Aluminium Phosphide Fumigation - Fires and Explosions

Loss Prevention Bulletin

The Club has experienced several fires and explosions in cargo holds on-board bulk carriers where aluminium phosphide tablets had been applied to fumigate agricultural products.

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Fumigation using Aluminium PhosphideTablets

Aluminium phosphide tablets are designed to react with moisture in the air and release phosphine (hydrogen phosphide, PH3), a colourless, highly toxic and flammable gas, to kill off any insect infestation in the cargo. As phosphine gas is slightly heavier than air it will slowly sink down through the cargo filling the hold. Depending on the composition of the fumigant product the tablets may also release ammonia and carbon dioxide to reduce the potential for ignition of a phosphine gas / air mixture.

Pure phosphine gas is odourless; however, where impurities are present, as is usually the case with aluminium phosphide tablets, it may smell of garlic, decaying fish or carbide. When the tablets have completed releasing phosphine gas the remaining residue consists of aluminium oxide or aluminium hydroxide, a grey /white powder which, although non-toxic, the dust can present a hazard to health when handling residues. However, it needs to be considered that if the tablets are not fully reacted then there remains the potential for phosphine to be produced.

Fires and Explosions caused by Aluminium Phosphide Tablets

Problems have been encountered when aluminium phosphide tablets have not been evenly distributed across the cargo either on the surface or sub-surface; instead they have been piled on the cargo surface in a handful of locations, usually Aluminium Phosphide Fumigation – Fires and Explosions when the fumigation is rushed. When aluminium phosphide tablets react with moisture in the air and in the cargo, they produce heat as well as releasing phosphine gas. Clusters of fumigant tablets can result in localised elevated concentrations of phosphine and high temperatures, increasing the potential for the ignition of cargo and the formation of a flammable mixture of phosphine and air.

The presence of free water, such as from rain lying on the cargo surface, water ingress via nonweathertight hatch covers or from ship or cargo sweat can substantially hasten the reaction of the tablets, increasing the rate at which heat and phosphine gas are produced still further. The heat produced by a pile of reacting aluminium phosphide tables, particularly in the presence of free water, can in some cases be sufficient to start a smouldering cargo fire. The heat from reacting tablets or the presence of a smouldering cargo fire can ignite a flammable phosphine / air atmosphere in a cargo hold. Phosphine gas has a Lower Explosive Limit (LEL) in air of 1.8%, (the Upper Explosive Limit (UEL) has not been determined.)

Where tablets are grouped together there is a greater likelihood of the atmosphere near the tablets being flammable due to the quantity of phosphine gas produced. When a flammable phosphine / air atmosphere forms, it can be ignited by:

- The presence of an impurity such as diphosphine in the aluminium phosphide tablets, which will spontaneously ignite moist phosphine at ambient temperatures.
- The heat of the reacting tablets or a smouldering cargo fire igniting pure moist phosphine gas (without impurities) which has an autoignition temperature of 38˚C.
- The heat of the reacting tablets or a smouldering cargo fire igniting moist phosphine gas (with impurities) which has an auto-ignition temperature of 150˚C.
- Glowing combustion or sparks from a smouldering fire, or flames from a flaming fire, which could ignite phosphine at ambient temperatures.
- Non-intrinsically safe cargo hold lights which have been left switched on.
- Non-intrinsically safe internal recirculation fans or blow.

Aluminium phosphide fumigant tablets will usually start reacting 2 to 4 hours after being set. The generation of phosphine gas can typically continue for between 48 and 72 hours. Although most fumigant explosions occur within 24 hours of the tablets being set, there have been occasions when explosions have occurred several days after fumigation commenced.

Where the cargo grains have an excessive moisture content or have been wetted, they will expand, clump together and restrict the migration of the phosphine gas through the cargo, possibly concentrating the gas in the upper reaches of the stow and in the headspace between the cargo and the hatch covers. Such a restriction on the movement of phosphine gas may increase the probability of a flammable phosphine / air mixture forming.

The size of any explosion will depend on the quantity of flammable gas ignited; in some cases, the explosion of a phosphine gas / air mixture has been of sufficient force to cause access hatches or hatch covers to be blown upwards and displaced whilst hatch cleats, hatch coamings and the hatch covers have been severely damaged, presenting the potential risk of serious injury to personnel and delays to the voyage. The passage of the flame through the flammable atmosphere within the hold can also cause blackening of the surface of the cargo and the steel structures within the cargo space.

