Permeation of MEK, Turco, aviation fuel and diesel through a breathing hose over an extended time

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Chemical permeation of the breathing hoses used with supplied air respirators has largely been neglected. This study investigates the long-term permeation of methyl ethyl ketone (MEK), Turco paint stripper, aviation fuel and diesel through the wall of Arbin Rinba brand breathing hose. The testing used a new, simple test method that involves filling a short length of breathing hose with the chemical. While MEK and components of MEK permeated in a few hours, it took several weeks for significant permeation of the aviation fuel and diesel to occur. The main implication of this work is that hoses need to be kept clean, as chemicals like MEK and Turco that permeate easily can contaminate the breathing air, while chemicals that permeate more slowly, like aviation fuel and diesel, show a potential for significant permeation if the breathing hose is stored contaminated. These findings affect the selection, service life and maintenance of breathing hoses.

KEYWORDS

- BREATHING HOSES
- CHEMICALS
- PERMEATION
- RESPIRATORY PROTECTION
- JP-8

Introduction

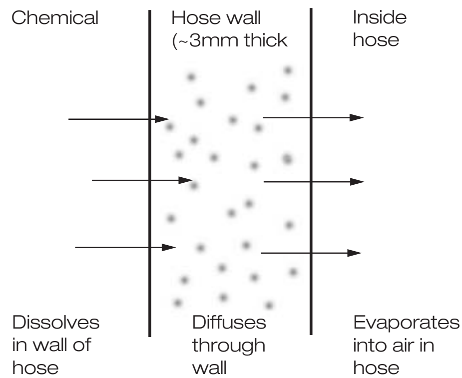
Inside a breathing hose, the air should be pure and the concentration of toxic chemicals should be low. In a demand respirator, all of the air from the hose is inhaled, and for a continuous flow respirator, the proportion of the supplied air inhaled depends on factors like the flow and breathing rates.

Chemical permeation of the hoses used with supplied air respirators has largely been ignored, perhaps through a belief that the pressure inside a hose will counter any tendency for a chemical to enter the hose. However, chemical permeation is driven by chemical gradients, not hydrostatic pressure. Hydrostatic pressure can drive penetration through holes and leaky junctions but, if the hose is usually pressurised, this may be small.

In the workplace, pools of chemical can exist, particularly on the ground and inside process vessels that are being maintained. While some workplaces prudently keep breathing hoses out of contact with chemicals, the dangers associated with chemical contact with hoses are not well recognised and no guidance on the matter could be found in books or standards.

The chemical permeation process involves a chemical dissolving in the wall of the breathing hose, diffusing through the thickness of the wall, and evaporating into the airstream supplying the user of a supplied air respirator. Unlike gloves, where the chemical has to then cross the skin to enter the body, contaminated air is delivered inside the body to the lungs for direct entry into the bloodstream. The skin keeps chemicals out and has a total area of less than 2 m^2 with most people. A very small fraction of that area is exposed when a hand is exposed as a result of permeation of a glove, even if the skin is hydrated due to occlusion by the glove. The alveoli facilitate easy gas exchange and have an area approximately the same as a tennis court. These two factors would be expected to somewhat outweigh even whole-body exposure of vapour to the skin, making inhalation a significant route for exposure (see Figure 1).

FIGURE 1
Permeation into an air hose



Some preliminary work has been carried out for the F-111 Deseal/Reseal Board of Inquiry.[1] It was found that strong polar solvents like methyl ethyl ketone (MEK) rapidly permeated through Esdan PVC Air Breathing Hose.[2] However, no permeation of aviation fuel was detected after one week, though some aviation fuel had diffused into the walls of the hose (evidenced by a weight gain of the hose sample). It would have been reasonable to conclude at this point that the breathing hose would be effectively "impermeable" by most kerosene-like fuels. A low permeation rate was to be expected, as aviation fuel tends to be non-polar and breathing hoses tend to be made of polymers like PVC (polyvinyl chloride), which is polar. The chemistry adage "like dissolves like" means that PVC hoses will tend to be resistant to non-polar chemicals but have poor resistance to polar chemicals, including many solvents.

This article explores the permeation of chemicals that do not permeate hoses easily (such as aviation fuel and diesel), and the implication of this for the selection, care and maintenance of breathing hoses.

