SVERIGES ÅNGFARTYGS ASSURANS FÖRENING
The Swedish Club
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Member Alert
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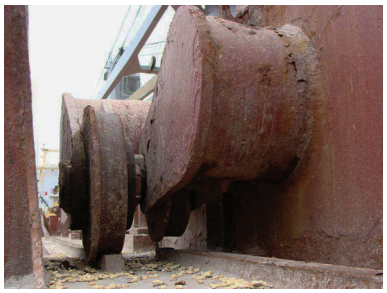
Phosphine Fumigant Explosions

The Club has recently been informed of an explosion which occurred on board one of our members' ships shortly after a cargo of maize had been loaded and the holds had been set for fumigation continued in-transit with phosphine gas produced from aluminium phosphide tablets.

Whilst fortunately no crew member was injured in the explosion, the hatch covers to the hold concerned suffered extensive damage as a result, with the hatches being blown upwards off their normal seating position, the securing cleats ripped out, a hole approximately 1m^2 blown in the weather deck and the structure of the hatches severely distorted.

Although such phosphine explosions are not a particularly common occurrence, this is not the first time this has occurred.

A recent explosion tore up a 1m^2 hole in the deck...



...and dislocated the hatches.

Spontaneous ignition

Phosphine is the common name given to phosphorous trihydride (PH_3), also known as hydrogen phosphide or less commonly as phosphane. It is a toxic, highly flammable gas which burns when its concentration exceeds its lower flammable limit of 1.8% volume by volume (v/v) in air. If an air/phosphine mixture in which the phosphine concentration exceeds this level, (i.e. above 1.8% v/v) is ignited in an enclosed space, then an explosion is likely to occur. The auto-ignition temperature for phosphine is reported by some sources to be as low as 38°C, although other sources state higher temperatures of about 85°C are required.

In any case, it should be noted that mixtures of phosphine in air, in which the phosphine concentration exceeds the lower flammable limit, may ignite spontaneously.

Smells like garlic

Pure phosphine itself is odourless, but in preparations produced from commercially available aluminium phosphide tablets it has a noticeable odour reminiscent of 'garlic' or rotten fish, due to the presence of trace impurities such as the spontaneously flammable diphosphine (P_2H_4). It is generally believed to be the presence of traces of diphosphine which increases the risk of spontaneous ignition of phosphine/air mixtures and which may account for some of the particularly low reported self-ignition temperatures.

To generate phosphine, tablets containing aluminium phosphide are placed in the cargo by qualified fumigation companies. These tablets also contain other minor ingredients, such as ammonium carbamate, the purpose of which is to act as a source of ammonia and carbon dioxide which help reduce the potential for spontaneous ignition or explosions. The tablets are usually placed on

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and under the surface of the stow once loading and trimming has been completed, using various methods such as handheld tubes pushed into the stow down which the tablets are dropped as well as placing of 'socks', containing tablets, on the surface.

Other application methods include deep probing and recirculation methods. The aluminium phosphide tablets then react with water vapour (moisture) in the air to generate phosphine gas, leaving aluminium oxide powder residue as a by-product. The rate of this reaction depends upon prevailing atmospheric temperatures and humidity, as well as to some extent the moisture content of the grain cargo. It is usual for the tablets to react fully within the first 24 to 48 hours of the fumigation having been set, although under some circumstances a longer period than this may be required.

Trace impurities in phosphine fumigation tablets generates an odour of garlic or rotten fish. These impurities might also contribute to the self-ignition of the fumigation substance.

Risk of explosion peaks after 12 to 24 hours

Fumigations of grain cargoes with phosphine are routinely continued during transit as an effective means of killing live insects present in the grain. The normal recommended dose of phosphine is in the order of 1 to 3 grams of phosphine gas per cubic metre of hold space. In order to achieve this with a surface application method, sufficient tablets to generate the desired final concentration of gas for the whole-hold volume (empty basis) must be placed in the surface layers of the stow.

As a consequence, during the early stages of the fumigation, the concentration of phosphine in the head space of the hold increases to high levels, probably exceeding the lower flammable limit in the majority of cases, before it penetrates into and diffuses throughout the stow. During this period, if ignition occurs, an explosion will result. In real terms this means that a potential explosion risk exists in the first 48 hours after the fumigation has been set and the hatches sealed.

Avoiding explosions

In cases where an explosion has occurred, the source of the ignition is often difficult to identify conclusively. However, potential candidates are over-heating of the tablets as a consequence of being placed too close together (such as in a pile) or through wetting resulting in tablet temperatures which exceed the auto-ignition point of the gas, static discharge, sparks, or through improper manufacture of the tablets possibly leading to increased diphosphine levels. As the explosion risk depends on the initial headspace gas concentrations, it can be reduced by using sub-surface application methods such as deep-probing or recirculation, and by avoidance of excessive fumigant doses.

It is important to note that aluminium phosphide tablets are used routinely in fumigations of shipments of grain annually and that the vast majority of these pass without incident.

Advise to members

We would advise members therefore that when fumigations are being conducted, particularly in the ports of the developing world that the presence of crew members on deck adjacent to the cargo spaces being fumigated is kept to a minimum during the first 48 hours after the fumigation has been set.

Club contact

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