American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

Service Lives of Respirator Cartridges versus Several Classes of Organic Vapors

R. W. FREEDMAN , B. I. FERBER & A. M. HARTSTEIN

To cite this article: R. W. FREEDMAN , B. I. FERBER & A. M. HARTSTEIN (1973) Service Lives of Respirator Cartridges versus Several Classes of Organic Vapors, American Industrial Hygiene Association Journal, 34:2, 55-60, DOI: 10.1080/0002889738984884

To link to this article: https://doi.org/10.1080/0002889738984884

Service Lives of Respirator Cartridges versus Several Classes of Organic Vapors

R. W. FREEDMAN, B. I. FERBER, and A. M. HARTSTEIN

Pittsburgh Mining and Safety Research Center, Bureu of Mines, U. S. Department of Interior,
Pittsburgh, Pennsylvania 15230

The effective service life of chemical respirator cartridges varies with the organic vapor absorbed on the charcoal. Life versus various compounds was determined by exposing chemical cartridges to vapors, some of which were of fairly high toxicity. An apparatus was assembeld to produce dynamic mixtures containing 1000-ppm concentrations of organic vapors. The effluent was continuously monitored to determine cartridge service life using hydrogen flame ionization detection. Service Life depends on the compound to which the cartridge is exposed. Breakthrough patterns for several compound classes may serve as a rough guide for untested compounds within a homologous series.

Introduction

ACTIVATED CHARCOAL-FILLED RESPIRATORS have long been used for protection against nonacidic organic gases and vapors. Coarse-mesh coconut charcoal is generally used because of its favorable adsorption and flow properties.

The U. S. Bureau of Mines routinely conducts permissibility tests of commercial chemical cartridges respirators against organic vapors. Test conditions are described under U. S. Bureau of Mines Schedule 23B.[1] The lattter specifies carbon tatrachloride as the test material.

The conditions used in the Bureau test procedure involve set concentrations of carbon tetrachloride in air at specified flow rates. The service life of two cartridges in parallel is then defined as the time taken for the organic component of the gas mixture to break through and reach an effluent concentration of 5 ppm, as measured by a nondispersive infrared (NDIR) instrument.

Materials less toxic than carbon tetrachloride have been considered for use as standard test vapors. In a prior study at the Bureau,[2] chemical cartridges were exposed to Freon 113 and carbon tetrachloride and the average service lives were compared, using a separate, specific NDIR detector for each compound.

In an unreported study at the Bureau, an attempt was made to employ hydrogen flame ionization detection (FID) because of its senistivity and nonspecific response to most organic compounds. However, at that time the FID was eliminated from consideration for routine testing because of electrical leakage due to contamination of high impedance connections with hydrogen chloride from chlorine-containing test compounds.

In the same study, we conducted preliminary experiments using conventional chromatographic columns filled with activated charcoal taken from respirator cartridges. However, this proved impractical, owing to greatly different geometry and elution behavior.

Any given compound cannot be assumed to be representative of the volatile organic compounds to which respirator wearers may be exposed. Therefore, service-life information on chemical cartridges for noxious

---

Reference to trade names does not imply endorsement by the Bureau of Mines.

compounds other than carbon tetrachloride is important in performance evaluation. Interest in the behavior of cartridges toward other organic compounds is growing, as evidenced by experiments conducted for the Atomic Energy Commission[3,4] at Lawrence Radiation Laboratory, Livermore, California. In this work, a variety of organic vapors of varying concentrations were monitored upstream and downstream from cartridges by hydrogen flame ionization detectors. Steady- and cycled-flow programs were employed and breakthrough concentrations determined down to the part-per-billion level.

In our present investigation we decided to measure cartridge service lives against a variety of volatile organic compounds with boiling points up to 126°C (butyl acetate). Several of the compounds with toxicities approaching that of carbon tetrachloride could be hazardous if cartridge service lives were consideraly lower than for carbon tetrachloride. In our experiments, we decided to confirm fairly closely to the conditions imposed by Bureau Schedule 23B. This was done to provide reasonably good comparisons with results obtained during official scheule testing of commercial cartridges. In addition, variables such as geometry, flow rate, and concentration would be eliminated, enabling a close comparison of service lives to be made. In the case of two organic compounds of widely differing volatility—namely, ethyl formate and methyl bromide—we decided to observe complete breakthrough to the input concentration (1000 ppm). This would give us a time-weighted estimate of wearer exposure as related to the threshold limit value (TLV).[5] It should be borne in mind that time-weighted exposure is not a linear integrand, and effects vary greatly with the compound in question.

Experimental Procedure

Several limitations of variables were imposed during the tests. Chemical cartridges were selected from one manufacturer's lot. Two cartridges were tested in parallel at a total flow of 64 liters/min with an input concentration of 1000 ppm, as called for in the schedule. Under these conditions, cartridge breakthrough time or service life was defined as the time required to reach an organic effluent level of 5 ppm.

