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Review of Influential Factors Affecting the Performance of Organic Vapor Air-Purifying Respirator Cartridges

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Industrial hygienists must consider numerous diverse factors prior to selecting a respirator. An accurate evaluation of environmental conditions as well as work functions is essential if an organic vapor air purifying device is to be properly chosen. Environmental factors which need careful consideration are oxygen level, contaminant composition, contaminant concentration, contaminant's warning properties, temperature, and relative humidity. In addition, work rate and numerous other work-related factors must be carefully evaluated to assure worker safety. In fact, safety precautions are built into the regulations themselves (30 CFR Part 11) by imposing environmental and use limitations for organic vapor respirator cartridges. These include: 1. not for atmospheres which are immediately dangerous to life and health (IDLH), 2. not for use against gases or vapors with poor warning properties (unless permitted by MSHA/OSHA), and 3. not for use against gases or vapors which generate high heats of reaction with the sorbent. Further, there are concentration limitations for use of an organic vapor chemical cartridge respirator: the IDLH concentration of the specific organic vapors, a maximum use concentration (MUC) of 1000 PPM for organic vapors, and the allowable faceseal and exhalation valve leakages. Chemical cartridge respirators are not approved for use at concentrations above the *lower* of these three values. Thus, extreme care must be exercised when selecting organic vapor cartridges due to these constraints. It is therefore essential that one be knowledgeable concerning the influential factors affecting cartridge performance. This paper reviews and discusses some critical cartridge performance factors (environmental and other) which must be considered prior to the appropriate selection of an organic vapor air purifying cartridge respirator.

Introduction

Organic vapor and gas air-purifying respirators are designed to reduce the exposure of the wearer to toxic vapor or gas contaminants in the ambient atmosphere. Generally, these devices remove the contaminants on inhalation by interaction of the molecules with granular porous materials called sorbents. Presently, these organic gas and vapor respirators are certified by the National Institute for Occupational Safety and Health (NIOSH) according to 30 CFR Part 11 Subparts I, L, M, and N, which concern "Gas Masks," "Chemical Cartridge Respirators," "Pesticide Respirators," and "Special Use Respirators," respectively. Further, chemical cartridges are approved for protection against specific types of substances as follows: ammonia, chlorine, hydrogen chloride, methylamine, organic vapors, sulfur dioxide, and vinyl chloride (30 CFR Section 11.150). Certifications can be obtained for a single vapor or gas or for a combination (paint spray, pesticide, chlorine and sulfur dioxide, chlorine and organic vapor, etc.). This discussion will be limited to the factors influencing the performance of organic vapor cartridges.

Air-purifying respirators, including their corresponding cartridges, are routinely used in diverse industrial environments. Thus, numerous factors such as contaminant concentration, composition, temperature, relative humidity, work rate, facepiece fit, etc., must be considered to assure that the proper respirator and cartridges have been selected. Of course, this assumes that the worker is aware of the need for respiratory protection, that it is available, and that he or she can use it correctly — factors which do not always exist. Further compounding the situation is the user's belief that these certified respirators, including cartridges, are safe and effective against most toxic vapor and gas contaminants. In reality this is not the truth.

Many limitations are placed on organic vapor cartridge usage in 30 CFR Part 11. In fact, when the constraints of 30 CFR Part 11 are considered, it is apparent that very little is known about the effectiveness and performance of these devices under real world environmental conditions. Actually, the only laboratory test data obtained on respirator cartridges stamped "NIOSH/MSHA APPROVED" for organic vapors is that they have provided protection for 50 minutes against 1000 PPM carbon tetrachloride in 50 ± 5% relative humidity air at 25 °C and at a test air flow rate of 64 liters/minute for the "as received" cartridges. This says nothing about the ability of a respirator cartridge to adsorb other vapors or gases. Further, 30 CFR Part 11 limits their use to only those gases and vapors with adequate warning properties. Adequate warning properties provide the user with some indication that the effectiveness of the sorbent is exhausted and protection is at an end. These devices are not approved for use in atmospheres which are immediately dangerous to life and health (IDLH), nor against concentrations greater than 1000 PPM (lower if the compound produces an IDLH at a concentration $\leq$ 1000 PPM). In addition, other limitations may be imposed due to factors such as lower flammable limit, toxicological effects, etc.

