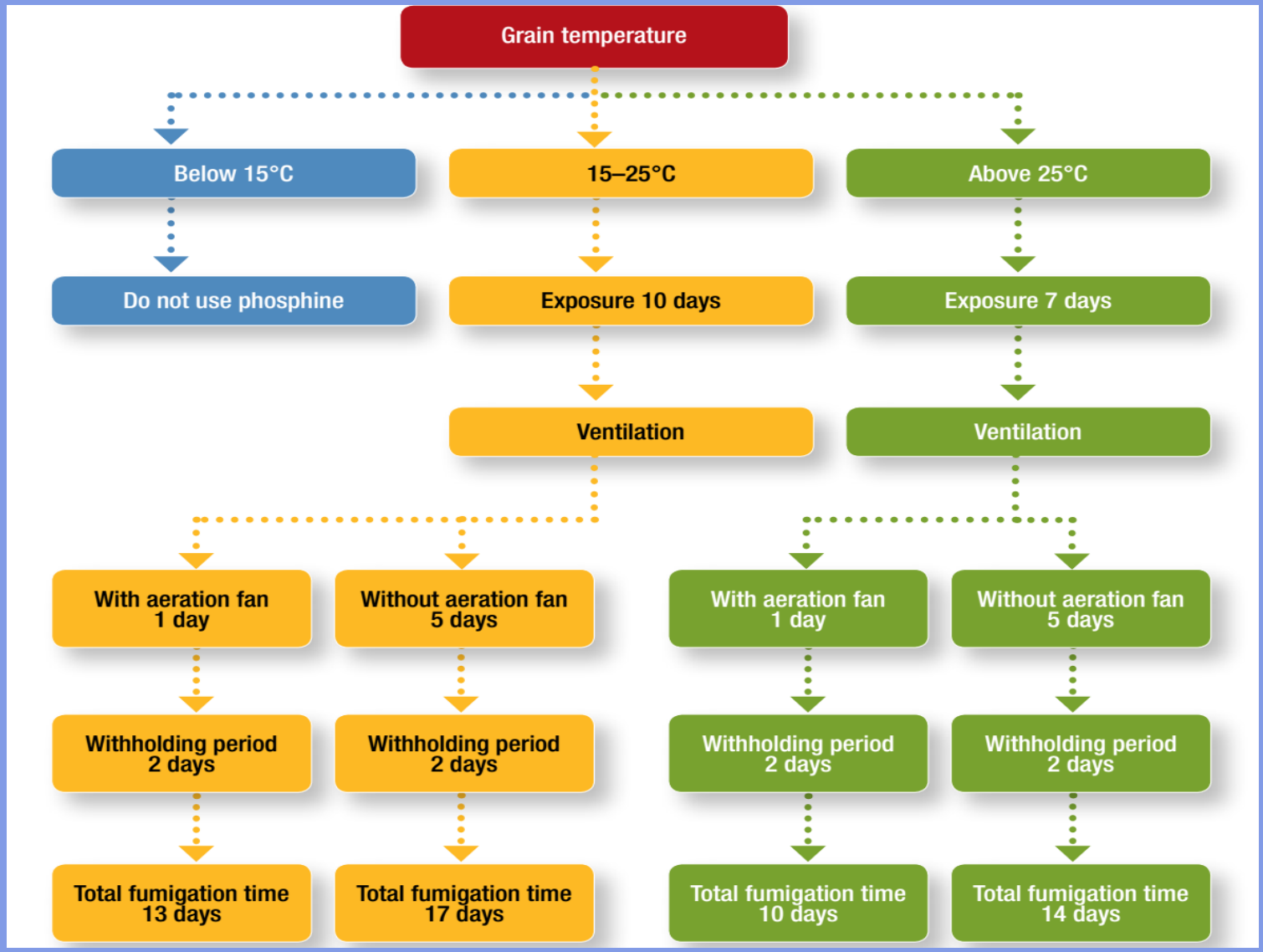


In-transit fumigation (7)

Relevance of air ambient temperature at load port

Temperature	Minimum Exposure Periods for GASTOXIN® Pellets	Tablets
40°F (5°C)	Do not fumigate	Do not fumigate
41°-53°F (5-12°C)	8 days (192 hours)	10 days (240 hours)
54°-59°F (12-15°C)	4 days (96 hours)	5 days (120 hours)
60°-68°F (16-20°C)	3 days (72 hours)	4 days (96 hours)
above 68°F (20°C)	2 days (48 hours)	3 days (72 hours)

Source: Applicator's Manual as found in US EPA 2010 re-registration Notice of GASTOXIN fumigation tablets



Fumigating with phosphine. GRDC (Australia). 2011. Chart source Kondinin Group

7. Back to the 66,000 T maize case

Relevant data not made available to shipmaster

"The complete label for this product consists of the container label and applicator's Manual which must accompany the product"

Source: Applicator's Manual as found in US EPA 2010 re-registration Notice of GASTOXIN fumigation tablets

Contents ex Applicator's Manual

TRAINING REQUIREMENTS FOR RECEIPT OF INTRANSIT VEHICLES UNDER FUMIGATION

The trained person(s) must be trained by a Certified Applicator following the EPA accepted product applicator's manual that must precede or be attached to the outside of a transport vehicle

Contents ex Applicator's Manual (2)

Respiratory protection is required when concentration levels of phosphine are unknown

Contents ex Applicator's Manual (3)

A NIOSH/MSHA approved full-face gas mask - phosphine canister combination may be used at levels up to 15 ppm

Above 15 ppm or in situations where the phosphine concentration is unknown, a NIOSH/MSHA approved, SCBA must be worn

NIOSH approved full-face gas mask – PH_3 canister combination sets may be legally used in countries that allow them only

The problem lies with countries such as EU member states where no manufacturer has available canisters expressly marked for PH_3 as they have not involved any CE marking notified body to attest it

Add to the above there is no internationally accepted standard to test PH_3 canisters

Contents ex Applicator's Manual (4)

Glass detection tubes used in conjunction with the appropriate hand-operated air sampling pumps are widely used

Electronic devices are also available for both low level and high phosphine gas readings

Contents ex Applicator's Manual (5)

Exposures to phosphine must not- exceed the·8-hour time-weighted average (TWA) of 0.3 ppm or the 15 minute short-term exposure limit (STEL) of 1.0 ppm phosphine.
All persons are covered by these exposure standards

8. CONCLUSIONS

Need to raise awareness

Convenience of updating the IMO Circular to better inform shipmasters