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Chemical Permeation Testing of Air-Supply Hoses

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Permeation of chemicals through the walls of air-supply hoses used with respirators is an underrecognized problem in industry. Transport of chemicals through the wall of a hose occurs in the same manner as through gloves and chemical suits—driven by the chemical concentration gradient—but for air-supply hoses, the chemical evaporating inside the air-supply hose is inhaled. A simple method based on the mathematical equivalence of filling a homogeneous hose with a chemical, to immersing it in a chemical, has been developed. The method requires a short section of hose to be filled, plugged, and weighed at intervals to determine the breakthrough detection time and the cumulative permeation per meter. The method has been tested experimentally, and calculations show that permeation of an air-line respirator hose could be a significant source of respiratory exposure, particularly for users of demand-type, supplied-air respirators.

Keywords air supply hoses, chemicals, permeation, respiratory protection

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Often work has to be performed in a contaminated environment such as cleaning or maintaining process vessels or near pools of chemicals where a worker uses a respirator attached to an air-supply hose. The worker may also be using gloves or wearing a chemical suit, and chemicals will not only permeate the chemical protective clothing but also the air-supply hose. Permeation may sometimes be evident only by the taste or odor in the air from the supply hose. In many situations requiring the use of an air-line respirator, the outside of the hose can become contaminated with chemicals, particularly if the hose lies on the ground or on the floor of a vessel. Prevention of contamination of the hose and regular replacement do occur in some industries, but common practice is to use a hose until it fails mechanically.

Permeation is a molecular process, first described by Graham(1) in 1829. For an air-line respirator hose, the process involves molecules of a chemical entering the pores of the hose polymer, diffusing through it (driven by the chemical concentration gradient), then evaporating on the inside (Figure 1).

The science of permeation testing of chemical protective clothing (CPC) is well developed, following the 1974 Occupational Safety and Health Administration (OSHA) requirement(2) to provide CPC that is “impervious” to carcinogens. Test methods for gloves and chemical suits were developed using the American Standards for Testing Materials (ASTM) ASTM F739 standard,(3) but hose permeation has not received the same attention. However, the permeation process for hose is identical to that for gloves.

An infrequently cited National Institute for Occupational Safety and Health (NIOSH) test protocol for testing the permeation of air-supply hose by gasoline(4) requires that (Figure 2).

> “The permeation of the hose by gasoline will be tested by immersing 7.6 m (25 feet) of hose and one coupling in gasoline, with air flowing through the hose at the rate of 8 liters per minute for 6 hours. The air from the hose shall not contain more than 0.01 percent by volume of gasoline vapor at the end of the test.”

This test method is unusual as it contains elements of both penetration of a coupling and permeation of the hose wall. Gasoline penetration through a coupling seal would increase with depth of immersion and would be reduced by hose pressure. Permeation would be unaffected by depth of immersion (once fully immersed) or hose pressure. The method does not appear to have been generalized to other chemicals.

This test method has a number of practical problems, including the use of 7.6 m of air-supply hose and several hundred liters of gasoline. The gasoline leaches plasticizer from the hose, making it unsuitable for normal use and creating a waste disposal problem. The cost of the setup effectively precludes more than one test at a time.

The purpose of the research reported here was to investigate a simplified gravimetric method for studying chemical permeation of air-line respirator hoses. Filling the hose with chemical and measuring the permeation rate out of the hose provides for a much simpler experimental technique.

BACKGROUND

Consider a plain, homogeneous sheet of polymer exposed on one side to a chemical. The permeation characteristics of the material can be measured in a suitable cell(3) and they are

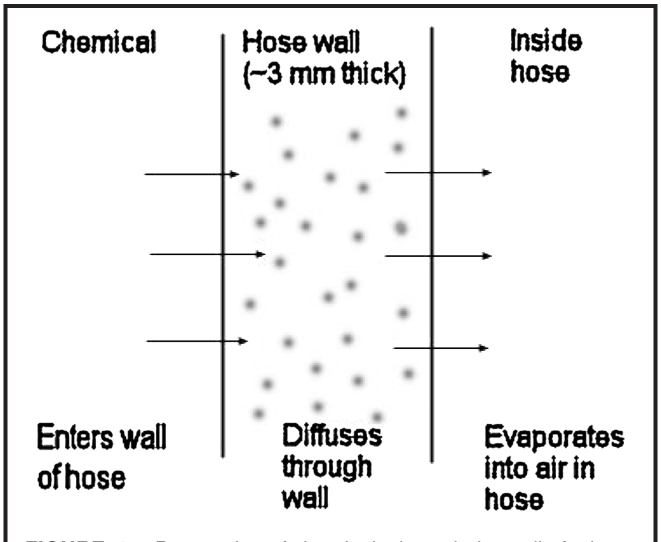

FIGURE 1. Permeation of chemicals through the wall of a hose

independent of which side of the material is exposed, provided that the material is homogeneous.

The case for a hose is not as obvious, as the exposed area on the outside is much greater than the exposed area on the inside. However, we have shown (see Appendix) by solving the diffusion equations(5,6) in cylindrical coordinates that the transient and steady-state permeation rate at the hose surface (predicted by filling a simple hose with a chemical) are the same as immersing the air-supply hose in the same chemical. With both immersed and filled hose, the flux of chemical through the walls of the air line is governed by the internal surface area of the hose. The model also assumes that the hose material is homogeneous.

When a hose is constructed of layers of dissimilar material it is not homogeneous and the model is inadequate. However, if the permeation properties of these layers are similar, then the approximation to homogeneity should be adequate to rank choices. The factors involved in the choice and service life of a breathing hose, which are often layered, parallel the choice and its service life of chemical gloves and extend beyond permeation parameters to other factors, such as temperature, mechanical stresses, product variation, and actual usage conditions.(7) The equivalent scenario with a layered glove for testing a filled or immersed hose would be to wear the glove inside out and perhaps obtain either better or worse chemical protection.

For a hose approximating a homogeneous hose, the model permits the testing to be greatly simplified because filling an air-supply hose requires a smaller volume of chemical than immersing the hose in a bath, as required by the NIOSH method. The testing can also be performed on a short section of hose, further reducing the volume of test chemical. Permeant evaporating from the outside of the hose is easily measured by weighing the section of hose filled with chemical with a laboratory balance at selected time intervals. This gravimetric approach is well established, with permeation tubes used to generate standard atmospheres. As long as there is some liquid chemical inside the tube, the permeation rate is unaffected.(8) The method also eliminates the need for costly chemical analysis, flow meters, and pumps that are required by the NIOSH method.

