



SAFETY INVESTIGATION REPORT

201212/020

REPORT NO.: 21/2013

December 2013

The Merchant Shipping (Accident and Incident Safety Investigation) Regulations, 2011 prescribe that the sole objective of marine safety investigations carried out in accordance with the regulations, including analysis, conclusions, and recommendations, which either result from them or are part of the process thereof, shall be the prevention of future marine accidents and incidents through the ascertainment of causes, contributing factors and circumstances.

Moreover, it is not the purpose of marine safety investigations carried out in accordance with these regulations to apportion blame or determine civil and criminal liabilities.

NOTE

This report is not written with litigation in mind and pursuant to Regulation 13(7) of the Merchant Shipping (Accident and Incident Safety Investigation) Regulations, 2011, shall be inadmissible in any judicial proceedings whose purpose or one of whose purposes is to attribute or apportion liability or blame, unless, under prescribed conditions, a Court determines otherwise.

The report may therefore be misleading if used for purposes other than the promulgation of safety lessons.

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MV THEOFYLAKTOS Explosions in four cargo holds at Rio Grande Outer Anchorage 22 December 2012

SUMMARY

In the early morning of 22 December 2012, the bulk carrier *Theofylaktos* anchored at Rio Grande outer anchorage. A few hours earlier, fumigation of her cargo of wheat was completed by a shore-based contractor whilst in port.

In-transit fumigation was planned to ensure cargo disinfection by the time the vessel reaches her discharge port.

During the afternoon, an explosion happened in cargo hold no. 4, followed by the escape of white smoke over the cargo deck area. Further explosions occurred in other cargo holds.

This culminated in a relatively violent explosion in cargo hold no. 2 at 1622. Eventually, the situation was brought under control and temporary repairs enabled the vessel to continue on her voyage for repairs.

The safety investigation concluded that the immediate cause of the explosions was an explosive mixture of phosphine and air.

The MSIU has issued two recommendations to the ship managers, intended to ensure appreciation of the hazards related to fumigation by phosphine gas.



MV Theofylaktos

FACTUAL INFORMATION

The vessel and her crew

Theofylaktos is a 7-hatch, gearless Panamax-size bulk carrier built in February 1995 at Daewoo Shipbuilding, South Korea and registered under the Maltese flag. She is owned by Kingsley Shipping Co. Ltd., managed / operated by General Maritime Enterprises Corporation, which is based in Piraeus, Greece, and classed by Lloyd's Register.

Theofylaktos is a vessel typical of her class, having a length overall of 225 m and a moulded depth of 32.20 m. She has a summer deadweight of 72610 tonnes at a corresponding draught of 13.8 m. Her cargo holds are fitted with Kvaerner side rolling hatch covers. *Theofylaktos* was exempted from the relevant SOLAS requirements for a fixed fire-fighting installation in her cargo holds; subject that the intended cargo is classified as a low fire risk.

Propulsive power is provided by a 6-cylinder B&W 6S60MC, slow speed direct drive diesel engine producing 9213 kW at 87 rpm. This drives a single, fixed pitch propeller to reach a speed of about 14.5 knots.

With the exception of the chief and second engineers, the vessel was manned nearly in its entirety with officers and ratings from South-East Asia. The master had been on board for just over a month whilst the chief and second mates had joined the vessel in May 2012.

When the first explosion occurred, the deck ratings were busy stowing moorings into the forecabin store while on the bridge the second mate and later the chief mate, were on watch.

Environmental conditions

The port of Rio Grande, located in the southern Brazilian state of Rio Grande do Sul, lies within the South Temperate Zone with generally a subtropical climate. During the loading period, between 17 and 21 December,

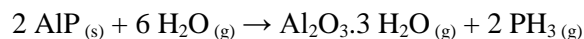
the weather was characterised by high relative humidity with some rain showers that necessitated cargo loading operations to be suspended and hatch covers closed. At the time of the cargo holds' explosions, the weather was good with a North-Easterly fresh breeze.

