3M Technical Data Bulletin

PSD

#212 – Respiratory Protection Against Phosphine

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Background

Phosphine is commonly used as a fumigant in agriculture. Phosphine gas is generated when calcium phosphide, aluminum phosphide or magnesium phosphide comes in contact with moisture. Occupational exposure may occur when workers apply pellets, strips, etc. or enter closed areas or open containers after the treatment. Phosphine exposure may also occur in semiconductor manufacturing, phosphine fires and explosions, and as a byproduct of illicit methamphetamine manufacturing.

Respirator Options

Exposure to phosphine should be minimized in as much as possible by replacement of phosphine with a less hazardous material, engineering controls such as ventilation, and administrative controls such as restricting access to areas where phosphine may be present. Respiratory protection may only be used to help reduce exposure if these methods are not adequate, or while they are being implemented. In the US, pesticides are regulated by the Environmental Protection Agency (EPA). EPA requires the pesticide manufacturer to include any requirements for respiratory protection. Please see the pesticide label for more information.

At this time 3M is not aware of any regulatory test method or approval for respirator cartridges used for phosphine. The US National Institute for Occupational Safety and Health (NIOSH) does have a 1500 ppm phosphine test method and approval for respirator *canisters*. In some countries, canisters may be used to escape from environments that are immediately dangerous to life or health (IDLH). Yet, customers may object to the size and weight of certain full facepiece canister respirators or the use of mouth-bit type canister respirators.

NIOSH also includes a 300 ppm phosphine test for air-purifying respirators certified for chemical, biological, radiological, nuclear (CBRN) applications. CBRN respirators are designed to filter a variety of gases and vapors and withstand permeation of chemical warfare agents. Therefore, CBRN respirators are often expensive and subject to export control regulations.

3M has traditionally recommended supplied air respirators if worker exposure is higher than applicable occupational exposure limits. However, supplied air systems are not always practical due to the need for a compressed air source. Also, a worker's movement is restricted due to being tethered to a supplied air hose.

Because of the limitations of the above options, 3M has received numerous requests for simpler respirators that may be used to help reduce exposure to phosphine during pesticide application. Specifically, some users have established that their exposure levels are minimal, but they still wish to wear a cartridge style respirator to further reduce exposure. As previously mentioned, there is no phosphine test method or approval for industrial respirator cartridges.

Testing of 3M cartridges

Test conditions should be at or beyond potential use conditions. The maximum use concentration is either the occupational exposure limit (OEL) times the respirator protection factor, or concentrations that are immediately dangerous to life or health (ILDH); whichever is lower. OELs vary by country and publishing organization, but generally are 1 ppm or less for phosphine. Respirator protection factors also vary by country, but are often 10 for half masks and higher for full facepieces. The NIOSH 1990 IDLH level for phosphine is 200 ppm.

So, for example, if the local exposure limit is 0.3 ppm and the respirator protection factor is 10, then the respirator could be used up to 3 ppm phosphine. Full facepieces could potentially be used in higher concentrations, depending on the local exposure limit, respirator protection factor and IDLH limit.

The following tests were performed at various phosphine concentrations. A flow rate of 32 L/min was used (representing 64 L/min for a pair of cartridges) to approximate a heavy work rate. Temperature in the lab was approximately 25C. Service life to 0.3 ppm breakthrough was measured. The 30 ppm and 60 ppm tests were intermittent: 8 hour exposure and then 16 hours no exposure. This intermittent pattern was repeated for 5 days for a total of 40 hours exposure.

Concentration (ppm)	**Relative humidity**	**Service life (minutes)**	**Comments**
300	85%	466	
300	25%	290	Cartridge front cover melted and carbon leaked out.
300	25%	> 600	No phosphine detected. During the test, air temperature exiting cartridge was about 30C and the cartridge body was barely warm to touch. After removal from testing, the cartridge heated up rapidly, the front cover melted and carbon leaked out.
60 / 0 (intermittent)	25%	> 2400	No phosphine detected. During the test, air temperature exiting cartridge was about 27C, but no cartridge warming or melting.
30 / 0 (intermittent)	50%	> 2400	No phosphine detected above 0.3 ppm limit. 0.05 ppm phosphine was briefly observed at the end of one of the 8 hr challenge cycles.

A small amount (0.05 ppm) of phosphine briefly came through the cartridge at the end of one of the intermittent tests. It is thought that since phosphine is removed via catalytic processes, very small amounts may come through the cartridge for an instant until steady-state conditions are re-established in the carbon bed. The amount detected was less than the 0.3 ppm limit.

The front cover of the cartridge melted during or after the 300 ppm test at 25% RH, but not at 85% RH. It is possible that some unreacted phosphine built up in the carbon bed and began to react as more humid room air entered the cartridge inlet. Cartridges **must not** be used at high phosphine concentrations.

Conclusion

Please consult an Industrial Hygienist or Safety Professional to assess worker exposure and determine appropriate respirators for your application. There is no phosphine test method or approval for industrial respirator cartridges. If phosphine exposure levels are less than both 60 ppm and local maximum use concentrations, then the following cartridges may be used with 3M™ 6000, 7000 and FF-400 Series half and full facepieces to help reduce phosphine exposure:

- 3M™ Mercury Vapor/Chlorine Gas Cartridge 6009
- 3M™ Mercury Vapor/Chlorine/Sulfur Dioxide Gas Cartridge/Filter 6009S
- 3M™ Mercury Vapor/Chlorine Gas, P100 Cartridge/Filter 60929
- 3M™ Mercury Vapor/Chlorine/Sulfur Dioxide Gas, P100 Cartridge/Filter 60929S
- 3M™ Gas & Vapour, Particulate & Combined Protection A1HgP3 6096

Respirators must be used in conjunction with a respirator program that meets applicable local standards (e.g. OSHA 29 CFR 1910.134 or CSA Z94.4). This includes, but is not limited to, training, fit testing, respirator maintenance, developing cartridge change schedules, etc. Please see local standards for more information.

The odor threshold for phosphine is 0.14 ppm. This is lower than the occupational exposure limit in some countries, but odor threshold varies widely between individuals. In certain countries (e.g. United States, Canada), a cartridge change schedule must be developed instead of relying on contaminant warning properties.

Service life is expected to be at least 40 hours for concentrations less than 60 ppm phosphine and normal breathing rate. Cartridges must be discarded earlier if taste, smell or irritation is noted, or if the cartridge is physically damaged.

Cartridges **must not** be used for non-respirator applications such as scrubbing phosphine from process or waste streams. The high vapor concentrations that can occur in these applications could potentially cause ignition of the carbon sorbent as a result of the highly exothermic oxidation of phosphine.

For more information, please contact:

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