METHODS AND MATERIALS

Two Australian brands of poly vinyl chloride (PVC) hose were selected, these being Nylex (Melbourne, Australia) and Esdan (Danderong South, Australia). The formulation of the hose polymers is unknown but would include plasticizers, fillers, and colorants.

The Nylex hose had an internal diameter of 6 mm and an external diameter of 12 mm and minimum wall thickness of 3 mm, excluding the small external ribs on the hose. The Esdan hose was larger with an external diameter of 18 mm and wall thickness of 4 mm. The Nylex hose was sealed with 3/8″ (9.52 mm) ball bearings and the Esdan hose with 7/16″ (11.11 mm) ball bearings. Trials were performed with new Nylex hose and both new and used Esdan hose.

Sections of the hose were cut with a box cutter and weighed on a laboratory balance (Mercury AND model 202 with 120 g

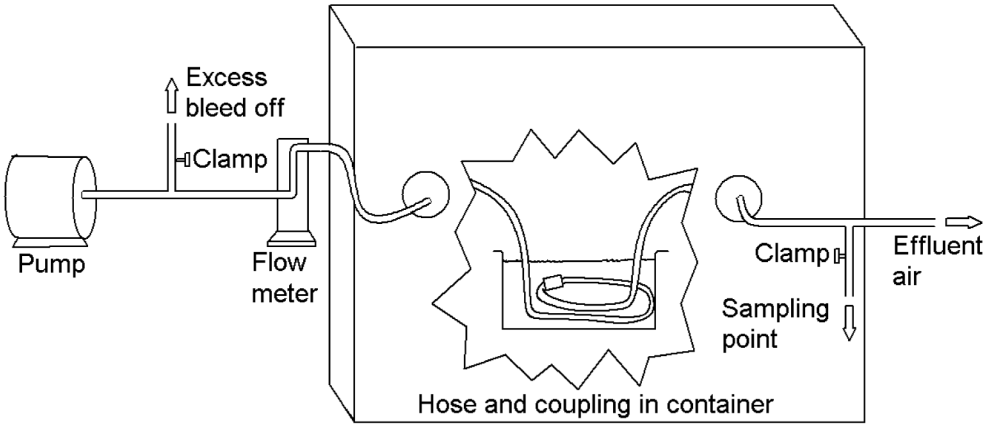

FIGURE 2. NIOSH hose permeation test rig (simplified)

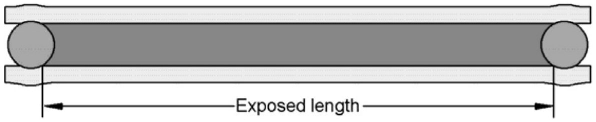

FIGURE 3. Hose filled with chemical

capacity, sensitivity 0.1 mg, Thebarton, South Australia). The samples were equilibrated for temperature for 24 hours in the laboratory, which was maintained at 20 ± 1°C. A ball bearing slightly larger than the bore of the hose was inserted into one end of each sample. Each section and a second ball bearing were weighed to give the empty weight. The samples were gently squeezed with pliers and filled with either methyl ethyl ketone (MEK) or water. The grip of the pliers on the hose was gently released as the second ball bearing was inserted to accommodate the volume of the ball bearing and prevent pressurization of any small bubble of air next to the ball bearing. Trapped, pressurized air could eject the ball bearing. The ball bearing had to be inserted so that it was totally inside the hose sample to ensure it did not fall out when the hose polymer softened under the influence of the chemical. O'Keeffe and Ortman(9) used this same technique with early permeation tubes and also found a ball bearing seal was adequate and that the ball had to be inserted 2 or 3 cm. The experimental setup is shown in Figure 3.

A water-filled hose was used as a control experiment to demonstrate whether water seeped past the ball bearing seals. Water does not permeate through PVC to any significant extent. If the ball bearings did not provide a good seal, then both the MEK and water should begin to change weight immediately, although the weight change would be dependent on a number of factors, including the viscosity of the fluid, hydrostatic pressure, diffusivity, and size of the leak. Once the material appears on the outside of the hose, the MEK will evaporate about 10 times faster (relative evaporation rates of MEK and water are 4.03: 0.3600, relative to n-butyl acetate).(10) If the ball bearing seals were patent, then no initial weight change would be expected for the hose sample containing water.

The sample lengths are expressed in terms of their "exposed length," the actual length of hose exposed to the chemical (Figure 3). This approach ignores nonradial permeation at the seals, but if the exposed length is large compared with the bore of the hose, then this effect could be expected to be small. The exposed length was estimated on completion of the trials using the edge of the visible indents made in the bore of the hose by the ball bearings (4 mm width for the Nylex hose and 5 mm width for Esdan hose) to indicate the edge of the ball bearing seal. There was axial swelling of the hoses during the trials, but the initial distance between the centers of the ball bearings was measured and the width of the ball bearing indent subtracted from this figure to give the exposed lengths shown in Table I.

The hose markings, diameters, distances between the ball bearings, fill time, empty and filled weight of the filled samples, plus temperature and humidity were recorded.

TABLE I. Hose Characteristics

Trial	Hose Brand	Exposed Length (mm)	Solvent
1	Nylex	61	MEK
2	Nylex	65	Water
3	Esdan	117	MEK
4	Esdan	108	MEK
5	Esdan	47	MEK
6	Esdan	80	MEK
7	Esdan	115	MEK
8	Esdan (used)	115	MEK

RESULTS

The results for the cumulative weight loss for the Nylex hose samples are shown in Figure 4 using linear scales and a time scale of 72 hours. The experiment was continued for 1000 hours and the additional data is shown on the log-log scale in Figure 5.

The sensitivity of the balance was 0.1 mg and this is directly applicable to the data in Figures 4 and 5, where the data have not been divided by the exposed length to normalize the data.

Surface MEK arising from the filling operation evaporated in the first few minutes (A). Low-level MEK permeation was observed within half an hour and persisted for 8 hours, as the solvent front moved through the air-supply hose (B). Once swollen with solvent, the permeation progressed at a higher rate (C) until liquid MEK was depleted and the permeation rate dropped after 1 day. This depletion of solvent was ascertained during preliminary trials by inspection during the period before and after the permeation rate dropped. At this stage (C), all residual MEK was in the walls of the air-supply hose, but the MEK continued to diffuse across the hose wall, driven by a reduced chemical gradient. This effect continued for the rest of the trial.

The results for water in the second trial are also shown in Figures 4 and 5. Water showed no measurable loss in the first 24 hours. The small loss after this time is not evident on the linear scale in Figure 4, though it is evident with the log scales in Figure 5.