Fumigation of grain bulk cargoes

In the case of organic products transported by ship, it is a standard practice to apply pesticides in order to ensure no infestation and contamination by pests. This is necessary for commercial reasons as well as to comply with international phytosanitary standards.

In the case of grain cargoes, a gas formulation of pesticide in fumigant form has been found to be very effective. Time savings are possible when fumigation of the cargo is commenced in port after loading is completed and continued whilst the vessel is at sea. This is known as 'in-transit fumigation' and it was the method applied on *Theofylaktos*.

The most widely used pesticide for in-transit fumigation is phosphine (PH₃) gas (also known as hydrogen phosphide). There are various ways to generate and apply the gas. However, almost all shipboard fumigation (as in this case) is carried out using a formulation of aluminium phosphide (AlP) or magnesium phosphide (Mg₃P₂) combined with other inert materials in tablet, pellet or granular forms. PH₃ gas is generated when the aluminium phosphide tablets react with the moisture in the air as follows:



There are diverse methods of fumigant application, the most common of which is surface application. The aluminium phosphide tablets are spread over the cargo surface and the PH₃ gas produced gradually permeates into the cargo. This is an acceptable, albeit rather slow process, when the depth of the stow is less than six metres. Variations, such as the 'trench-in method', are also used.

Where the cargo stow is deeper, *i.e.* in the region of 12 m to 20 m for Panamax-size vessels, the ‘J’ or ‘Recirculation System’ is utilised (Figure 1). In the Information Booklet provided to the vessel by the fumigation company, the ‘J System’ is described as a “patented... cargo hold fumigation system.”

In the ‘J System’, PH₃ gas is circulated through the cargo by means of perforated tubes and a special electrical fan. This results in a rapid, even and effective distribution of gas in the cargo hold.

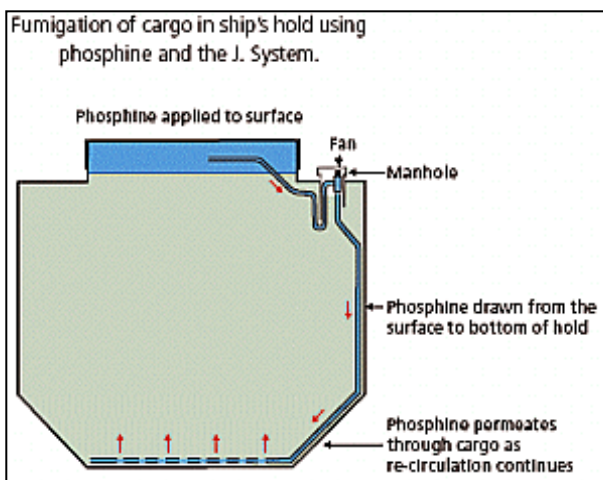


Figure 1: The ‘J System’

Source: UK P&I Club, “Carefully to Carry”

Aluminium phosphide in the form of tablets or pellets is distributed over the cargo surface. A fan then draws the PH₃ gas from the space above the cargo and distributes it through the plastic tubing to other areas of the stow.

Even distribution of the gas is essential in order to avoid an excessive concentration of PH₃ gas / air mixture in the space between the cargo surface and the cargo hold hatch cover.

Narrative

The vessel arrived at Bianchini Terminal, Rio Grande, late in the evening on 16 December 2012. Immediately after berthing, the necessary preparations to load wheat in bulk were made. Commencing at 2200¹, a draught

¹ Unless otherwise stated, all times are local.

survey, a hatch cover hose test, and a cargo hold inspection were carried out.

At the same time, personnel from the fumigation company laid out plastic pipes on the tank tops of each cargo hold, as part of the ‘J System’ of fumigation. They also installed fan motor blowers inside the cargo holds’ access trunking. The suction inlet of the ‘J System’ was also located in way of the cargo hold access trunk (Figure 2) rather than in the cargo hold above the cargo top layer (Figure 1).

