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Reuse of Organic Vapor Chemical Cartridges

Introduction

Traditionally gas and vapor cartridges and canisters were often changed when the user noted taste, smell or irritation from the contaminant. However, some contaminants don’t have good warning properties, and the ability to smell odors varies greatly between individuals. Therefore, change schedules are required for gas/vapor cartridges and canisters under local regulations such as US OSHA 29 CFR 1910.134 and CSA Z94.4-11.

Change schedules are often based on service life measurements or estimates. To best use the service life information, it is necessary to understand how chemical cartridges work. It is especially important when organic vapor cartridges are used against volatile chemicals during more than one work shift. These chemicals may desorb from the carbon when not in use. Inappropriate reuse of organic vapor cartridges can result in breakthrough occurring earlier than expected. The decision to reuse organic vapor cartridges may have an impact on worker protection and the respiratory protection program

Gas & Vapor Filtration

Chemical cartridges are used on respirators to help remove and lower worker exposures to harmful gases and vapors in the workplace. There are several types of chemical cartridges: organic vapor, ammonia, formaldehyde, mercury vapor and acid gases, such as hydrogen chloride, chlorine and sulfur dioxide.

All chemical cartridges consist of a container filled with a sorbent to filter gases or vapors from the air. Typically this sorbent is activated carbon or activated charcoal. Activated carbon is an amorphous form of carbon characterized by high adsorptivity for many organic vapors.

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Activated carbon for respirators usually comes from coconut shells or coal. It is 'activated' by heating to 800-900^{o}C with heat or steam, which results in a porous internal structure (honeycomb-like). The internal surface area of activated carbon averages 10,000 square feet per gram. This large surface area makes activated carbon ideal for removal of organic vapors by adsorption. Adsorption is the adherence of gas or vapor molecules to the surface of the activated carbon. The attractive force between the activated carbon and the chemical molecule is a relatively small, weak physical force. Adsorption works best for organic vapors with vapor pressure less than 100 mm Hg at room temperature.

To make cartridges more effective for filtering gases and volatile organic vapors, sorbents can be impregnated with chemical reagents. Impregnated activated carbon removes specific gas and vapor molecules by chemisorption. Chemisorption is the formation of bonds between molecules of the impregnant and the chemical contaminant. These bonds are much stronger than the attractive forces of physical adsorption. The binding is usually irreversible.

Table 1 shows the types of chemical cartridges and the mechanism used for removal of the gas or vapor.

Table 1. Chemical Cartridge Types and Removal Mechanisms

Chemical Cartridge Type	Removal Mechanism	Examples of Impregnant
Organic Vapors	Adsorption	N. A.
Ammonia/Methylamine	Chemisorption	Nickel chloride, Cobalt salts, copper salts, Acids
Acid Gases	Chemisorption	Carbonate salts, Phosphate salts, Potassium hydroxide, copper oxide
Formaldehyde	Chemisorption	Copper oxide + metal sulfates, Salts of sulfamic acids
Mercury Vapor	Chemisorption	Iodine, Sulfur
Hydrogen Fluoride	Chemisorption	Carbonate salts, Phosphate salts, Potassium hydroxide, copper oxide

Desorption of Organic Vapors

Generally, the more volatile the organic vapor, the less strongly adsorbed, or the more likely it will undergo desorption. Since only weak physical forces are involved in adsorption of organic vapors, the process can be reversed. Desorption is the process of an adsorbed material "letting go" from the activated carbon. It can occur naturally during periods of nonuse or if a less volatile organic vapor displaces a more volatile organic vapor.

A boiling point of less than 65°C is used as a guideline for identifying volatile organic vapors.[1] However, the boiling point of 65°C is not a fine line between organic vapors that desorb and those that do not. Organic vapors with higher boiling points can still desorb; it just may take longer for it to occur. The boiling point can be misleading for chemicals (e.g., alcohols) that undergo hydrogen bonding. The hydrogen bonding results in a higher boiling point than would be expected based on molecular weight. Experiments with ethyl acetate (BP = 77°C) have shown significant desorption after 63 hours of storage (non-use).[2]

Laboratory studies have also shown that a less volatile organic vapor can displace a more volatile organic vapor.[3] This may result in a breakthrough concentration that exceeds the concentration in the air. While this study was done with concurrent exposure to organic vapor mixtures, the same effect is very likely to occur from sequential exposures, e.g. workers who move between tasks with different exposures.

In contrast, desorption typically should not be a problem for cartridges that rely on chemisorption.

Migration of Organic Vapors

Desorption during storage or nonuse times can result in chemical migration. Migration is the movement of a previously adsorbed chemical through the chemical cartridge, even without air movement. During periods of nonuse, organic vapors may desorb and redistribute from the areas of high concentration to areas of lower concentration, *i.e.*, the back of the cartridge. When a worker reuses an organic vapor respirator, they may breathe the desorbed organic vapor when they first put it on and potentially for some time afterwards.[4]

Variables that appear to impact migration include[2]:

- Volatility – the more volatile the organic vapors, the greater the concern for migration. (For nonvolatile organic vapors, 3M studies indicate migration is minimal.)
- Water vapor coadsorption – use in atmospheres with high relative humidity (>50%) can increase the migration effect.
- Amount of material adsorbed onto the cartridge in the first use
- Storage time
- Vapor type

Change-out Schedule Recommendations

There have been various recommendations published regarding the potential reuse of organic vapor cartridges. The ANSI Z88.2-1992 standard recommends changing cartridges daily unless desorption studies suggest otherwise.[5] OSHA states in its compliance directive that cartridges exposed to organic vapors with boiling points less than 65^{o}C should be changed after every work shift, unless the employer has objective data (desorption studies) to the contrary.[6] Wood and Snyder use a mathematical model to predict migration and the potential reuse of organic vapor cartridges.[7]

A more practical solution for reuse of organic vapor cartridges may be a “running clock”. In other words, the estimated service life starts when the cartridge is first used and continues whether the cartridge is being used or stored. For example, if the estimated service life is 40 hours, then the organic vapor cartridge may be used for 8 hours, stored 16 hours and used for 8 hours (total time 30 hours) before being discarded. The effective cartridge change schedule would be every 2 days, except when used prior to a weekend, holiday, etc.

3M™ Service Life Software

The 3M™ Service Life Software uses an earlier method developed by Wood for determining service life for organic vapor cartridges by modeling the adsorption capacity and rate of adsorption of organic vapors from organic liquids.[8] The service life estimate is the continuous time cartridges would last until a breakthrough point is reached. In other words, a service life estimate of 16 hours means it would last 16 hours of continuous use. It does not mean necessarily that it will last two 8-hour shifts when stored overnight.

The software uses boiling points less than 65^{o}C to identify highly volatile organic vapors. When a service life estimate is made for a low boiling chemical, a warning is given to not use the cartridge more than a single work shift. However, the “running clock” method mentioned above may also be considered if the estimated service life is greater than a work shift. In Europe, Australia and New Zealand, the warning message also states that per local regulations, AX type cartridges are required for low boiling organic vapors instead of normal organic vapor cartridges.

Conclusion

Organic vapors can desorb and migrate through cartridges during storage, or if displaced by other less volatile organic vapors. This is mainly a concern for volatile organic vapors. Organic vapor cartridges should not be used for more than one shift without considering the volatility of the organic vapor(s), estimated service life, cartridge use/nonuse patterns, and desorption data (if available).

References

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