The crux of the matter is that knowledge of sorbent efficiency and service life appears to be a weak area in the

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The views expressed herein are those of the author and not necessarily those of NIOSH.

present standards of air-purifying respirator performance. This is due to numerous reasons such as: (1) all organic vapor and gas cartridges are evaluated for efficiency with only a single test vapor (carbon tetrachloride as specified in 30 CFR 11.62-8, Table II), (2) the reliance on warning properties to indicate breakthrough (end of the cartridge's effective service life), (3) the possible desorption of impregnating agents used on sorbents, (4) the desorption of adsorbed gases with low boiling points, (5) the potential for synergistic effects in multi-component contaminant environments, (6) the effects of environmental working conditions which are not completely compensated for, and (7) the lack of data and information characterizing sorbent materials. These factors, along with inadequate research in the area, especially regarding applications, are disturbing. The potential impact is only realized after evaluation of a study which showed that 51 of 121 organic compounds tested on commercially available cartridges had shorter service life times than carbon tetrachloride. Yet, these same cartridges are being used against a wide range of organic substances which have extremely diverse chemical and physical properties. Thus, workers wearing these safety devices in areas where there are numerous contaminants (some of which may not have adequate warning properties) may be protected by no more than a false sense of security. It must be remembered, however, that NIOSH does not recommend their use for substances which do not have adequate warning properties. Nevertheless, individuals using organic vapor (OV) cartridges do not always adequately investigate a substance's warning properties.

In order to help alleviate the situation, air purifying respirator research designed to fill the voids that exist is essential. The goal of such programs would be the establishment of an effective, scientifically sound program for evaluating sorbent materials against all types of organic vapors and gas contaminants in a timely fashion. This would help lead to the safe and effective use of these respirators in the field against only those organic vapors and gases for which adequate wearer protection has been demonstrated.

General Background

Organic respirator cartridges bind gas and vapor molecules by sorption mechanisms. Different types of forces can be involved and sorption is usually classified according to these types of interaction. For example, if only physical forces are involved, the process is called adsorption (activated carbon black, charcoal). Should the interaction be stronger (electron transfer mechanism), the phenomenon is termed chemisorption (soda lime, cupramite, acid-impregnated solid adsorbents, acidic alumina, amine-impregnated activated carbon and metal oxides). However, if the sorbate does not remain on the surface, but enters into the solid or its impregnant and reacts chemically with it, and thus changes the chemical nature of each, this is called absorption. In addition, the sorbent could act solely as a catalyst (*e.g.*, hopcalite) which decomposes and detoxifies the contaminant by formation of relatively innocuous substances which can be adsorbed, chemisorbed, or absorbed.

As expected, the amount of gas and/or vapor sorbed may be small or large depending on the physical and chemical nature of both the sorbent and sorbate. Porous granular sorbents having a large surface area are utilized to remove gas and vapor contaminants from environmental air during inspiration. Usually these sorbents, contained in layers of varying depths in cartridges, must function under varying conditions of concentration of contaminants, flow rate, temperature, humidity, etc. For example, concentration may range from less than one PPM to 1000 PPM (0.1%), and average flow rates (inspiratory) may range from 15 liters/min to over 200 liters/min. Through all this, the sorbent layer must reduce the contaminant's concentration below the threshold limiting value in a period of tenths of a second (air residence time in the sorbent bed). To accomplish this, properties which sorbents ideally possess are:

(1) Ability to sorb contaminants at a high rate
(2) High capacity (quantity) for contaminant adsorption
(3) High retention for sorbate so as to minimize desorption (valved respirators only)
(4) Ability of sorbent granules to retain their shape and size so that they do not crush
(5) Stability and retention of these properties under normal storage conditions and use conditions

Charcoal and charcoal impregnated with substances like iodine, nickel chloride, copper oxides, manganese, chromium, copper, and cobalt salts, etc., to enhance selective adsorption for certain vapors, are widely used. But, most organic vapor and gas cartridges employ non-impregnated charcoal. Many factors are at work in determining the effectiveness and efficiency of the sorbent against any one particular vapor. Unfortunately, no one physical characteristic (*e.g.*, boiling point, vapor pressure, molecular weight, polarizability) of the contaminant (gas or vapor), or the sorbent has been identified that consistently correlates with adsorption capacity and service life. Thus a dilemma exists, a situation where numerous unknown factors can determine the amount of a particular sorbent needed. Some factors known to be important include:

(1) Rate of flow and flow type (steady state vs cyclic or pulsating, laminar vs turbulent)
(2) Relative humidity of air and water content of sorbent
(3) Concentration of contaminant
(4) Temperature
(5) Physical-chemical properties of the sorbent (surface area, porosity, surface characteristics)
(6) Size of granules and relationship to surface area
(7) Activity of sorbent
(8) Capacity of sorbent
(9) Physical and chemical properties of the gases and vapors (polarizability, dipole moment, quadrupole moment, etc.)
(10) Desorption characteristics
(11) Void Fraction

Unfortunately, information dealing with air purifying cartridge performance under real world type conditions is limited. By far the most extensive treatment of the subject was a series of papers by Nelson *et al.*(1-8) concerning the testing of organic vapor and gas cartridges for breakthrough (penetration, service life) characteristics. Nelson's experimental design(1,2) was such that parameters like vapor concentrations (upstream and downstream), relative humidity, and flow rates could all be continually monitored over a wide range of test conditions. These important parameters and additional issues raised in other articles will be discussed in the body of this paper.

Flow Type

Nelson initially developed a mechanical breathing simulator(3) so a comparison study between steady state and pulsating flow patterns could be performed.(4) Ultimately, these studies found no significant service life difference between the mechanical breathing simulator at 0, 208, 415, 622, 830, and 1107 kg-m/min work rates and the equivalent steady state average flow rates of 14.0, 20.6, 29.8, 36.9, 53.3, and 71.4 liters/minute for exhalation valve respirators. This is consistent with basic equilibrium adsorption theory which predicts that the amount of contaminant adsorbed at a given temperature, humidity, and concentration is essentially independent of flow rate. Thus, the breakthrough time is governed by the average rate of flow through the cartridge rather than uniformity of flow, assuming negligible desorption. From this, it follows that the effective service life appears to be inversely proportional to the flow rate at a given concentration and set of experimental conditions.

Thus, the use of steady state flow for testing organic vapor and gas cartridge performance appears justified for air purified respirators which have exhalation valves. However, air-purifying respirators which do not have exhalation valves are different (exhaled air also cycled through sorbent bed) and probably need to be evaluated under pulsating flow, with a mechanical breathing simulator.

Relative Humidity

The effects of relative humidity on activated charcoal's ability to adsorb gases and vapors have been studied by Nelson *et al.,*(7) Balieu,(9,10) McGinnis and Fawcett,(11) Maggs and Smith,(12) and Burrage and Allmand.(13) In general, the relative humidity data have been generated on a rather small selection of solvent vapors and cartridge types. The overall data are relatively consistent and certain important trends exist. First, Nelson's(7) studies indicate that the pulsating and steady state flow breakthrough curves (service lives) are basically identical when tested at the same relative humidity and concentration/flow conditions.

Second, although the service life is approximately the same between 0 and 50% RH, significant differences are observed at higher relative humidities. As might be expected, this is a reflection of the amount of sorbate which can be adsorbed at these different RH conditions, which in turn depends on the amount of water vapor the sorbent can hold. From the literature reports it appears that at a test relative humidity of approximately 65% the dependence on humidity becomes highly significant, as reflected by a large shift to shorter or longer breakthrough times. In general, as the test RH increases, the breakthrough concentration vs time line is depressed toward shorter times with the degree of depression being a function of the sorbent material. But should the contaminant be highly water soluble, a shift to longer breakthrough times could occur. This latter phenomenon is also observed when samples are preconditioned at high RH conditions prior to testing. Thus, both preconditioning and varying test humidities can alter the cartridge service life. Further, it has been postulated that the test use humidity has a greater effect on service life than the preconditioning humidity, but this is still debated.