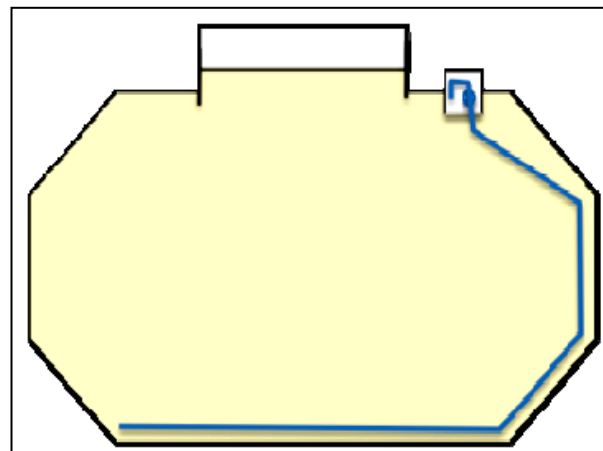


Figure 2: Location of suction inlet inside the cargo hold access trunk

At 0215 (17 December 2012) loading operations commenced in cargo holds nos. 2, 3, 5 and 6. The cargo operations were completed less than 24 hours later at 0200 on 18 December 2012. After the draught survey was completed, the vessel cast off and anchored outside the port, waiting for her berth to become available at the second loading terminal.

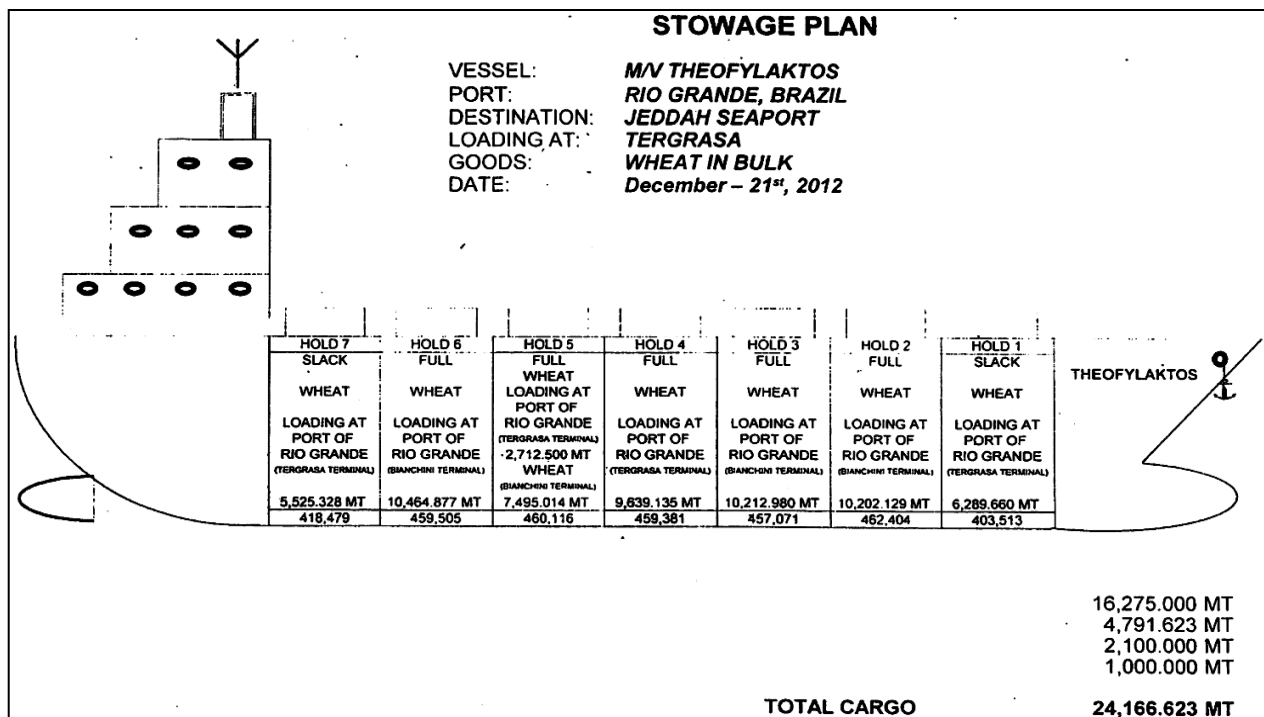


Figure 3: Cargo stowage plan

Theofylaktos was fast alongside at the second loading terminal (Tergrasa Grain Terminal) at 0054 on 20 December 2012. Loading of cargo holds nos. 1, 4, and 7 commenced at 0615 and was completed the next day at 2200 (Figure 3). Fumigation in the cargo holds was started shortly after at 2210.