The test apparatus is shown in Figure 1. Compressed air flows through a charcoal filter, which removes oil and hydrocarbons. It then passes through a flow controller and rotameter at 64 liters/min. The system is calibrated at 5 ppm using continuous syringe injection (from a syringe pump) to

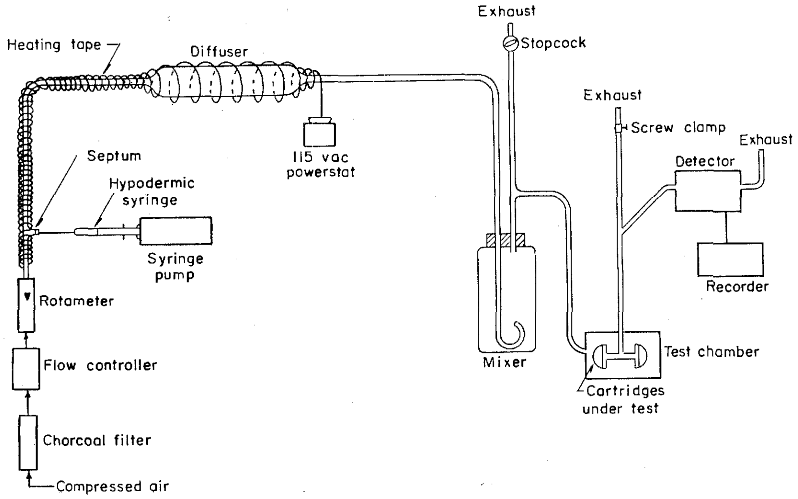

Figure 1. Cartridge test apparatus.

provide a gaseous flow rate of 0.32 ml/min into the main airstream. Gastight and liquid syringes are used for gases and liquids, respectively. Liquid flow from the syringe required to produce a flow of 0.32 ml/min of vapor is calculated from the following equation:

$$F_1 = \frac{(0.0001242)(F_v)(M)(T)}{(P)(D)}$$

where F_1 = liquid flow rate (ml/min) at room temperature.
F_v = vapor flow rate (ml/min) at room temperature.
M = molecure weight of organic compound.
T = room temperature (°K).
P = barometric pressure (mm Hg).
D = liquid density (gm/ml).

The calibrated mixture of vapor in air is forced into a diffuser consisting of two perforated porcelain filter disks stationed in a glass cylinder. A heating tape is wrapped around the diffuser and connecting glass tubing to keep the organic compound in the vapor state until a homogeneous mixture results.

Residual mixing of the vapor in the main airstream is assured by a mixing jar. A stopcock is provided for manual release of vapor. The 5-ppm mixture then enters the empty cartridge test chamber, which is arbitrarily kept at 46°C by powerstat setting. Its effluent flow is throttled down to provide an aliquot to the hydrogen flame ionization detector within a Beckman Model 400 hydrocarbon analyzer. This is capable of detecting less than 1 ppm of organic compounds.

After the system has been calibrated for 5 ppm, the aparatus is readied to generate 1000 ppm of organic vapor, by providing a flow of 64 ml/min of the vapor into the 64-liter/min main airstream. This involves using a larger syringe and selecting a higher syringe pump speed. Organic compounds that are normally gaseous at room temperature and pressure are metered directly into the main airstream by employing rotameter measurement of flow.

With the test cartridges in the test chamber, the airstream containing 1000 ppm of organic vapor is introduced and the service life is noted with the analyzer.

Chemical cartridges were tested against homologous series of alkanes, alcohols, aldehydes, formates, and acetates. In addition, several organic compounds of fairly high toxicity, such as halogenated hydrocar-

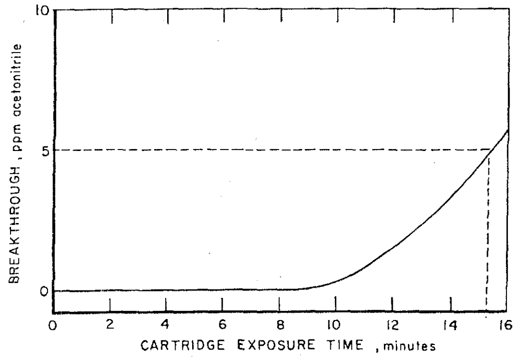

Figure 2. Cartridge breakthrough for acetonitrile.