Finally, it has been speculated that humidity has a greater effect on cartridge performance at low contaminant concentrations. This increased effect has been postulated to be due to the competition between contaminant vapor and water vapor for the same sorbent's active sites. These water/carbon and vapor/carbon interactions are dependent on each substance's physical and chemical properties. For example, Maggs and Smith(12) noted that preadsorbed moisture reduced the useful life of charcoal against halothane and chloroform by a factor of approximately three. Still, other anesthetics showed less of a dependence which led to the general opinion that a correlation between boiling point and intermolecular forces might exist (as boiling point increased, the effect of H_2O vapor decreased). In fact, empirical equations for predicting the dependence of breakthrough times on RH have been established by some researchers.(7,13)

30 CFR Part 11 now requires the testing of cartridges which have been preconditioned for 6 hours at 25 liters/minute flow of 85% or 25% relative humidity air (conditions are different for powered cartridges due to the greater sorbent volume). Preconditioned cartridges are then tested against 1000 PPM carbon tetrachloride at 50% RH and 25 °C with the one exception that the flow is reduced from 64 liters/minute to 32 liters/min. Although it is probably true that any cartridge sorbent that is highly susceptible to water vapor would not pass, this is not representative of real life conditions. In fact, what is taking place is that the reduction in flow is really off-setting changes due solely to the relative humidity preconditioning. Therefore, a realistic relative humidity challenge test which is more stringent, based upon experimental data, and which simulates actual work place environmental conditions and cartridge use, is necessary. Also data showing the effects that increased relative humidity has on sorbent efficiencies for various contaminants over a broad range of contaminant concentration (≤ 50 PPM to 1000 PPM) needs to be generated. This would help identify the conditions at which desorption by water vapor becomes important and critical to the removal of adsorbed organic vapors. Further, the differences observed from one class of compounds to another due to the variations in physical and chemical properties of the substances would be valuable information. This would be particularly desirable for compounds with low boiling points.

Temperature

In the literature little data is available on the effects of temperature on cartridge performance and efficiency. But, an increase in temperature would be expected to have an adverse effect on breakthrough time due to increased desorption. However, a positive effect (increased efficiency) would be observed if the mechanisms of chemisorption or decomposition were important. Yet, temperature as a factor has only been briefly addressed. In Nelson's(7) work, no temperature range studies were performed, but the general statement that for every 10 °C rise in temperature, the service life would be reduced from 1-10%, depending on the contaminant, was based solely on calculations using a selected adsorption isotherm. Some unpublished data by G.O. Wood at Los Alamos indicates that there may be as much as a twofold reduction in breakthrough times with a 5 °C temperature rise at a fixed RH, assuming that adsorption is the only mechanism of action.

This latter information suggests that the service life would be significantly shortened at elevated temperatures due to enhanced desorption. This is one area where research efforts could readily supply the data necessary to fill existing voids. Also, temperature effects observed would shed light on the possible effects anticipated with combination units like paint spray and pesticide cartridges. Indeed, an understanding of the temperature effects on cartridge performance and efficiency over the range from 25 °C to 55 °C is badly needed in order to determine pertinent environmental conditions during use. Simultaneously, one would learn what restrictions, if any, are needed in order to prevent wearer misuse and injury. In summary, a significant reduction in service life can occur with even nominal temperature increases.

Breakthrough Time, Service Life

Articles appear in the literature on the charcoal breakthrough characteristics against classes of compounds,(5,14,16) low boiling compounds,(17) anesthetics,(12,18,19) and specific compounds.(20,24) It is, however, difficult to directly compare results due to differences in experimental conditions and cartridge types. By far the most comprehensive evaluation was that of Nelson *et al.*(5) who tested a few commercially available organic vapor cartridges against 121 various organic vapors and gases. The standard conditions used in that study were as follows: C^{input} was 1000 PPM regardless of the compounds' TLV; relative humidity was 50%, room temperature (20 °C) was employed; and a continuous flow rate of 53.3 liters/minute which corresponds to a moderate-to-heavy work load was selected. The sample cartridges were dried and then stored in a cabinet for at least 2 days at 50% RH and 22 °C before use. The 121 compounds tested represented different classes (aromatic, alkanes, alcohols, monochlorides, dichlorides, trichlorides, tetrachlorides, pentachlorides, acetates, ketones, amines, miscellaneous). From the resultant breakthrough curves, the following trends were detected and general observations made:

(1) Attempts to predict the breakthrough time by relating it to a single property of the adsorbed vapor or gas proved to be unrealistic. Rather, the time is a complex function of the contaminant vapor, the sorbent (activated carbon), and the experimental conditions (flowrate, temperature, relative humidity, etc.).