Fumigation and subsequent explosion

Aluminium phosphide tablets were distributed on the cargo surface by personnel from the fumigation company. This process was recorded complete at 2350. On 22 December at 0105, the vessel sailed from her berth to anchor at the outer roads, pending clearance of documents from the customs authorities and final sailing permission from the Harbour Master.

On the advice of the fumigation company, measures were taken to ensure that the cargo hold hatches were effectively sealed and gas-tight. To this effect, expanding foam was applied around the hatch cover sides. In addition, the hatch cover joints were sealed with “ram-nek” adhesive tape.

An account of the events by several crew members suggested that on 22 December at 1432, the first explosion occurred in way of cargo hold no. 4, producing white and grey smoke escaping from the hatch cover joints. Four pieces of quick-acting cleats sheared off as a result of the explosion.

A second less violent explosion in cargo hold no. 4 was reported at 1600, also generating white and grey smoke escaping from the hatch cover joints (Figure 4). More smoke and a violent release of energy were observed on the port side of cargo hold no. 6 at 1620. About two minutes later, a larger explosion occurred in cargo hold no. 2. Crew members observed the hatch covers lift above the deck to an estimated height of between two to three metres and land on the hatch coamings (Figure 5).



Figure 4: Smoke from cargo hold hatch no. 4



Figure 6: *Theofylaktos* at Valletta 28 March 2013

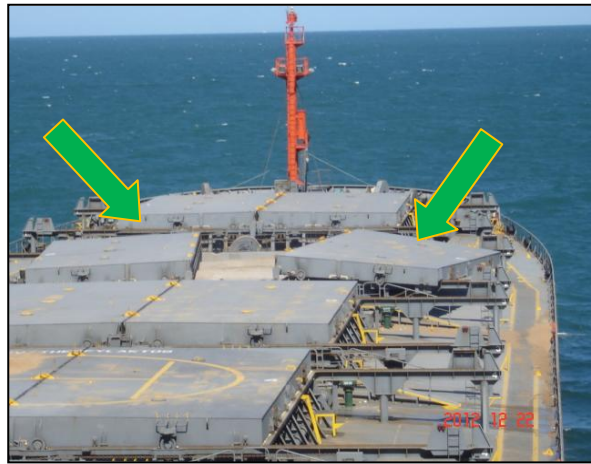


Figure 5: Cargo hold no. 2 with displaced hatch covers

Although there are no records as to whether the general alarm was sounded, the crew members retreated to the safety of the accommodation until the situation stabilised. The air-conditioning system was switched to re-circulation mode and the deck electrical power supply was shut off. *Theofylaktos* remained at Rio Grande anchorage for inspection and assessment of structural damage.

Further surveys and inspections were carried out after the vessel entered the port, where temporary repairs were carried out. On 09 January 2013, a short-term International Load Line Certificate was issued by the Classification Society on behalf of the flag State and the vessel sailed for Jeddah. Wheat in cargo hold no. 2 was eventually discharged for transshipment in Valletta, Malta on 28 March 2013 (Figure 6).

Structural damages

The structural damages were limited to the cargo area. Cargo hold no. 2 was the most affected. Plating in way of the hatch cover and hatch coamings was found buckled and displaced. A number of hatch cover transverse girders were also damaged. Damages were also found in the hatch cover rubber channels, stoppers, chain fittings and compression bars.

Cargo hold no. 6 hatch cover was also slightly affected and displaced upwards.