Explosions because of aluminium phosphide tablets having been incorrectly set may not only be caused by the ignition of a flammable phosphine gas / air mixture. There have been cases where smouldering cargo fires have been started by piles of aluminium phosphide tables creating considerable heat when reacting with moisture. A smouldering fire can cause thermal decomposition of the agricultural product producing a flammable combustion product / air mixture which is subsequently ignited by the smouldering fire, causing what is known as a “smoke explosion”. The introduction of fresh air into what might be an oxygen deficient environment in the closed hold, by opening an access hatch or vent, can feed the fire and allow for the formation of a flammable atmosphere.

Precautionary Measures

The fumigator's written instructions concerning the use of the fumigant product and the conduct of the fumigation after their departure from the vessel must be followed precisely.

The guidance contained in the Material Safety Data Sheets (MSDS) for the tablets and their residue must be left with the vessel and must be reviewed and understood.

It will be seen from the foregoing guidance that problems with aluminium phosphide tablets can arise when they are not spread evenly in cargo holds, instead being placed in piles on the cargo surface. The problem is further exacerbated by the presence of free water in contact with the tablets. Therefore, tablets should be evenly spread over the surface of the cargo or evenly placed sub-surface; the tablets should not be heaped together in one or a handful of locations.

When the tablets are evenly spread, there is less likelihood of excessive heat being generated and it is unlikely that sufficient phosphine gas to form a flammable atmosphere with the air in the hold will be produced. Piles of tablets usually occur when the fumigation operation is rushed by the fumigators; therefore, where practicable, it must be ensured that the fumigators are reminded to take their time to properly distribute the required number of tablets over or in the cargo, and that clusters of tablets are not set.

Vessels should be provided with gas detection equipment, instructions for its use and adequate spare parts to enable the measurement of concentrations of phosphine gas. An infrared handheld thermometer can also be useful for checking for hot spots on suspect hold steelwork. In addition, at least four sets of suitable respiratory protective equipment should be available onboard. If cargo hold fire alarms are activated, smoke / vapour (considering that phosphine gas is colourless) is seen issuing from hold openings, or if hatch covers, coamings or the main deck in way of the holds are found to be warmer than normal, then the cause of the problem must be investigated whilst always taking all necessary safety precautions. Where smoke tube fire alarms are fitted, it needs to be considered that the system will be continuously drawing phosphine gas from the holds and venting this outside the accommodation superstructure, therefore the risk of using the system should be fully evaluated prior to fumigation commencing.

If problems develop it is recommended that expert advice be sought at the earliest opportunity as some actions, such as opening a hold access hatch, may cause the situation to deteriorate. In the event of a problem, it is recommended that, where possible, gas monitoring for oxygen, carbon monoxide and flammable gases (% LEL) is conducted on the problematic hold using a suitably calibrated gas detector to support the expert with their provision of assistance.

As noted earlier, the presence of free water in contact with aluminium phosphide tablets will speed up the reaction causing higher temperatures and the production of more phosphine gas, heightening the possibility of a flammable atmosphere being formed in the hold. The cargo surface must therefore be kept dry, protected from precipitation during loading and, it should be considered that sweat may form on the cargo or on hold steelwork while the holds are sealed whilst fumigation is in progress.

It must also be ensured that the vessel is cargoworthy, with weathertight hatch covers, vents and access hatches, to prevent water ingress into the holds. As an additional precautionary measure to reduce the potential for moisture laden air to enter the hold, Ram-nek tape or expanding foam can be added to hatch cover joints although the creation of a fully airtight hold could potentially present problems of overpressure or a vacuum forming in the hold because of temperature changes.

If it is necessary for crewmembers to handle the residue of spent aluminium phosphide tablets; then the fumigator's instructions in this regard should be followed as well as the guidance contained in the MSDS for the spent product. Appropriate safety measures should be followed and personal protective equipment, which will usually be cloth gloves and a dust mask, should be worn.

It must also be noted that when aluminium phosphide residues are collected and stored together, they may spontaneously ignite due to the presence of unspent chemical.

The toxicity of phosphine gas must never be underestimated; it is worthwhile considering the Workplace Exposure Limits (WEL) for phosphine compared to another well-known toxic gas, hydrogen sulphide.

The long-term exposure limit (8-hour Time Weighted Average (TWA)) for phosphine is 0.1 ppm (parts per million) / 0.14 mg/m3 and the short-term exposure limit (15 minute TWA) is 0.2 ppm / 0.28 mg/m3, the corresponding figures for hydrogen sulphide are 5 ppm / 7 mg/m3 and 10 ppm / 14 mg/m3.

The "Recommendations on the Safe use of Pesticides in Ships Applicable to the Fumigation of Cargo Holds", contained in MSC.1/Circ.1264 and MSC.1/Circ.1396 (Amendment) should also be followed by all vessels undertaking the fumigation of cargo holds.

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Members requiring any further guidance or advice on this topic should contact the Loss Prevention department.

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