(2) In general, activated carbon has a greater affinity for less volatile materials.

(3) Volatile materials, especially the first members of each homologous series, exhibited relatively short breakthrough times.

(4) In general, the higher the boiling point of the solvent (contaminant), the greater is the weight of solvent adsorbed.

(5) Usually, the most volatile solvent within a given class or series breaks through first. However, as the boiling point of the solvents within a class increase, the trend eventually reverses until at some point the breakthrough time actually decreases with rising solvent boiling point.

(6) Within each solvent class the weight adsorbed is both an increasing function of the boiling point and a decreasing function of the vapor pressure, the two being interrelated.

Although trends in the breakthrough characteristics of compounds do exist, no *one* physical characteristic of the gas or vapor or the sorbent consistently correlates with breakthrough time. Use of no *one* single agent is capable of accurately assessing the breakthrough behavior of all organic vapors and gases. For example, it seems unrealistic to establish one substance against which all pesticides could be rated due to the highly diverse chemical structures of routinely employed pesticides. However, what seems realistic might be the development of a predicting scheme based on multiple substances which are representative of organic compounds possessing diverse chemical and physical properties. In addition, studies of thermodynamic factors, such as heats of adsorption and their relationship to physical adsorption are desirable to obtain a fundamental understanding of the adsorption process. A complete evaluation and characterization of such critical sorbent/contaminant interactions might lead to a model for predicting sorbent efficiencies for various classes of substances based upon the sorbent, sorbate, flow conditions and their interactions.

Concentration

The contaminant's concentration imposes major restrictions on organic vapor respirators. These devices are not approved for entry into atmospheres which are immediately dangerous to life or health (IDLH). 30 CFR Part 11; (11.1510 Footnote 7) also states that they are not for use against gases and vapors which have poor warning properties. Further, 30 CFR 11.150 specifies the maximum use concentrations for chemical cartridge respirators and adds that the maximum use concentrations are lower for organic vapors which produce IDLH atmospheres at concentrations equal to or lower than those specified in 11.150. Additional factors like lower flammable limits, toxicological effects, faceseal, etc., could lead to other restrictions.

Concentration effects on the breakthrough characteristics of charcoal have been discussed in the literature.(6,23,25) In particular, Nelson(6,25) showed that when one plots the log of the service life time at selected breakthrough percentages against the log of the concentration, a family of straight lines is obtained. Similarly, a plot of log concentration versus log 10% breakthrough time for various flow rates again gives a family of straight lines. This was found to be true for numerous organic contaminants tested. Also, this linear relationship was verified for concentrations ranging from 50 to 3000 PPM. Little or no work was or has been done since at concentrations below 50 PPM, but a study by Smith and Giesler(23) found that vinyl chloride gave a linear relationship when the log of concentration was plotted versus the 10% breakthrough time over the concentration range from 100 to 5000 PPM. These reported differences (log/log vs log/linear) raise some questions about concentration effect on breakthrough times for different contaminants. More importantly, one must remember that a lower percentage of the sorbate is adsorbed at low concentrations, thus making it essential to study and define the concentration response at low concentrations for various types of vapors and gases which are routinely found in the work place. This is particularly important for substances with extremely low TLVs® (threshold limit values) where it is essential that not even tenths of PPMs be allowed to penetrate.

Multicomponent Environments

The evaluation of sorbents against mixtures of contaminants has received very little attention. One study on binary and ternary hydrocarbon adsorption on activated carbon has been done by Costa *et al.*(26) Their work discusses the aspects of theoretical prediction for these systems. But exactly what the situation is when various classes of organic vapors and gases are present is not known. Thus, another area where future research efforts are needed has been identified, and studies to determine the effects on sorbent efficiencies in multicomponent environments should be conducted. The issues that need to be considered are: (1) can a model be developed which will allow prediction of efficiencies for mixtures of sorbents under such conditions, (2) what is the competitive nature of various substances for active sorbent sites, (3) are toxic substances displaced by less toxic and inert substances like water vapor? (for example, could an accumulated low dose of a toxic substance suddenly be desorbed by a heavy dose of petroleum vapor?) and (4) what is the effect of the extent of loading on the potential adsorption and desorption characteristics?