ANALYSIS

Aim

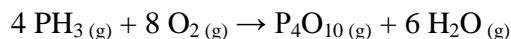
The purpose of a marine safety investigation is to determine the circumstances and safety factors of the accident as a basis for making recommendations, and to prevent further marine casualties or incidents from occurring in the future.

Immediate cause of the explosion

The observed mechanical and thermal damage to the ship were entirely consistent with the occurrence of gas phase explosions in the four cargo holds.

Considering the presence of PH₃ gas, it is concluded that the explosion was the result of the ignition of this gas in air.

The reaction is represented in the following chemical equation:



As indicated above, the burning of PH₃ gas forms phosphorus pentoxide (P₄O₁₀). P₄O₁₀ is a white gas (Figure 4).

Factors producing explosive air/gas mixtures

The main hazard normally associated with the use of PH₃ gas as a fumigant is its high toxicity. Indeed, it can endanger the lives of crew members and shore-based personnel if exposed to the gas without them wearing the necessary Personal Protective Equipment (PPE)².

Another hazard posed by PH₃ gas, and which is of relevance to this safety investigation, is its property as a flammable gas. PH₃ gas is both colourless and odourless.

Whilst no source of ignition was identified in the cargo hold, the auto ignition temperature of pure PH₃ gas is 38°C. However, the presence of impurities, particularly diphosphine, often causes PH₃ gas to ignite spontaneously at room temperature and to form explosive mixtures at concentrations greater than 1.8% by volume in air. It has also been noted by experts that the spontaneous ignition behaviour of PH₃ gas is very unpredictable.

The aluminium phosphide tablets utilised in fumigation are typically composed of aluminium phosphide and other inert ingredients. Literature suggests that in order to reduce the risk of fire, the tablets contain ammonium carbamate (NH₂CO₂NH₄), which releases ammonia and carbon dioxide, hence reducing the potential fire hazard posed by PH₃ gas. Although the ammonium carbamate reduces the potential danger of fire, it does not eliminate it.

² Vide MAIB Report No. 21/2013: http://www.maib.gov.uk/publications/investigation_reports/2013/arklow_meadow.cfm

As explained above, the aluminium phosphide tablets react with water vapour (moisture) in the air to generate PH₃ gas. The rate of this reaction depends on, *inter alia*, the prevailing atmospheric temperatures, humidity and to some extent the moisture content of the cargo. Moreover, the chemical reaction of aluminium phosphide with moisture in the air may sometimes produce small quantities of diphosphine. Diphosphine is also a gas which ignites spontaneously when it reacts with the oxygen in the air³.

Records covering the period between 17 and 22 December indicated that during loading, the relative humidity was on the high side with values in excess of 75%. It can be fairly stated that the generation of PH₃ gas commenced immediately after the hatch covers were closed and that its production may have been elevated due to the humidity level.

The MSIU was unable to determine the moisture content of the cargo and whether or not it was excessive. Although it was stated that the hatch covers were closed during rain showers on advice from the loading terminal, it is not excluded that some of the cargo was wet to a certain degree.

It was neither excluded that water originating from the condensation of humid air eventually came in contact with the tablets spread over the cargo stow.

One factor that may have contributed to an increase in the temperature in the head space of the cargo hold (and above the auto ignition temperature of PH₃ gas) was the distribution of the aluminium phosphide tablets on the cargo surface. The tablets were in very close proximity within the centre area of the cargo hold rather than spread out evenly⁴ (Figure 7).

³ Safety investigations into similar accidents revealed that this chemical reaction is likely to occur when there is an imbalance between aluminium and phosphorus during the manufacturing process.

⁴ This needs to be considered with a further increase in temperature because the generation of PH₃ gas is an exothermic chemical reaction.



Figure 7: Aluminium phosphide tablets distribution in cargo hold no. 2

It may have been possible that this high concentration of generated PH_3 gas would not have necessarily been a contributing factor to the explosions, had the efficient diffusion of the gas (*via* the ‘J System’) been achieved as intended. It is indeed doubtful whether the ‘J System’ effectively diffused the elevated rate of production of PH_3 gas through the entire stow.