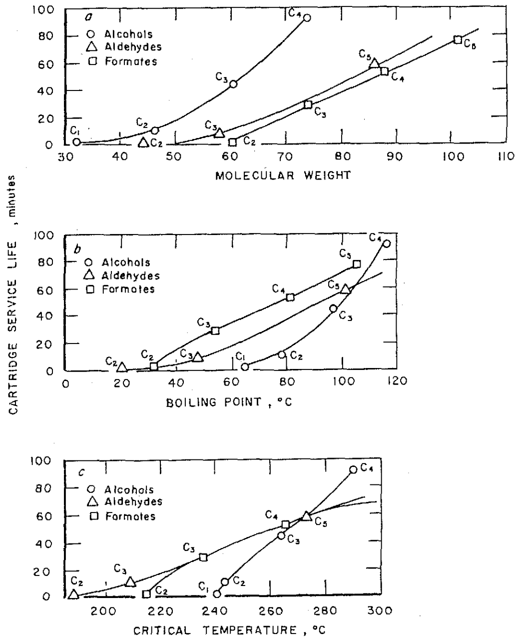

Figure 3. Service life versus several physical properties.

bons, benzene, acetic acid, carbon disulfide, acetonitrile, and ethylene oxide, were tested.

Extended breakthrough patterns were made with ethyl formate and methyl bromide. After the 5-ppm breakthrough had been determined, the testing was allowed to continue. Complete breakthrough (to the 1000-pph input concentration) was indicated by a leveling off of the recorder trace.

Results and Discussion

One of the typical curves demonstrating cartridge breakthrough is shown in Figure 2. In this case, adsorption in the cartridge packing occurred over a 9-minute period followed by 5-ppm breakthrough at 15.3 minutes. The corrosion that occurs when

TABLE I

Service Lives of Commercial Chemical Cartridges against 1000-Ppm Concentrations of Various Organic Vapors

Compound	Threshold Limit Value (ppm)	Life[a] (minutes)
Alkanes		
Butane—C_4H_{10}	—	10.7
Pentane—C_5H_{12}	500	34.9
Hexane—C_6H_{14}	500	55.3
Heptane—C_7H_{16}	500	60.9
Octane—C_8H_{18}	400	65.5
Alcohols		
Methanol—CH_3OH	200	2.2
Ethanol—C_2H_5OH	1000	10.9
Propanol—C_3H_7OH	200	44.1
Butanol—C_4H_9OH	100	92.1
Formates		
Methyl formate—$HCOOCH_3$	100	2.6
Ethyl formate—$HCOOC_2H_5$	100	28.1
Propyl formate—$HCOOC_3H_7$	—	52.5
Butyl formate—$HCOOC_4H_9$	—	76.2
Acetates		
Methyl acetate—CH_3COOCH_3	200	22.4
Ethyl acetate—$CH_3COOC_2H_5$	400	59.6
Propyl acetate—$CH_3COOC_3H_7$	200	62.1
Butyl acetate—$CH_3COOC_4H_9$	150	59.7
Aldehydes		
Acetaldehyde—CH_3CHO	200	1.0
Propionaldehyde—C_2H_5CHO	—	8.2
Valeraldehyde—C_4H_9CHO	—	57.1
Halides		
Bromides		
Methyl bromide—CH_3Br	20	1.2
Ethyl bromide—C_2H_5Br	200	17.3
Iodides		
Methyl iodide—CH_3I	5	22.1
Ethyl iodide—C_2H_5I	—	84.2
Miscellaneous compounds		
Benzene—C_6H_6	25	63.0
Acetic acid—CH_3COOH	10	105.1
Acetonitrile—CH_3CN	40	16.1
Chloroform—$CHCl_3$	50	23.5
Ethylene oxide—$(CH_2)_2O$	50	0.45

[a] Time to reach 5-ppm level.

hetero-atom organic compounds are burned (yielding mineral acids) is minimized by avoiding extended exposure to such combustion products.

Service lives against the organic vapors tested are given in Table I, together with threshold limit values. Service life has been plotted against molecular weight, boiling point, and critical temperature in Figure 3 for three families of compounds.

Curve patterns for molecular weight and boiling point are similar with a shift in position of the formate curves. The critical temperature plot displays somewhat different curve shapes. Plots of data in Table I shows that alkanes (C_4–C_8) and acetates (C_2–C_5) display sets of curves that rise and then level off at the higher molecular weights.

Attempts to obtain correlations with critical temperature, boiling point, molecular weight, dipole moments, compressibility, polarizability, polarity, and Van der Waals constants have been the subject of a great deal of effort by investigators in the field of activiated carbon. Some relationships to the basic Freudlich equation for gases, $X/m = k \log p$, can be obtained for hydrocarbons and other compounds with low polarizability (X/m = weight of sorbed vapor per gram of carbon, and p = applied partial pressure). If the liquid volume at breakthrough of the sorbed vapor per unit weight of carbon, V_1/m (the loading factor), is plotted against the activation energy expressed as the log of the ratio of the vapor pressure of sorbed vapor at 46°C, P_0, to the partial pressure of the sorbate, P, a linear curve is obtained for alkanes as shown in Figure 4. The liquid volume, V_1, is readily calculated from the known sorbate flow rate and breakthrough time. The value of P_0 is calculated from the empirical equation $\log_{18} P_8 = (-0.2185A/T) + B$, where P_0 = vapor pressure (mm Hg), T = temperature (°K), A = molar heat of vaporization (cal/gm-mole), and B is a constant. The quantities are avaliable from handbooks.