Methods and materials

The test method has been discussed in detail elsewhere but a brief outline is given below.[3]

Filling a length of breathing hose with a chemical has been shown with a mathematical model to be the same as immersing the same length in a chemical, both during transient and steady-state conditions.[3] Rather than testing a long length of hose in a bath of chemical using complex chemical analysis to detect the chemical, the mathematical model supports permeation measurements that are made using a short length of breathing hose filled with the chemical and weighed at intervals to measure the evaporation of the permeant.[4] The approach is essentially the same as the permeation tube method for generating standard atmospheres.[5]

Materials

Hose

The Arbin Rinba brand hose was supplied by the Department of Defence for evaluation following the development of the permeation test method for the F-111 Deseal/Reseal Board of Inquiry.[1,6] It is likely that the outer layer of the hose is EPDM, an ethylene propylene diene methylene rubber (or a mixture of similar co-polymers), which has many good properties but poor oil resistance. The inner layer is likely to be NBR, an acrylonitrile-butadiene copolymer (NBR or nitrile rubber is reputed to have good oil resistance). The hose dimesions are set out in Table 1.

TABLE 1
Hose dimensions

Dimension	*mm*
Outer diameter (excluding ribs)	19
Inner diameter	9
Wall thickness	5
Thickness of black outer layer (excluding ribs)	3
Thickness of light brown inner layer	2

Chemicals

Four chemicals (and an unfilled blank) were tested to determine the permeability of the hose. A range of workplace chemicals with different chemical properties were chosen:

1. MEK — methyl ethyl ketone is a volatile solvent that is widely used in the surface coatings industry. It is a good solvent for oils and, being small and polar, it will rapidly permeate many polymers. Analytic grade (Merck) MEK was used for the trials.

2. Turco — the Turco 5351 paint stripper is a viscous yellow liquid, with a distinct smell of methylene chloride. The constituents of Turco 5351 (as reported by Chemwatch®) are listed in Table 2.

For Turco, it was expected that methylene chloride (dichloromethane) would be the main permeant as it is a powerful polar solvent. The phenol, sodium chromate and water would be expected to permeate the breathing hose much more slowly. As the methylene chloride is diluted with other chemicals, the permeation rate could be expected to be lower than for the pure substance.

3. Fuel — aviation turbine fuel (JP-8, Jet A), a universal aircraft fuel, is over 98% kerosene with additives such as antioxidants, metal deactivators, static dissipater, corrosion inhibitors, fuel system icing inhibitors, octane enhancers, ignition controllers, detergents and dispersants.[8] The American Conference of Governmental Industrial Hygienists (ACGIH) considers it to be an "A3 — confirmed animal carcinogen with unknown relevance to humans", but limits its recommendations to vapours, not aerosols. Skin exposure is warned as a route of exposure.[9]

4. Diesel — Shell diesel (Tasmanian winter formulation) was chosen as it has more volatiles and would be expected to have the highest permeability. Diesel is considered by the ACGIH to be an A3 carcinogen with advice to "avoid prolonged and repeated skin contact to diesel fuels which can lead to dermal irritation and may be associated with an increased risk of skin cancer".[10]

To explain the differences in permeation curves for the aviation fuel and diesel, both were analysed using gas chromatography/mass spectrometry (Agilent 55973 GC system, Agilent 5793M mass selective detector, Gerstel CIS4 inlet) by the standard Alltech method 6890.[11] The results are presented in Figure 7. The MEK was not analysed as it was a pure analytical grade solvent, and the analysis for the Turco data by a similar method is not presented as it adds little to the published formulation.

TABLE 2
Turco 5351 formulation

Name	*CAS*	*%*	*TLV (mg m⁻³)*	*Skin*
Methylene chloride	75-09-2	30–60	174	
Phenol	108-95-2	10–30	19	Yes
Sodium chromate	7775-11-3	< 10	–	
Water	7732-18-5	10–30	–	

CAS: unique chemical abstract service number for a chemical.
TLV®: threshold limit value.[7]
Skin: skin exposure should be considered.