Further to the elevated production rate of PH_3 gas, ineffective distribution of the gas could have been a contributing factor as a result of the location of the suction pipe of the ‘J System’ in the upper part of the access trunk for each cargo hold (Figure 8), making it difficult to draw the generated gas from the surface of the cargo.

The safety investigation has also considered the possibility of blockages in the plastic tubing hence preventing the free transfer of the gas. However, there was no evidence to substantiate this hypothesis.

It is also pertinent to highlight that the explosions occurred about 14½ hours after the fumigation had commenced. This was considered to be the time when explosive mixtures of air and phosphine would have been reached⁵.

⁵ UK P&I Club Bulletin 289 - 02/03 – ‘Fumigation (Phosphine) Explosions’ clearly indicates that very



Figure 8: ‘J’ system inlet of suction pipe and recirculation fan in the cargo hold access trunking

The effect of these explosions was more severe in cargo hold no. 2, although the safety investigation could not accurately establish the reasons behind this.

In-transit fumigation and risk perception

Whilst the IMO recommends that in-transit fumigation should be carried out at the discretion of the master⁶, the latter has to take several technical factors when considering the various aspects of the fumigation process.

A detailed Brief by one P&I Club on the subject matter explained that PH_3 gas is only effective if a lethal concentration is maintained for a period of time, which can be as little as three days or as much as three weeks.

The duration of the lethal concentration would depend on the cargo temperature, insect species that may be present, and the adopted

potential explosive mixtures of air and phosphine are frequently encountered during the first 12 to 24 hours of phosphine fumigations, when the phosphine concentration in the upper areas of the cargo hold reaches a peak concentration.

⁶ *Vide* MSC.1/Circ.1264, as amended.

system of fumigation. Thus, the in-transit fumigation is a crucial aspect since the voyage time would ensure that the fumigation process has been effective.

From a safety aspect, in-transit fumigation is not free from risks. Toxicity is one component, whilst the hazard of flammability as explained elsewhere has to be factored in. However, there was no evidence to suggest that flammability was a specific concern on board.

Information on the fumigation and the release of PH₃ gas as a fumigant were provided to the master by the fumigator-in-charge. The document explained in detail the gas, its detection, fumigation process, and ventilation of the cargo holds (which had to be carried out two days before berthing at the discharge port). Precautions were also explained and quantities used were recorded. Adequate PPE was also provided on board.

The Material Safety Data Sheet (MSDS), which formed part of this document, detailed the hazards related to fire and explosions in Section III. Although it was clearly stated that PH₃ gas “may ignite spontaneously in air at concentrations above its LEL of 1.8% v/v,” this information was somewhat limited. Thus, whilst (concise) information on the fire and explosion hazards was available on board, it did not raise particular concern amongst the crew members.

It was acknowledged that once a fire / explosion occurred inside the cargo holds, the crew members would have been very limited in the actions which they could have taken, except for limiting the damage and extinguishing the fire without endangering themselves and the ship⁷. However, during the loading operation, what seemed to be the uneven distribution of the tablets across the cargo hold (leading to an elevated rate of

production of PH₃ gas) was missed and not queried by any of the crew members.

One of the main aims of risk assessments is to identify whether a system is acceptable in its current state or changes in its parameters are required so that an acceptable status is achieved. Nonetheless, risk assessment is only one process, which follows risk perception.

The crew members were not involved in the fumigation process, given that they were neither trained nor qualified to oversee the fumigation process. In fact, the fumigator-in-charge stated that during the fumigation process, only the fumigation team (wearing their PPE) remained in the vicinity of the cargo hold being fumigated. Therefore, the potential issue of risk perception was already present at this stage.

Empirical research in other domains on the subject matter demonstrates that hazard perception comes from an array of factors, which range from detection to cognitive inferences.

These factors are listed below in order of strength:

- perception of human senses;
- comparison with standards;
- perceptible events that could have been related to hazardous conditions; and
- memory recall.

