Technical Data Bulletin

OH&ESD

#142, May 1999

Reuse of Organic Vapor Chemical Cartridges

Introduction

One of the most significant changes in the Occupational Safety and Health Administration's (OSHA's) new 1910.134 respiratory protection standard is the requirement to establish change schedules for chemical cartridges used for gases and vapors. 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 the organic vapor cartridges can result in breakthrough occurring earlier than predicted by the service life estimate. For example, when the organic vapor cartridge has been used for chemicals that migrate through the cartridge during the storage or nonuse period, it should not be reused. The decision to reuse the cartridge may have an impact on worker protection and the respiratory protection program

Background

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.

It is important to understand how the different cartridge types work. All chemical cartridges consist of a container filled with a *sorbent*. A chemical cartridge *sorbent* is a granular porous material that interacts with the gas or vapor molecule to remove it 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 gases and vapors.

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The carbon is obtained by destructive distillation of wood, nutshells, animal bones or other carbonaceous material. 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. The strength of the attraction depends in part on the chemical. Since only weak physical forces are involved, the process can be reversed. This is called *desorption*. Desorption is the process of an adsorbed material "letting go" from the activated carbon. Desorption can occur naturally during periods of nonuse or by the presence of another more strongly adsorbed substance displacing a less strongly adsorbed chemical (*i.e.*, a more volatile chemical). Generally, the more volatile the chemical the less strongly adsorbed, or the more likely it will undergo desorption. 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. Variables that appear to impact migration include:

- Volatility – the more volatile the chemicals, the greater the concern for migration;
- Water vapor coadsorption – coadsorption [from 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; and
- Vapor type.[1]

The potentials for desorption and migration makes reuse of organic vapor cartridges a concern.

Not only are the more volatile chemicals more likely to desorb but the capacity of the carbon is generally lower for these chemicals. This includes many inorganic gases and organic vapors. Inorganic gas desorption is prevented by the use of special cartridges. For organic vapors Europe uses a boiling point of less than 65^{o}C as a guideline for identifying the more volatile chemicals.[2] These chemicals are often classified as low boiling chemicals. Typical organic vapor cartridges would be expected to have lower capacity for these materials and desorption could be a major concern.

To make the cartridges more selective for certain chemicals, 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. Reuse of chemical cartridges that work on the principle of chemisorption typically should not be a problem. 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

This table indicates organic vapor chemical cartridges are the ones for which desorption and migration are the biggest concern. In combination chemical cartridges, such as organic vapors and acid gases, the organic vapors are predominantly removed by adsorption.

Desorption/Migration

Caution needs to be exercised in establishing a change schedule with reuse of organic vapor cartridges used for:

- Volatile chemicals that are likely to desorb during non-use;
- Two or more different chemicals adsorbed sequentially and the subsequent chemical is more strongly adsorbed.

Reuse for volatile chemicals

After use of a chemical cartridge the vapor is collected on the first layers of carbon in the cartridge. During the period of nonuse, the chemical, depending upon its volatility and other conditions, may desorb and redistribute itself from the areas of high concentration to areas of lower concentration, *i.e.*, the back layers of carbon where no vapor has been collected. Eventually the chemical will reach the back of the cartridge. When it desorbs from the back of the cartridge it goes into the air. This can result in the worker breathing the chemical vapor when they first put on the respirator (and potentially for some time afterwards) without wearing it in the contaminated area.[3]

Reuse in a different environment

Less volatile chemicals can cause desorption and early breakthrough of the poorly adsorbed, more volatile chemicals. For example, a maintenance worker wears a respirator for exposure to chemical A. The use period is shorter than the service life for chemical A so no breakthrough occurs. The next day the worker goes to a different area with exposure to a different organic chemical, chemical B. Chemical B is less volatile than chemical A. Since the service life was not used up with chemical A, the organic vapor cartridges are reused. Before chemical B breaks through, it displaces the more volatile chemical A. If the change schedule does not consider this effect, chemical A may break through and the worker is exposed to chemical A. Laboratory studies have shown that a more strongly adsorbed chemical can displace a relatively weakly adsorbed chemical.[4] This may result in a breakthrough concentration that exceeds the concentration in the air. While this work has been with mixtures, the same effect is very likely to occur from sequential exposures to two chemicals. For a maintenance worker, a compliance officer, or someone else that may use an organic vapor respirator in different environments, reuse may not be appropriate under any situation.