Permeation experiment

Sections of 100 mm-long hose were cut with a box cutter and numbered with a permanent marker. The samples were weighed on a laboratory balance (Mercury AMD model 202, 120 g capacity, sensitivity 0.1 mg). The samples were equilibrated for temperature for 24 hours in a laboratory that was maintained at 20 ± 1 °C, relative humidity 60–74% (uncontrolled). A ball bearing slightly larger (7/16", 11.11 mm) than the bore of the hose (10 mm) was inserted into one end of each sample. Each section and a second ball bearing were weighed to give the empty weight of the sample. Samples were then gently squeezed with pliers and filled with the four chemicals, with duplicates for each sample. After almost filling each tube, the pliers were released as the second ball was inserted to ensure that the second ball bearing did not pressurise the hose during insertion. Two tubes were also left unfilled as controls (see Figure 2).

FIGURE 2
Hose filled with chemical and sealed with ball bearings

The samples were placed in a tray lined with domestic aluminium foil (to ensure that, if a sample leaked, the chemical was trapped) and weighed at geometrically increasing time intervals. The weight difference with time was used to calculate the permeation rate per unit length. After the 10-week trials, the samples were examined to determine the length of the indent forming the seal between the ball bearing and the hose. This length was subtracted from the distance between the centres of the balls to give the best estimate of the true exposed length.[3] This enabled the permeation to be expressed as milligrams per metre (mg m^{-1}).

Results

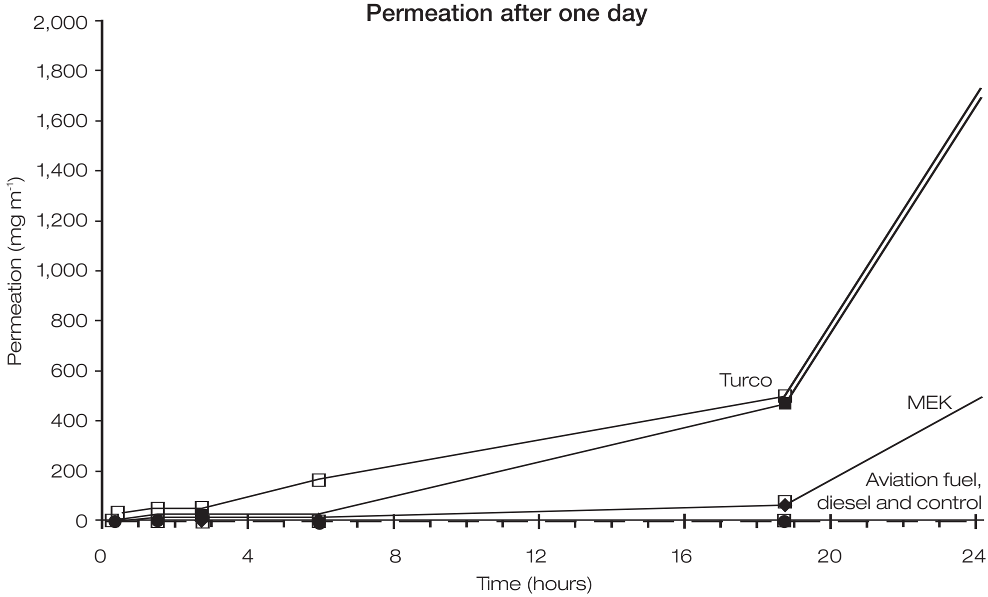
The trials were replicated and the datasets for each chemical are shown with solid and open boxes in Figures 3 to 6 to enable the replicability of measurements in the trial to be demonstrated.

On the first day, breakthrough by Turco was evident within a few hours, followed by low-level permeation of MEK within eight hours (Figure 3). As previously suggested, it is likely that the high permeation rate for Turco was due to the methylene chloride component.

Within the first day, there was little evidence of breakthrough of the aviation fuel or diesel. The zero weight change for the unfilled controls shows the stability of the balance.

After one week (168 hours), the permeation rate for Turco and MEK slowed and there was still little evidence of permeation by the aviation fuel and diesel (Figure 4). Note the closeness of the permeation curves for the duplicate samples.

FIGURE 3
Permeation after one day



After several weeks, permeation by both the aviation fuel and diesel was evident (Figure 5). The trials were extended to 10 weeks to determine whether the shape of the permeation curves changed.