The log scales in Figure 5 reveal an initial sudden jump (A) as minute amounts of water or MEK evaporate from around the ball bearing from the filling process. This is an experimental artifact with a time scale of several minutes and is not evident on the linear scale in Figure 4. This jump is difficult to avoid, and one solution is to measure weight loss relative to a weight measurement several minutes into the trial when traces of surface solvent have evaporated and the sample weight is stable.

With lengthy exposure, water is seen to permeate the Nylex PVC hose after a day but at a much lower rate than for MEK. The MEK permeation rate slows as the reservoir of liquid MEK disappears, leaving the permeation to be driven at a lower rate

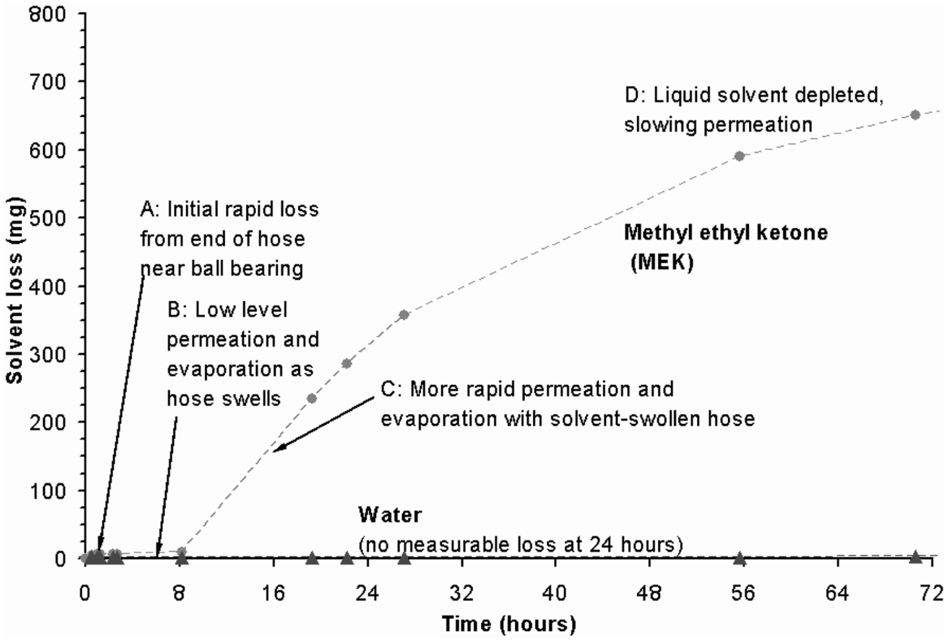

FIGURE 4. MEK and water permeation through Nylex PVC hose

by MEK vapor inside the wall of the hose, as previously noted. At this stage the experiment can be terminated.

Parallel trials were performed by filling short lengths of new and, in one case used, Esdan hose with MEK and then sealing the hose and weighing the samples at intervals, with different exposed lengths of hose (Table I). The normalized cumulative permeation from these trials are shown in Figure 6 in milligrams of chemical per exposed meter of hose. The detailed history of the used Esdan hose sample is unknown, but the hose was slightly abraded and marked and may have been in use for months with intermittent chemical exposures.

In Figure 6, three successive 8-hour work shifts are also indicated to highlight the increasing chemical respiratory dose from MEK permeating the walls of a hose under conditions of continuous exposure. In each shift, the additional respiratory dose from MEK per meter of exposed hose, is the increase in permeation in that shift.

For the five new Esdan air-supply hose samples (Trials 3 to 7), the results are similar. However, the sample of used