3M Service Life Software

The 3M Service Life Software uses a 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.[5] The service life estimate is the time the cartridge would last until the selected breakthrough point is reached. For organic vapors it is the time cartridges would be expected to last with one continuous use. In other words, a service life estimate of 16 hours means it would last 16 hours if used continuously under the conditions of the estimate. It does not mean necessarily that it will last two 8-hour shifts when stored overnight. For nonvolatile chemicals 3M studies indicate service life is very close to the estimate even with periods of nonuse. This is not true for the more volatile chemicals.

The 3M Service Life Software uses boiling points less than 65^{o}C to identify the highly volatile chemicals. Many of the service life estimates for the more volatile chemicals will be short due to the lower capacity of the carbon for these chemicals. Some, however, may be longer than 8 hours. When a service life estimate is made for a low boiling chemical that is longer than 8 hours, a warning is shown that advises that the chemical cartridge be disposed of after the shift. These chemicals are likely to desorb and migrate throughout the cartridge during short periods (few hours to overnight) of non-use. However, the boiling point of 65^{o}C is not a fine line between chemicals that desorb and those that do not. 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. Chemicals with higher boiling points can still desorb and migrate; it may take a little longer for it to occur. Experiments with ethyl acetate (BP = 77^{o}C) have shown significant desorption after 63 hours of storage (non-use).[1] So for this chemical, reuse after a short nonuse period may be okay, but reuse after a weekend probably should not be attempted.

Change-out Schedule Recommendations

Unfortunately, there has not been much information published for evaluating the effect of desorption or migration on cartridge service life. The two safest approaches when the service life estimate is longer than the use period are:

- Never reuse an organic vapor chemical cartridge; dispose of it after the period/shift in which it is used.
- Conduct desorption studies in a laboratory mimicking the conditions of use/reuse at your work site. Use these data when establishing the change schedule.

The ANSI Z88.2-1992 standard recommends desorption studies unless cartridges are changed daily.[6]

OSHA states in its compliance directive that where contaminant migration is possible (chemicals with boiling points below 65°C), respirator cartridges should be changed after every work shift where exposure occurs.[7] If the employer has specific objective data (desorption studies) showing the performance of the cartridge under the conditions and schedule of use/nonuse found in the workplace, daily change would not be required.

Using 65°C as the indicator for migration does not take into account those materials that may migrate after slightly longer periods of nonuse. Another possibility is to establish guidelines for reuse based on the volatility of the chemical. Three or four levels of volatility could be established. Different periods of nonuse would be acceptable for highly volatile chemicals, moderately volatile chemicals and low volatility chemicals. No guidelines are presently available to say what boiling points, or other indicator of volatility, should be used as the cutoff between moderate and low volatility. As the volatility increases, the reuse of cartridges for organic vapors should be restricted.

- Cartridges used for organic chemicals that are very volatile should never be reused. For example chemicals with boiling points less than 65°C should never be used for more than one shift.
- Cartridges used for chemicals of moderate volatility should never be reused after periods of nonuse of a few days. For example, never reuse the cartridge if a cartridge change schedule results in storage over a weekend.
- Cartridges used for chemicals of low volatility should never be reused after some longer period of use that is still less than the service life estimate. For example, cartridges used for these types of organic chemicals should never be used longer than one or two weeks.

For mixtures the acceptable nonuse or storage period should probably be based on the most volatile component of the mixture. As more information becomes available in the future, firm recommendations about reuse can be made.

Conclusion

Before setting the change schedule, the volatility of the chemical, the cartridge use/nonuse patterns, and desorption data (if available) should all be evaluated. The prudent practice is to never reuse organic vapor cartridges when the service life estimate is greater than one work shift if desorption data are not available. For organic chemicals that migrate through the cartridge during the storage or nonuse period, the organic vapor cartridge must not be used for more than one shift.

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