Desorption of Vapors, Gases, and Impregnating Agents

So far, several factors have been discussed which affect the breakthrough times of cartridges. Yet, the important issue of desorption, one factor which is not directly considered and tested for under 30 CFR Part 11 has not been explored. Basically, the desorption of adsorbed compounds during normal cartridge use, is indirectly tested for when the breakthrough characteristics are determined. In general, compounds which have low boiling points have increased desorption properties; plus, the capacity of the sorbent against such compounds is generally lower. Also, some particular classes of compounds, such as alcohols, show increased rates of desorption and lower sorbent capacity than expected.

This raises the question as to whether the sorbent's capacity is sufficiently high. Two additional questions are: (1) will desorption take place if the sorbent is partially used and then reused after a short period (hours) of non-use, and (2) do sorbent impregnating agents desorb from the sorbent during use and upon storage?

Conventional desorption experiments(27,28) can be found in the literature, but articles which directly address the questions raised above are sparse. The desorption issue concerning compounds which possess low boiling points was covered by Balieu(17) at the NIOSH International Respirator Research Workshop (September, 1980). To sum up the importance of this issue, Balieu concluded by saying that the new draft for a European Standard (CEN) states, ". . . filters [sorbents] for use against substances boiling below 65 °C shall be capable of passing a desorption test in addition to the normal sorption test." Further, Maggs(29) has tried to take advantage of the desorption phenomenon by using rapidly desorbing agents to establish a small dose, nondestructive test method for routine 100% cartridge testing. Although difficulties were encountered, this appears to be a viable approach to the establishment of such a vitally needed procedure. In a later article Maggs and Smith(30) proceeded to emphasize the importance of the consequences of desorption with methyl bromide. They concluded that use restrictions are needed for respirators employed for protection against agents which desorb readily, like methyl bromide. In particular, even if specially designed for an agent, the respirator should *not* be worn intermittently due to desorption which gives rise to a redistribution of preceding doses which can lead to hazardous effluent concentrations during subsequent usage even if in an uncontaminated work area.

Finally, a few words should be said about the desorption of impregnating agents. This is an area which has not really been investigated. In fact, a recent study at Los Alamos by G.O. Wood(31) is the only work extensive enough to warrant mentioning. The study found that triethylene diamine (TEDA) and C-alkyl substituted TEDA used as impregnating agents to enhance adsorption of methyl iodine were being desorbed but at levels below the TLV for similar amines. This raises a red flag, especially since studies on other impregnants have not been reported.

The effects of extended storage time on impregnated charcoal has been investigated. Hjermstad and Berg(32) demonstrated that aging has an effect on the sorbent's ability to remove contaminants. In their study they showed that copper-chromium impregnated charcoal gradually lost some of its capacity for cyanogen chloride over extended storage times. They attributed this to a change in the crystal structure of the impregnant. This structural change occurred due to a small amount of moisture in the cartridges even though in general impregnants are very water insoluble. In addition, it should be noted that the formation of substances like ammonia in cartridges can increase the pH or result in complex formation which could result in increased impregnate solubility. This is a potential with copper-chromium impregnated charcoal for cyanogen chloride removal, which functions according to the following scheme:

$$\mathrm{ClCN} + 2\,\mathrm{H_2O} \rightarrow \mathrm{NH_4Cl} + \mathrm{CO_2}$$

In addition, the possible catalytic conversion of contaminant to more toxic species must be studied. Thus, two additional important questions have been brought to light. First, what is the effect of aging on impregnated sorbents as well as unimpregnated materials? Second, what factors lead to and cause the increased desorption of impregnating agents, which in some cases are toxic heavy metals or acids?

Conclusions

There are numerous environmental factors which must be evaluated prior to actually selecting an organic vapor cartridge respirator. This holds true for all other respirators as well, but the specific environmental and use limitations which are mandated for this specific type far outnumber the others. Therefore, if an accurate assessment of the contaminant, its concentration, and its warning properties are not made, worker safety cannot be assured. In fact, if those steps are not taken, it is highly likely that the worker's safety may be jeopardized.

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