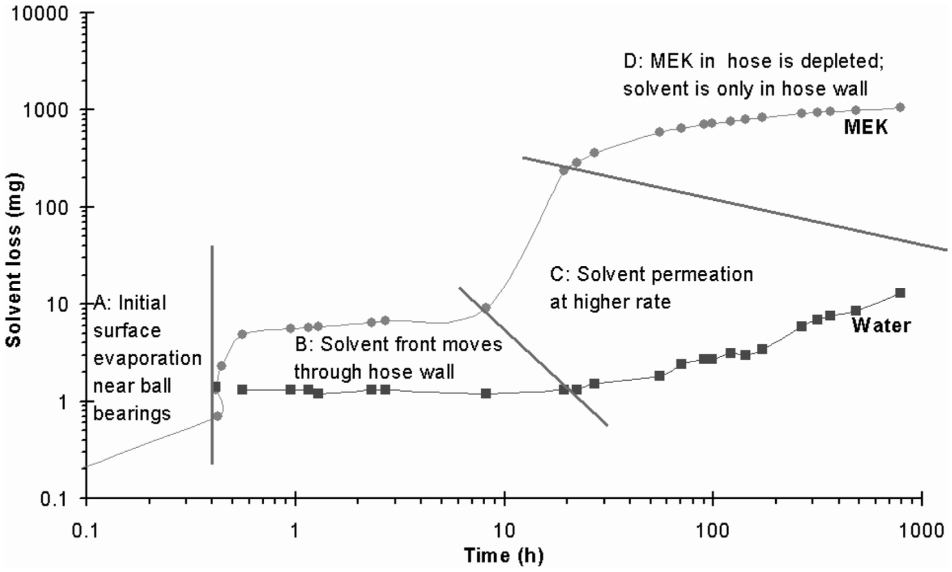

FIGURE 5. Extended MEK and water permeation through Nylex hose, log-log scales

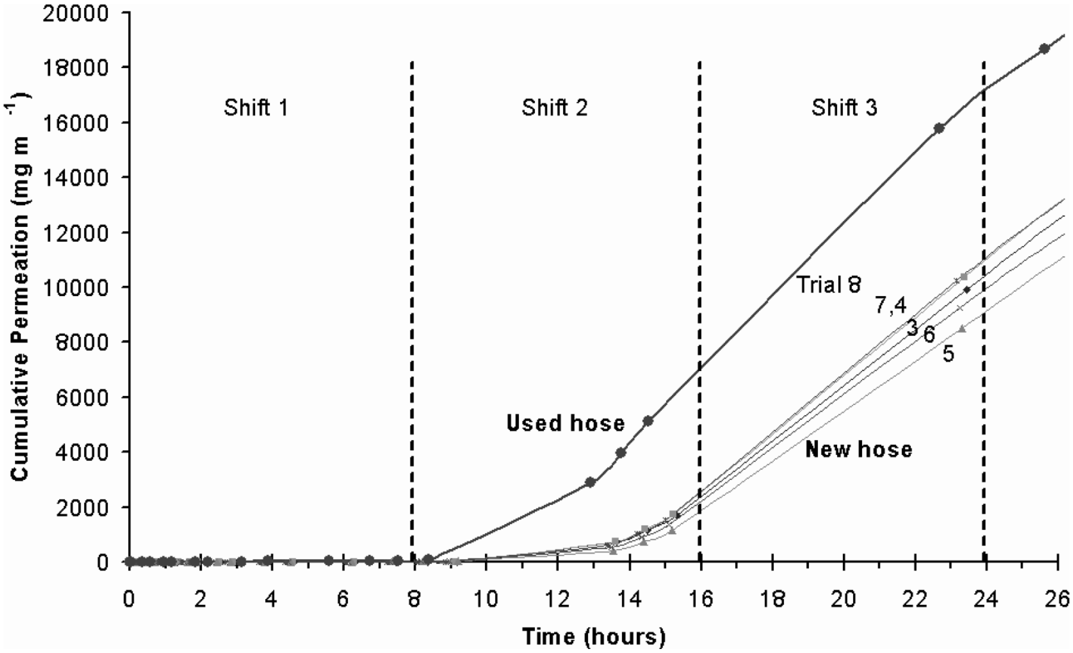

FIGURE 6. MEK permeation through new and used Esdan hoses

Esdan hose (Trial 8) shows earlier breakthrough and a slightly higher permeation rate (slope of permeation curve). Whether this is due to batch differences in the samples, prior chemical exposure of the hose, or perhaps microscopic cracks in the hose is not known.

DISCUSSION

Seals

No measurable loss of water was measured in the first 24 hours with the Nylex hose, confirming that the ball bearings provided a sufficient seal even though water, like any chemical, would eventually permeate the PVC hose.

MEK and Water Permeation

The MEK permeates the hose initially at a low rate but then at a much higher rate. While the permeation may not be significant at room temperature (20°C) in the first 8 hours, not all chemicals have good warning properties such as taste and smell to indicate that significant permeation has occurred. There is a significant increase in permeation after 10 hours' exposure. For a workplace using the same hose during a shutdown and working around the clock, particular care would have to be taken to avoid chemical exposure to the hose and subsequent elevated permeation rates.

The fact that water permeates in measurable amounts in 24 hours should also be of concern, as PVC air lines are common, and many formulations (particularly in agriculture) are water based. It has been found with gloves(11,12) that the carrier solvent can facilitate the permeation of other components of the formulation; this may also occur with hoses.

Detection Limits

Perkins and Pool(13) defined the breakthrough detection time (BDT) for gloves using a similar gravimetric method as "the weighing time just prior to when the weight loss first exceeded the LOD" (limit of detection), and then monotonically increased. This criterion for BDT is also applied here. The detection limit for the method was derived using the initial Nylex water permeation data, as they showed no measurable permeation in the first 20 hours. The standard deviation (SD) for these data ($n = 12$) was 0.06 mg or a LOD of 0.18 mg. In this investigation, 3 SD above background gives a LOD for use in calculating the BDT of 3.6 ± 2.0 hours ($n = 5$) for new Esdan hose.

Accurate estimates of the BDT depend on the interval between weighings being significantly less than the spread of weight changes in the early stages of the trials. Near 3 hours, the intervals between weighings was 22 min and at the next weighing near 4 hours it was 57 min. A weighing robot could enable automation of the process at shorter intervals with more samples. However, manual weighing would detect a "popped" ball bearing and avoid contaminating other samples and the balance.

Repeatability

Perkins and Pool(13) performed gravimetric permeation tests with 2-ethoxyethanol acetate (selected for minimal swelling in the gloves) on four batches of Ansell-Edmont nitrile gloves. These data are compared with the Esdan hose data to determine whether the repeatability of the methods was comparable (Table II). The steady-state permeation rate (SSPR) is the slope of the permeation curve before the MEK is depleted. The coefficient of variation (CV) of the new Esdan hose samples at

TABLE II. Repeatability of Gravimetric Methods for Glove and Hose Permeation

	CV SSPR	CV BDT
Perkins and Pool (n = 5 for each batch)	0.07–0.62	0.26–0.78
Esdan hose at 24 hours (n = 5)	0.08	0.56

24 hours is the standard deviation of the permeation rates of the samples divided by the mean permeation rate of the samples.

It appears that the repeatability for the hose permeation method is at least comparable to gravimetric permeation methods for gloves.

The temperature control in the room was to ±1°C, and a rule of thumb(14) for permeation tubes is that each 1°C increase in operating temperature results in a 10% change in permeation rate. In these parallel trials, the samples experienced the same temperature variations, so greater repeatability of permeation indices could be expected than in trials run in sequence.

Used Hose

The effect of use on hose appears to be real, but the used Esdan hose (Trial 8) may have been from a different batch than the new Esdan hose (Trials 3 to 7), which may account for some of the difference. However, there was less difference in cumulative permeation at 24 hours between the new Esdan hose samples (SD 771 mg m^{-1}) than between new and used Esdan hose (6122 mg m^{-1}) (Figure 6). It appears that used hose is likely to provide less protection to the user than new hose.

This finding has significant implications in determining the service life of hoses and their storage conditions. Not only will extended exposure of new hose to chemicals result in increased permeation, but hose that has been used and stored is also less effective at protecting the user. For any pre-exposed hose, the permeation process will continue in the absence of chemical contact with the hose, driven by a residual chemical gradient. A good practice for any hose that has been exposed to chemicals would be to blow clean air through the hose before using it again for breathing, even after a short break. For a hose 20 mm long with a bore of 10 mm and an airflow of 30 L/min, it would take 10 sec to flush it with 3 volumes of air. This would remove most of the pool of permeant in the hose but not necessarily below toxic amounts.

Specific air testing for the contaminating chemicals would be needed to determine whether this flushing was adequate, so this verification would be impracticable in most workplaces. Flushing would not stop the permeant pool reforming between tasks nor would it stop ongoing permeation during use. The residual permeation rate may determine whether the hose has reached its service life, but the emphasis should be on avoiding chemical exposure to the hose in both use and storage, rather than continued use of contaminated hose.

Investigations are needed to determine the best methods of decontaminating hose after use and it may be that warm soapy water(15) is the best method to remove surface contamination.

Inhalation Dose Estimates for Demand-Type Air-Line Respirators

MEK permeation was easily detected through the hose within a workday. It is difficult to translate this to a comparison with the total inhalation dose for demand-type air-line respirators without making some assumptions. Consider the following conditions, corresponding to a confined space where MEK is liberally used.

- One meter of Esdan air-supply hose continuously wet with MEK. In one case, new hose is used, in the other it has been pre-exposed for 24 hours to MEK.
- The supply air to the hose is uncontaminated.
- The work is performed for 8 hours.
- The worker breathes in 10 m^3 a day (20 L/min × 480 min = 9600 L).
- The respirator is a demand-type and all the supplied air is inhaled.
- The temperature is 20°C (the temperature of the experiment).
- The protection factor (PF) afforded by the respirator is 20.
- The MEK concentrations in the workplace are one and ten times the occupational exposure limit (TLV) of 590 mg m^{-3}, giving 590/20 × 1 × 10 = 295 and 2950 mg, respectively, of MEK in 8 hours to the exposed person through limitations of the respirator.