The permeation of Turco and MEK had levelled out, probably due to the depletion of volatiles in the sample. Observations of the samples after the trials indicated that the tubes containing the single chemical (MEK) were empty, but the tubes with complex mixtures or formulations (Turco, aviation fuel and diesel) still contained some liquid chemical, but were probably depleted in the smaller and polar molecules. This phenomenon has also been observed with permeation tubes.[5,12]

After about 400 hours, the MEK permeation exceeded the Turco permeation. This is probably because the phenol, water and sodium chromate in the Turco formulation would dissolve less easily in the hose polymer.

Some of the early details and the similarities between the permeation curves can be more easily understood on the logarithmic scales in Figure 6.

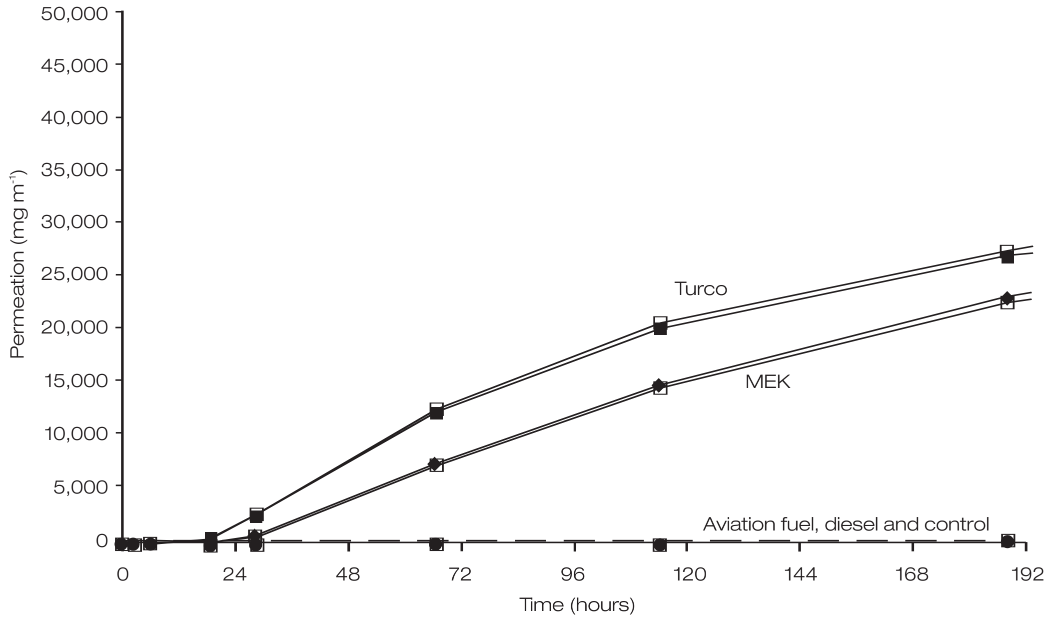
The variability of the data at the start of each permeation curve is exaggerated on a log scale, but the replicability of the data for each chemical becomes evident as the curves climb and converge. The shapes of the permeation curves are seen to be similar, so it is mainly a scaling factor (solubility in the hose, concentration of chemical inside the hose, and diffusivity of the permeating chemicals) that differentiates the curves.

Chemical analysis of aviation fuel and diesel

The chemical analysis of the aviation fuel and diesel revealed a large number of components, as shown in Figure 7. The relative amount is plotted against the chromatographic retention time in minutes. Each of the thousands of peaks could be identified with the mass spectral library.

The diesel has few light components, presumably to prevent pre-ignition and tends to have a heavier composition (nonane C9 to heptadecane C17 on the main hump). In contrast, the aviation fuel has an abundance of lighter fractions and the main hump ends at hexadecane (C16).

FIGURE 4
Permeation after one week (168 hours)



Discussion

The theoretical shape of the permeation curve for both immersed and filled hoses is shown in Figure 8, along with the permeation indices of breakthrough time (BT), lag time (LT) and steady state permeation rate (SSPR) that are also used to measure the performance of gloves.[3,13]

Unlike the permeation curves in Figure 5, the theoretical curve does not level off, as the supply of permeant is infinite in the model.

Estimates of BT, LT and SSPR from the permeation data are given in Table 3. This provides a quantitative measure of the performance of the Arbin Rinba hose with these chemicals at 20 °C and could be used to rank choices of hose and determine service life under conditions of full immersion of sections of hose.

