Risks of in-transit fumigation - phosphine gas explosions

We recently published an [article](https://gard.no/insights/beware-of-the-danger-of-in-transit-fumigation/) focusing on the toxicity of phosphine gas and the potential danger this poses to the crew when agricultural bulk cargoes and forestry products are undergoing in-transit fumigation with aluminium phosphide. In that article, we very briefly mentioned another potential hazard that can arise at the initial stage of the process – phosphine gas explosions. In this article, our guest author, Dr Nicholas Crouch, focuses on the risk of explosion in port and the steps that can be taken to reduce the risk.

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Generation of phosphine gas from aluminum phosphide fumigant products

Aluminium phosphide, the precursor compound from which phosphine gas is generated, is available in different forms and can be supplied in aluminium bottles as tablets of about 3g each or as pellets of about 1g. Alternatively it can be supplied in fabric 'socks' or strips of cojoined paper sachets which enable the fumigant residues to be easily removed in the situation where it is undesirable to have fumigation residue remaining in the cargo. Generally, and as a rule of thumb, Degesch state that one 3g tablet of aluminium phosphide formulation will generate about 1g of phosphine gas.

Usually, the quantity of aluminium phosphide applied per hold is calculated based on the volume of the hold rather than the quantity of cargo it contains, with a common target concentration of phosphine deemed to be effective of 1g of gas per cubic metre, although sometimes higher concentrations are used. The recommended dosages of aluminium phosphide /phosphine used in fumigation of bulk cargo stows onboard ships, as set out by the United Nations Food & Agriculture Organisation (FAO) and by a major producer of aluminium phosphide, Degesch, with these tabulated below:

RECOMMENDED

Dosage of Solid Aluminium Phosphide [Formulation with 55% AlP wt/wt] (g/M3)

Dosage of Phosphine Gas (g/M3)

Dosage of Phosphine Gas (g/MT)

FAO

3 - 6

1 - 2

3.7 – 7.4

Degesch

3.2 - 7.1

1 - 2.4

3.9 – 8.7

Accumulation of phosphine gas in the hold headspace

When arranging an 'in-transit' fumigation, the lead fumigator will calculate the required quantity of aluminium phosphide on a hold-by-hold basis and the fumigation crew will then apply this across the surface of the cargo stow, sometimes using pipes to place a proportion of the fumigant beneath the surface of the stow. Once exposed to water vapour in the air, i.e., atmospheric moisture, the aluminium phosphide reacts generating phosphine gas and aluminium oxide as a byproduct. It should therefore be appreciated that all the phosphine for the entire hold is generated on the surface or near the surface of the stow where a considerable proportion will accumulate in the headspace before dispersing/diffusing into the cargo.

The overall fumigation operation can be divided into four distinct phases with these being:

1. Phosphine gas generation and accumulation in the headspace of the hold as the aluminium phosphide reacts with moisture,

2. Diffusion of the gas into the interstitial spaces between the kernels of grain or soybeans leading to reduced concentration of phosphine in the headspace,

3. The contact period during which any live insects are exposed to the fumigant, and

4. Release and dispersal of any remaining fumigant by ventilation following the designated period of contact and prior to discharge.

Inflammability of Phosphine and risk of explosion

Phosphine and a related compound, diphosphine, have long been recognized by chemists to be highly reactive and quite unstable chemicals with both being prone to self-ignition. This is especially so for diphosphine, which can be formed when there is an imbalance in the amount of aluminium and phosphorus in the aluminium phosphide tablet or pellet formulation. The chemical literature points to the presence of diphosphine as being responsible for self-ignition of phosphine as the paragraph below, taken from 'The Chemistry of Phosphine' by Prof. Dr. Ekkehard Fluck of the Institut fur Anorganische Chemie der Universitat Stuttgart, indicates:

"*Our experience has shown that the hydrolysis of aluminium phosphide with cold water is the most suitable method for the laboratory preparation of phosphine. Here it is important that the aluminium phosphide be as pure as possible in order to avoid the formation of spontaneously inflammable phosphine. The presence of small quantities of diphosphine and also higher phosphines are responsible for this spontaneous inflammability. It appears, however, that these are only formed when P-P bonds are already present in the phosphide. Accordingly, the hydrolysis of aluminium phosphide, prepared from the elements with phosphorus in slight excess, always leads to spontaneously inflammable phosphine*."

The manufacturers of aluminium phosphide formulations include ammonium carbamate in the mixture as this decomposes on exposure to water vapour to generate carbon dioxide and ammonia. These gases are believed to suppress the likelihood of ignition by decreasing the inflammability of the phosphine. However, at concentrations of 1.8% or above in air, phosphine is inflammable and will support 'combustion' producing dense white fumes of phosphorous pentoxide (i.e., P2O5) which is a severe respiratory tract irritant due to formation of orthophosphoric acid on contact with water, such as in the lungs. In the presence of an ignition source, such elevated concentrations of phosphine will ignite andin an enclosed space, such as the headspace of a hold, result in explosion.

Although many 'in-transit' fumigations are set daily in the ports of grain exporting countries, comparatively few fumigant explosions occur. However, they can, and indeed do, occur and it is important that Shipowners and their crews are aware of this potential danger.

Potential sources of ignition are:

- Hot work on the hatch covers,
- Exposure to temperatures above phosphine's self-ignition temperature,
- Direct inadvertent wetting of the fumigant tablet; this can rapidly produce very high phosphine concentrations and because the phosphine producing reaction is exothermic, temperature conditions above the self-ignition point of phosphine.
- Unwanted production of diphosphine from the fumigant formulation as discussed above.
- Sparks from say static electricity in hatch cover structures or direct inadvertent metal on metal contact,

In the many cases that Brookes Bell have investigated it is usually impossible to identify the source of ignition with absolute certainty, but there are generally common features which point to them being in some way part causative. These include the following:

- Explosions generally occur within the first 8 to 24 hours presumably due to the high phosphine concentrations in the headspaces during this period, but Brookes Bell are aware of one explosion which occurred after 29 hours,

- Use of high doses of aluminium phosphide/phosphine which leads to higher initial phosphine concentrations during the first phase of the fumigation,

- High prevailing ambient temperatures and high humidity, both of which increase the rate of phosphine generation,

- Intense tropical sunshine which can heat the hatch covers possibly exceeding the autoignition temperature of the phosphine,

- Surface application of the fumigant may result in higher headspace concentrations of phosphine, and

- Comparatively small headspaces above the cargo stows which lead to higher phosphine gas concentrations during the initial phase of the fumigation.

Fumigations on board ships is entirely the responsibility of the fumigators over which Masters and crew have no control or influence. Consequently, once an "unsafe" fumigation has been set there is nothingthe crew can do to minimize the risk of a fumigant explosion from occurring. Nevertheless, as a general safety precaution in the early period of fumigations in ships' holds,we would recommend that as little time as possible is spent on deck and close to the hatch covers by the crew during the first 24 to 36 hours after the fumigation has been set. After this period, it is reasonable to expect that most of the aluminium tablets will have reacted to release the phosphine gas with a proportion of that gas diffusing into the cargo, thereby reducing the concentration of phosphine in the headspace of the hold and therefore reducing the risk of explosion.