Estimates of MEK respiratory dose for a person employing a demand air-line respirator with a new Esdan hose (first shift and again in subsequent shifts) are given in Table III, for two ambient air concentrations and one meter of hose immersed in MEK. Further assumptions would have to be made for continuous flow respirators as to the proportion of supplied air that was inhaled.

TABLE III. Respiratory MEK Dose in Successive 8-Hour Shifts

	Shift 1 (mg)	Shift 2 (mg)	Shift 3 (mg)
New Esdan air-supply hose dose in shift with 1 meter immersed in MEK	19.6	2318	7330
Respirator dose (PF 20, at TLV)	295	295	295
Percentage of TLV by new Esdan hose and respirator at TLV	5%	44%	129%
Respirator dose (PF 20, 10 times TLV)	2950	2950	2950
Percentage of TLV dose by new Esdan hose and respirator, at 10 times TLV	50%	89%	174%
Used Esdan air-supply hose dose in shift with one meter immersed in MEK	75	6963	10047

Note: Atmospheres of 1 and 10 times the TLV for MEK.

In the scenarios in Table III, the total respiratory dose for new Esdan hose is between 5% and 50% of the TLV in the first shift and is dominated by contributions by the respirator. If a greater length of hose was immersed or the temperature was higher, the permeation from the hose permeation could be much higher. By the third shift, the hose permeation (7330 mg) into the 10 m^3 of air breathed somewhat exceeds the TLV of 590 mg/m^{-3} (or 10 L × 590 $mg/m^{-3} = 5900$ mg). When used Esdan hose is employed, the dose in the first shift is increased by permeation through the hose (75 mg), and the dose in the second shift is similar to the dose in the third shift with "new" Esdan hose.

For a chemical with poor warning properties, there may be no taste or smell and toxic exposures can unknowingly occur.

CONCLUSIONS

Evidence has been presented to suggest that hose permeation can be an important contributor to the overall exposure of workers using air-line respirators in certain work conditions. A simple gravimetric method has been developed that makes permeation testing of air-supply hoses easy and affordable, using a laboratory balance. Hose seals using ball bearings have been shown to be acceptable.

At present the mathematical model supporting the method is based on the assumption of homogeneous (single-layered) hoses, but if the chemical permeation properties of the layers are similar, then ranking of choices should still be possible. Further experimental and theoretical work is needed to determine whether the method can be reliably extended to hoses with more than one layer.

Far less of the chemical under test is needed than with the NIOSH method, almost eliminating chemical waste disposal cost. Pumps and flowmeters are also dispensed with and many samples can be tested at the same time with different chemicals.

It is possible for air-supply hose permeation to dominate the respiratory dose, particularly with pre-exposed hose. This finding is not adjusted for hose wall thickness and hose diameter, so caution should be exercised in generalizing potential respiratory dose to other hose sizes.

It is prudent to avoid direct contact of air-supply hoses with chemicals. Where there is significant contact with liquid chemicals over a length of air-supply hose, daily or weekly replacement may be warranted.

ACKNOWLEDGMENT

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REFERENCES

1. **Graham, T.:** Notice of the singular inflation of a bladder. *Royal Institute J.* 88–89 (1989).
2. "13 Carcinogens (4-Nitrobiphenyl, etc.)," *Code of Federal Regulations Title 29,* Part 1910.1003.
3. **American Society for Testing and Materials (ASTM):** *F739 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact*. West Conshohocken, Pa.: ASTM, 1999.
4. **National Institute for Occupational Safety and Health (NIOSH):** *Test Procedure No 6. Determination of Gasoline Permeation Test for Air-Supply Hoses and Couplings for Type A, B, C, and CE Supplied Air Respirators*. Morgantown, W.Va.: NIOSH, 1980.
5. **Crank, J.:** *The Mathematics of Diffusion*. Oxford, England: Clarendon Press, 1970.
6. **Carslaw, H.S., and J.C. Jaeger:** *Conduction of Heat in Solids*. Oxford, England: Clarendon Press, 1990.
7. **Klingner, T.D., and M.F. Boeniger:** A critique of assumptions about selecting chemical-resistant gloves: A case for workplace evaluation of glove efficacy. *Appl. Occup. Environ. Hyg. 17*:360–367 (2002).
8. **Lucero, D.P.:** Performance characteristics of permeation tubes. *Anal. Chem. 43*:1744–1749 (1971).
9. **O'Keeffe, A.E., and G.C. Ortman:** Primary standards for trace gas analysis. *Anal. Chem. 38*:760–763 (1966).
10. **Archer, W.L.:** *Industrial Solvents Handbook*. New York: Marcel Dekker Inc., 1996.
11. **Schwope, A.D., R. Goydan, D. Ehntholt, U. Frank, and A. Nielsen:** Permeation resistance of glove materials to agricultural pesticides. *Am. Ind. Hyg. Assoc. J. 53*:352–361 (1992).
12. **Forsberg, K., and S. Faniadis:** The permeation of multi-component liquids through new and pre-exposed glove materials. *Am. Ind. Hyg. Assoc. J. 47*:189–193 (1986).
13. **Perkins, J.L., and B. Pool:** Batch lot variability in permeation through nitrile gloves. *Am. Ind. Hyg. Assoc. J. 58*:474–479 (1997).
14. **Washenfeldera, R.A., C.M. Roehl, K.A. McKinney, R.R. Julian, and P.O. Wennberg:** A compact, lightweight gas standards generator for permeation tubes. *Rev. Sci. Instrum. 74*:3151–3154 (2003).
15. **Perkins, J.L.:** Decontamination of protective clothing. *Appl. Occup. Environ. Hyg. 6*:29–35 (1991).
16. **Abramowitz, M., and I.A. Stegun:** *Handbook of Mathematical Functions*. New York: Dover Publications, Inc., 1965.

APPENDIX—ADDENDUM PERMEATION THROUGH THE WALLS OF PIPES

Consider the radial diffusion of a chemical through the walls of a pipe, hose, or walls of a hollow cylinder, as shown in Figure A1.