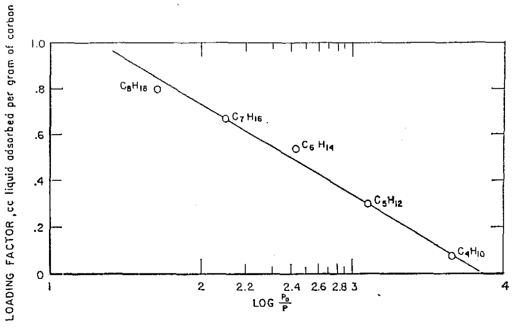

Figure 4. Loading factor versus log (vapor pressure/partial pressure) for *n*-alkanes.

The linear alkane plots could be of value in predicting breakthrough times for these compounds, but unfortunately plots of the other compound series result in curved lines.

From the preceding information it is readily seen that the breakthrough curves can serve at best as a rough guide for untested compounds within a homologous series.

The extended breakthrough patterns showed that ethyl formate (TLV = 100 ppm), with a 5-ppm breakthrough time of 28 minutes, broke through completely (1000 ppm) at 58 minutes. Methyl bromide, with a TLV of 20 ppm, had a 5-ppm breakthrough time of 1.2 minutes. The level rose rapidly to 1000 ppm in 5 minutes. In both of these extended breakthrough patterns, the concentration increases linearly after the 5-ppm breakthrough point. In a Bureau schedule test, these cartridges should protect for at least 50 minutes against 1000 ppm of organic vapor. With methyl bromide, a person wearing these cartridges would receive a 1000-ppm exposure for more than 45 minutes with a material having very little odor and a low threshold limit value (20 ppm). Such exposure could even be more serious with very volatile organic compounds, which have much lower threshold limit values. For example, acrolein (b.p.53°C) has a TLV of 0.1 ppm. Cartridge life against it should be similar to the 8.2 minutes of protection that a cartridge offers against propionaldehyde (b.p.49°C).

Summary

The results indicate that the service life of a charcoal respirator cartridge depends on the compound to which it is exposed. It is difficult to predict service life at a known concentration and flow rate based on physical and chemical calculations alone. Important determining factors are vapor pressure, molecular weight, structure, and polarizability. Breakthrough patterns for several compound classes can at best serve as a rough guide for untested compounds within a homologous series.

References

1. U. S. Bureau of Mines: Respiratory Protective Apparatus, Test for Permissibility; Fees, Schedule 23B, 8 pp, August 8, 1959. *Federal Register 24:*6619 (August 14, 1959).
2. Swab, C. F., and B. I. Ferber: Freon 113 as a Test Material for Chemical Cartridge Respirators. *U. S. Bur. Mines Rept. Invest. 7380:* 5 pp. (May 1970).
3. Ruch, W. E., G. O. Nelson, C. Lindekin, R. Johnson, and D. J. Hodgkins: *Respirator Cartridge Efficiency Studies:* I. *Experimental Design.* Presented at American Industrial Hygiene Conference, Toronto, Ontario, Canoda, May 28, 1971, Paper 167.
4. Nelson, G. O., and D. J. Hodgkins: *Respirator Cartridge Efficiency Studies: II. Preparation of Test Atmospheres.* Presented at American Industrial Hygiene Conference, Toronto, Ontario, Canada, May 28, 1971, Paper 168.
5. American Conference of Governmental Industrial Hygienists: *Threshold Limit Values of Airborne Contaminants and Intended Changes.* 27 pp., Cincinnati, Ohio (1970).

Received May 29, 1972

Noise Course Repeated

Two presentations of the Institute on Noise Control Engineering have been scheduled to accommodate the growing enrollment. The seventh presentation of the Institute will be August 20-24, 1973, at The Dearborn Inn in Dearborn, Michigan. The eighth presentation will be at The John Marshall in Richmond, Virginia on March 25-29, 1974.

The Institute provides training in the solution of factory, environmental and product noise problems, including compliance with laws and regulations. Concurrent sessions permit specialization of training according to registrant interest. The course explains noise, its measurement, the adverse effects and legal consequences. Characteristics of noise generated by various types of equipment are identified. Methods of noise reduction at the source, along transmission paths and at the receiver are explained. These principles are illustrated by numerous examples of applications in different industrial or community situations.

For additional information write to James H. Botsford, Director, Institute on Noise Control Engineering, P.O. Box 3164, Bethlehem, Pennsylvania 18017.