Theofylaktos crew members had none of these factors available until after the accident happened. Their ability to assess the fire and explosion risk was also limited as a result of the combination of these factors and the limited emphasis on the fire and explosion characteristics of PH₃ gas.

⁷ Water should never be used to extinguish metal phosphide fires.

Information on PH₃ gas

In 2008, the Maritime Safety Committee adopted the “Recommendations on the Safe Use of Pesticides in Ships Applicable to the Fumigation of Cargo Holds” (MSC.1/Circ.1264). The Circular, which applied to the carriage of solid bulk cargoes, including grain and, *inter alia*, detailed the measures to be taken, giving due regard to the poisonous nature of fumigant gases.

MSC.1/Circ.1264 made no reference to the flammable properties of PH₃ gas and the risk of explosive air/gas mixtures. However, an amendment to MSC.1/Circ.1264, which was adopted in 2011, made specific reference to fire risks *i.e.*, “[w]hen Phosphine generating formulations are used to fumigate, any collected residue may ignite.”⁸

Besides these two circulars, there is other information on the hazards posed by PH₃ fumigation, which is publically available. The UK’s M1718, MGN86 and MGN284 all address fumigation. M1718 cautions that, “[s]ome of the gases and other agents commonly used for fumigation are flammable and, unless used strictly in accordance with manufacturer's instructions, may create a fire hazard. All the recommended fumigants are highly toxic and must be used only by qualified operators.”

The US Department of Agriculture Fumigation Handbook cautions that PH₃ gas is “flammable at concentrations above 1.79 percent by volume in air.” More detailed information and advice regarding PH₃ gas explosions has been published by P&I Clubs *via* bulletins and circulars sent to their members. This is also a free valuable source of information.

CONCLUSIONS

1. The immediate cause of the explosions in cargo holds nos. 2, 3, 4 and 6 was a result of a spontaneous ignition of a flammable air / PH₃ gas mixture.
2. The high level of humidity inside the cargo holds contributed to the elevated production rate of PH₃ gas.
3. The temperature between the cargo stow and the hatch cover was in excess of the PH₃ gas auto ignition temperature because of the exothermic reaction of the tablets, which were also dispersed in close proximity to each other.
4. In all probability, the PH₃ gas was not distributed effectively within the cargo hold because of the location of the suction pipe of the ‘J System’ and the elevated rate of production of the gas.
5. The uneven distribution of the tablets was not identified.
6. The crew members were unable to assess the risk of fire and / or explosion on board their ship.

RECOMMENDATIONS

General Maritime Enterprises Corp. is recommended to:

21/2013_R1 issue a Company Circular to ensure that safety literature on the subject matter, including this safety investigation report, is brought to the attention of the crew members serving on board ships under its management and shore-based personnel;

21/2013_R2 ensure that shore technical advice is readily available to crew members when fumigation is scheduled to be carried out.

⁸ *Vide* MSC.1/Circ.1396.

SHIP PARTICULARS

Vessel Name:	THEOFYLAKTOS
Flag:	Malta
Classification Society:	Lloyd's Register
IMO Number:	9081112
Type:	Bulk Carrier
Registered Owner:	Kingsley Shipping Co. Ltd.
Managers:	General Maritime Enterprises Corp.
Construction:	Steel
Length Overall:	224.8 m
Gross Tonnage:	39027
Minimum Safe Manning:	16

VOYAGE PARTICULARS

Port of departure	Rio Grande
Port of arrival	Jeddah
Type of voyage	International
Cargo information	Wheat in bulk
Manning:	20

MARINE CASUALTY INFORMATION

Date and time	22 December 2012 1432 LT
Type of marine casualty or incident	Serious Marine Casualty
Location of casualty	Rio Grande Outer Anchorage in position 32° 14.6'S 051° 55.0'W
Place on board	Cargo & tank areas – Cargo Holds
Injuries/Fatalities	None
Damage/environmental impact	None
Ship operation	Normal service – On anchor
Voyage segment	Departure
External and internal environment	Clear weather with good visibility. The sea was calm with a North-Easterly Fresh breeze.
Persons on board:	20