The internal radius of the pipe is r = a, and the external radius is r = b, where the radial coordinate is in millimeters. Where the pipe is long compared with its diameter, the diffusion is principally in the radial direction, assuming angular symmetry. The concentration $c = c(r, t)$ of chemical is then a function only of the radial distance r and of time t. The linear diffusion of chemical through the walls of the pipe is governed by the diffusion equation in cylindrical coordinates as given by Crank.(5)

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r K \frac{\partial c}{\partial r}\right), \quad a \le r \le b, \ t \ge \infty, \tag{1}$$

where K is the diffusivity in millimeters squared per second. Since this is a linear partial differential equation, the concentration may be normalised so that the saturation concentration $c^* = 1$.

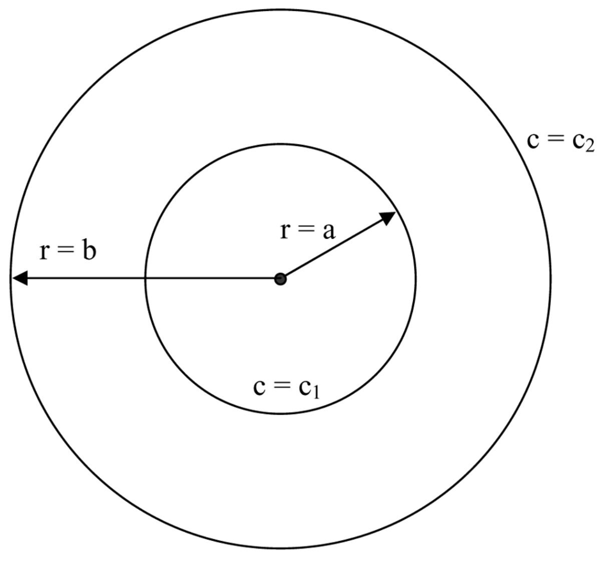

FIGURE A1. Coordinate system for radial diffusion through walls of pipe

Boundary conditions may be taken in the form

$$\begin{aligned} c(r, t = 0) &= c_0 \quad a \le r \le b, \\ c(r = a, t) &= c_1 \quad t \ge 0, \\ c(r = b, t) &= c_2 \quad t \ge 0, \end{aligned} \qquad \textbf{(2)}$$

where c_0, which is constant, is the initial concentration of chemical in the wall of the pipe, and c_1 (and c_2) is the concentration of chemical at the inner surface (outer surface) of the pipe (both are constants). Note that the case

$$c_1 = 1, \quad c_2 = c_0 = 0,$$

corresponds to a fresh pipe being filled with chemical, which then diffuses outward and evaporates. Further, the case

$$c_1 = c_0 = 0 \quad c_2 = 1,$$

corresponds to a fresh pipe being immersed in chemical and an internal airflow removing the permeating chemical from the pipe. Thus the boundary conditions can be adjusted to represent the two sets of experimental conditions.

The analytical solution of Eq. 1, subject to the boundary conditions in Eq. 2, is given by Crank, Eq. 5.62$^{(5)}$

$$\begin{aligned} c(r, t) = {} & (c_1 \ln(b/r) + c_2 \ln(r/a))/\ln(b/a) \\ & + \pi c_0 \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n)u_0(r\alpha_n)\exp\left(-K\alpha_n^2 t\right)}{J_0(a\alpha_n) + J_0(b\alpha_n)} \\ & - \pi \sum_{n=1}^{\infty} \left(\frac{c_2 J_0(a\alpha_n) - c_1 J_0(b\alpha_n)}{J_0^2(a\alpha_n) - J_0^2(b\alpha_n)} \right) \\ & \times J_0(a\alpha_n)u_0(r\alpha_n)\exp\left(-K\alpha_n^2 t\right) \end{aligned} \qquad \textbf{(3)}$$

where J_0 is the zero-order Bessel function of the first kind

$$u_0(r\alpha_n) = J_0(r\alpha_n)Y_0(b\alpha_n) - J_0(b\alpha_n)Y_0(r\alpha_n)$$

is a parabolic cylinder function, and Y_0 is the zero-order Bessel function of the second kind.$^{(16)}$ The quantities α_n, n = 1, 2, 3, … are the roots of the function $u_0(a\alpha_n) = 0$, and there is an infinite number of these roots. Some of the roots α_n are given in Carslaw and Jaeger$^{(6)}$ (Appendix IV, Table IV) although these roots are now easily evaluated by computer. Carslaw and Jaeger also give a reasonably complete discussion on how the solution in Eq. 3 is constructed.

The first group of terms in Eq. 3 represent the steady-state concentration that is attained for large time. These solutions for the two cases

$$\begin{array}{llll} \text{(i)} & c_1 = 1, & c_2 = 0 & \text{pipe filled with chemical} \\ \text{(ii)} & c_1 = 0, & c_2 = 1 & \text{pipe immersed in chemical} \end{array} \qquad \textbf{(4)}$$

are shown in Figure A2. These steady-state concentration profiles are not the same due to the radial geometry. Where the pipe is filled, the inner wall at r = a controls the steady-state permeation of chemical into the wall of the pipe. After entering the wall of the pipe, the chemical diffuses outward into a radially expanding space until it exits through the outer wall.

Where the pipe is immersed, the chemical enters through the outer wall and diffuses inward into a radially contracting space. The chemical needs higher concentrations and concentration gradients toward the inner wall to enter the inner hollow section.

The second term in Eq. 3 involves the initial concentration c_0 and represents the effects of retesting a pipe where there are residual amounts of chemicals still in the walls of the pipe. Where a fresh pipe is tested, it may be assumed that $c_0 = 0$ and the fresh pipe is not contaminated. Then the second term is zero and does not enter the discussion. This term is a sum of exponentially decaying (with time) terms, and these effects (with $c_0 \neq 0$) die away as time increases.

The third group of terms in Eq. 3 involves c_1 and c_2, and represents the nonsteady or time-dependent effects arising from the boundary conditions. Each term in the sum is governed by an exponentially decaying (with time) term. For small times, this group of terms controls the solution. As time becomes large, this group of terms decays to leave the steady-state profile.

Now consider the permeation rate or total flux per unit length of pipe for the two experiments at Eq. 4. The total flux per unit length is given by Crank$^{(5)}$

$$\text{Flux} = -2\pi K\left(r\frac{\partial c}{\partial r}\right), \qquad \textbf{(5)}$$

where c(r, t) is given by Eq. 3. The experimental processes involve estimating the permeation rate at the inner (r = a) or outer (r = b) wall of the pipe. Consider the case of Eq. 4(i), where the pipe is filled with chemical, and let $F_i(r = b)$ be the permeation rate at the outer wall. Similarly, $F_i(r = a)$ is the permeation rate at the inner wall for the case in Eq. 4(ii). Calculating the permeation rate involves calculating

$$\left(r\frac{\partial u_0(r\alpha_n)}{\partial r}\right)_{r=b} = -\frac{2}{\pi}$$

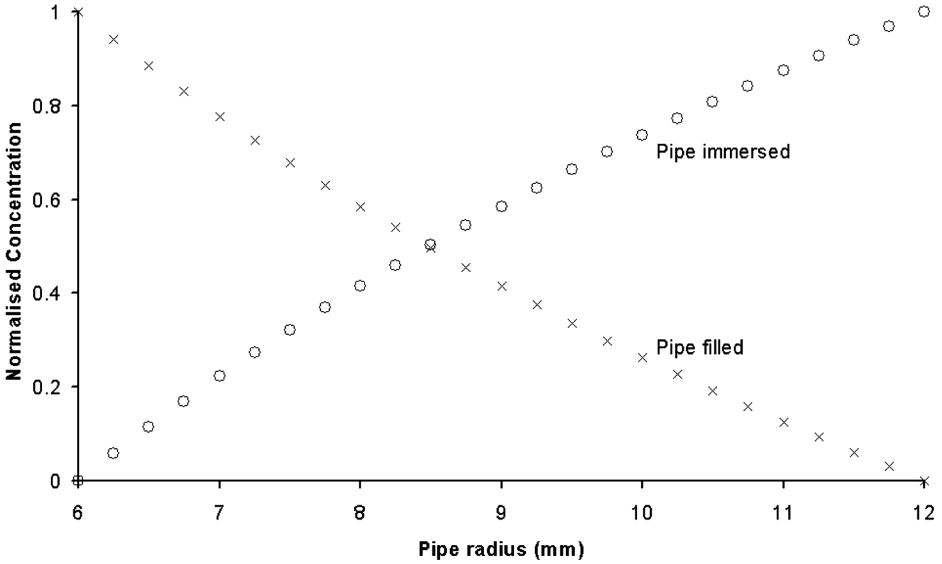

FIGURE A2. Steady-state concentration profiles for pipe filled and immersed

(see Carslaw and Jaeger, Section 7.10)(6), and thus

$$F_i(r = b) = \frac{2\pi Kc_1}{\ln(b/baa)} + 4\pi c_1 K \sum_{n=1}^{\infty} \left(\frac{J_0(b\alpha_n)J_0(a\alpha_n)}{J_0^2(a\alpha_n) - J_0^2(b\alpha_n)} \right) \times \exp\left(-K\alpha_n^2 t\right), \tag{6}$$

with $c_1 = 1$. The first term represents the steady-state flux, while the second group of terms represent the unsteady or transient flux when the pipe is filled with chemical.

When the pipe is immersed in chemical, the permeation rate F_{ii} $(r = a)$ is the flux of chemical over the inner wall of the pipe. In this case,

$$\left(r\frac{\partial u_0(r\alpha_n)}{\partial r} \right)_{r=a} = -\frac{2}{\pi p_n},$$

where

$$p_n = \frac{J_0(a\alpha_n)}{J_0(b\alpha_n)}$$

is the ratio of two Bessel functions. Then

$$F_{ii}(r = a) = -\frac{2\pi Kc_2}{\ln(b/ba)} - 4\pi Kc_2 \times \sum_{n=1}^{\infty} \frac{J_0^2(a\alpha_n)\exp\left(-K\alpha_n^2 t\right)}{\left(J_0^2(a\alpha_n) - J_0^2(b\alpha_n)\right)p_n}, \tag{7}$$

with $c_2 = 1$. Substituting for p_n in Eq. 7, then

$$F_i(r = b) = -F_{ii}(r = a), \tag{8}$$

where the change of sign refers only to the direction of permeation. The magnitudes of the permeation rates are the same at all times t. Thus, for Eqs. 4(i) and 4(ii), the permeation rate at the outer wall of the pipe when it is filled with chemical is identical to the permeation rate at the inner wall when the pipe is immersed. This equality holds for the steady state and for the nonsteady state. The permeation rates at the unexposed surface are shown in Figure A3.

Finally, consider the permeation rates at the exposed surface $F_i(r = a)$ and $F_{ii}(r = b)$, which are shown in Figure A4. These are not equal but do exponentially alter to give the same steady-state permeation rate for large times. The term $F_i(r = a)$ gives the permeation rate at the inner wall when the pipe is filled with chemical. Initially at $t = 0$ just inside the wall, $c_0 = 0$ and there is an infinite concentration gradient. This is a modeling artifice, since Eq. 1 is an approximation that is not valid in such circumstances. The numerical solution also has difficulty for small times, and many terms are needed in the summations to adequately represent c(r, t) and the permeation rate for small time. The same features occur in considering $F_{ii}(r = b)$.

Note that Eqs. 6 and 7 are identical only in magnitude provided $c_1 = 1$ in Eq. 6, and $c_2 = 1$ in Eq. 7; that is, the wall in contact with the chemical is saturated. In addition, $c_0 = 0$ and the pipe must be free of chemical to start with. If $c_0 \neq 0$, then the second group of terms in Eq. 3 needs to be considered in calculating the fluxes in Eq. 5. In this set of terms, there is no fortuitous dependence on c_1 or c_2, and no fortuitous cancellation arising from p_n in Eq. 7. In these cases, the permeation rates will not be equal in magnitude.

The fluxes $F_i(r = b)$ and $F_{ii}(r = a)$ correspond to the breakthrough curves as discussed by Crank(5,p.48) for a plain sheet of material. The total amount of diffusing substance per unit length Q(t), which penetrates the pipe in time t is given by

$$Q(t) = \int_0^t F_i(r = b)dt,$$

where the pipe is filled with liquid and $c_2 = 0 = c_0$. A similar result is obtained for the immersed pipe. Performing

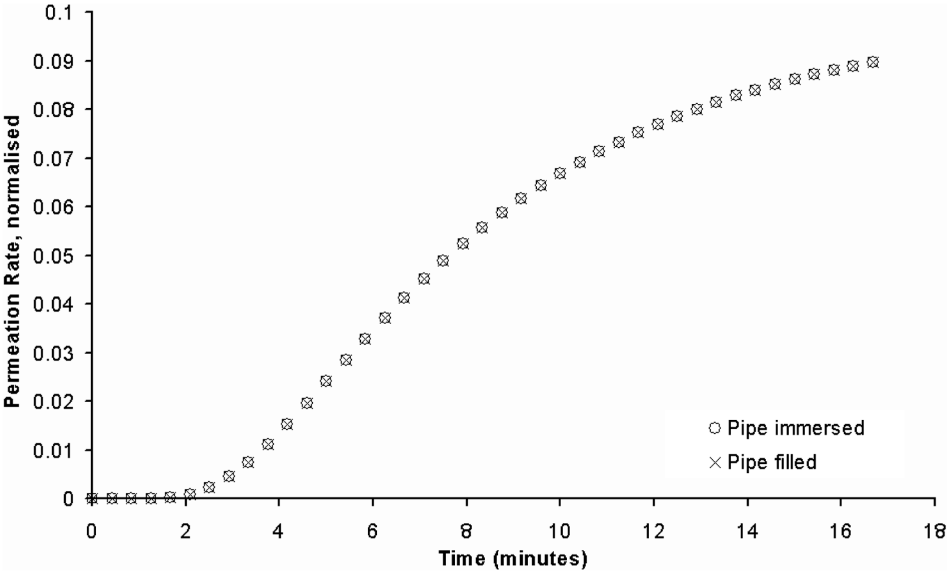

FIGURE A3. Permeation rates at unexposed surface, for pipe immersed and filled

the integrations leads to (with $c_1 = 1$)

$$Q(t) = \frac{2\pi K}{\ln(b/ba)} t + 4\pi \sum_{n=1}^{\infty} Z_n - 4\pi \sum_{n=1}^{\infty} Z_n e^{-K\alpha_n^2 t},$$

where $Z_n = J_0(a\alpha_n)J_0(b\alpha_n)/\left(\alpha_n^2\left(J_0^2(a\alpha_n) - J_0^2(b\alpha_n)\right)\right)$.

As t → ∞, the last summation approaches zero, and Q(t) approaches a straight line of the form

$$Q_1(t) = 2\pi(tK/\ln(b/a) + B),$$

where $B = -2\sum_{n=1}^{\infty} Z_n$. The intercept, T, of this straight line on the t-axis is given by

$$T = \left(2\sum_{n=1}^{\infty} Z_n\right) \ln(b/a)K.$$

Summing the series may be feasible analytically, but the solution would not be a simple scaling of the form for Lag Time as for a plane sheet. However, some numerical answers for

$$S_M = \left(2\sum_{n=1}^{M} Z_n\right)$$

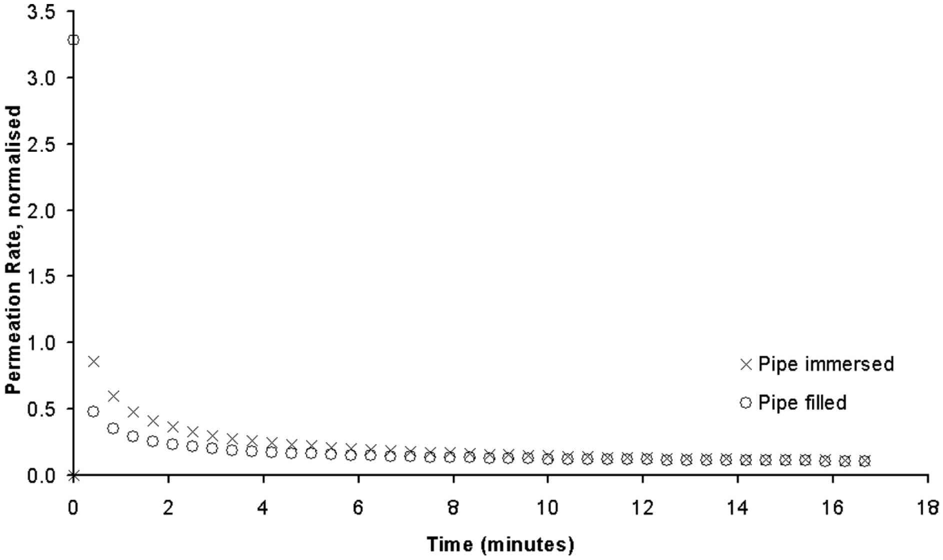

FIGURE A4. Permeation rates at exposed surface, for pipe immersed and filled

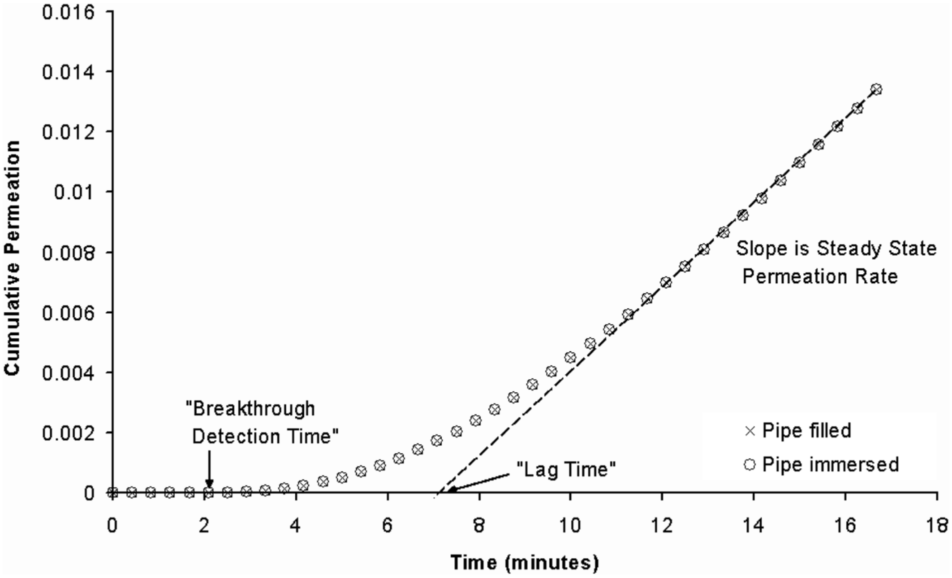

FIGURE A5. Theoretical permeation curve for a homogeneous hose

with a = 6 mm, b = 12 mm, $K = 0.011\ \text{mm}^2/\text{sec}^{-1}$ are:

$$M = 24 \quad S_M = -54.866$$
$$M = 28 \quad S_M = -54.777$$
$$M = 32 \quad S_M = -54.786$$

and the changes are small for such a large number of terms.

Example of a Calculation for a Hose

If the diffusion coefficient $K = 0.011\ \text{mm}^2/\text{min}^{-1}$ and the concentration of the liquid in contact with the pipe or hose is set to unity, the inside and outside radii being 6 and 12 mm, respectively, (the same dimensions as for the Esdan hose), then the theoretical permeation curve for permeation through the wall of a pipe or hose has the form shown in Figure A5. The metrics familiar to glove testing of Breakthrough Detection Time, Lag Time and Steady State Permeation Rate have been shown in Figure A5. Unlike gloves, where there is a simple mathematical relationship between Lag Time, glove thickness, and diffusion coefficient, for breathing hoses this does not exist.

The form of this permeation curve is similar to the experimental curves in Figure 6, even through the Esdan hose.