TABLE 3
Arbin permeation at 20 ºC

Chemical	*Breakthrough time (hours)*	*Lag time (hours)*	*Steady state permeation rate (mg $m^{-1}h^{-1}$)*
Turco	3	3	260
MEK	~8	2	180
Aviation fuel	100	100	30
Diesel	200	200	7

Limitations of the test method

The test method assumes complete immersion of a length of hose, something that may occur with a pool of chemical. More likely, partial immersion would occur. The test method and present theoretical model cannot easily simulate partial immersion, but permeation will still occur at a reduced rate. There are also theoretical limitations to the method for layered hose, where one layer has very different properties from another layer. This would not be expected to significantly affect the permeation data in this study.

Implications of extended exposure to chemicals

With extended or repeated use, permeation theory predicts that all chemicals (solid, liquid or vapour) in contact with a breathing hose will permeate and

FIGURE 5
Permeation after 10 weeks

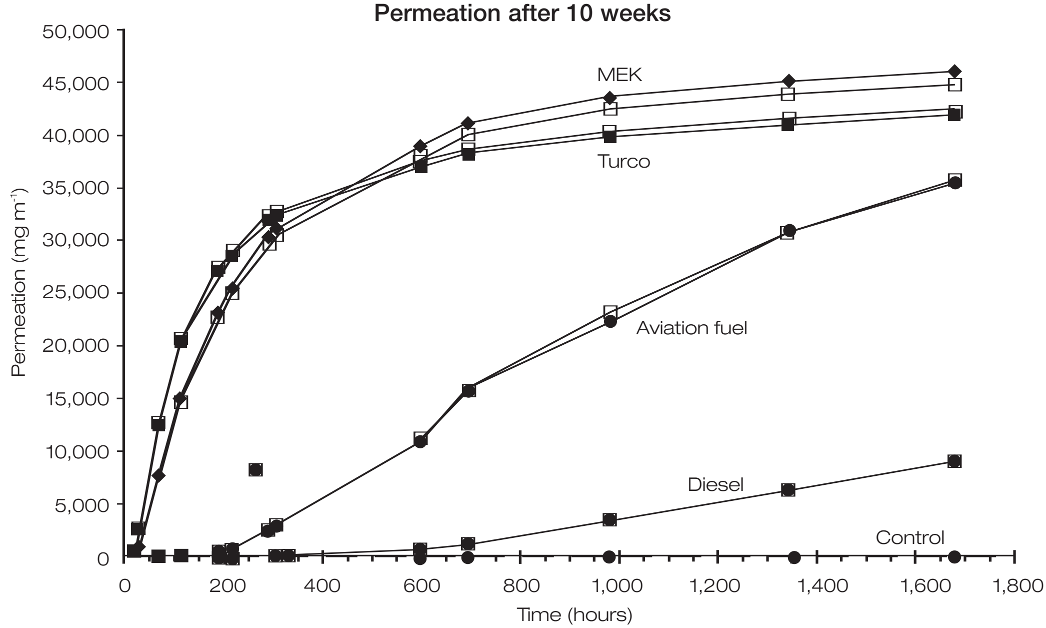


FIGURE 6
Permeation after 10 weeks, log–log scales

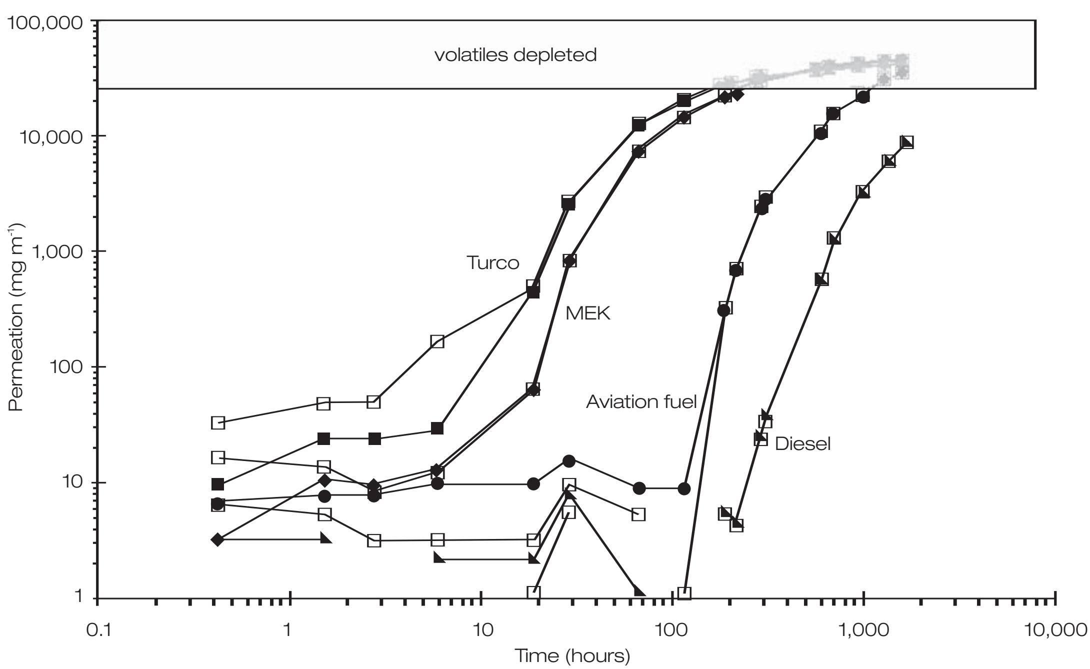
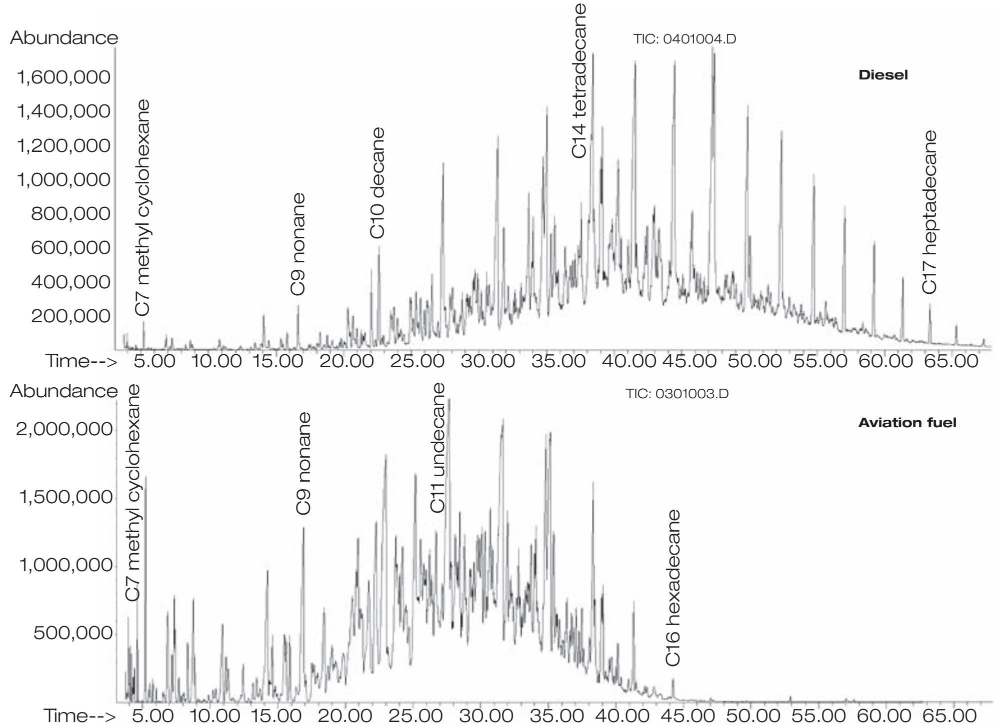


FIGURE 7
Composition of diesel and aviation fuel



contaminate the air inside the hose.[14] This study shows that it is only a matter of time before significant amounts of the chemical have permeated.

If the chemical is volatile, then it is more likely that the chemical will permeate easily during use, but the chemical on the hose surface would evaporate after use. For chemicals like aviation fuel and diesel, the more volatile and probably more permeable components would evaporate first, leaving the less volatile residue to permeate on storage. A thin film of chemical on a hose is the same as immersing the hose in a chemical. This implies that caution would be needed with the use of breathing hoses with any chemical.

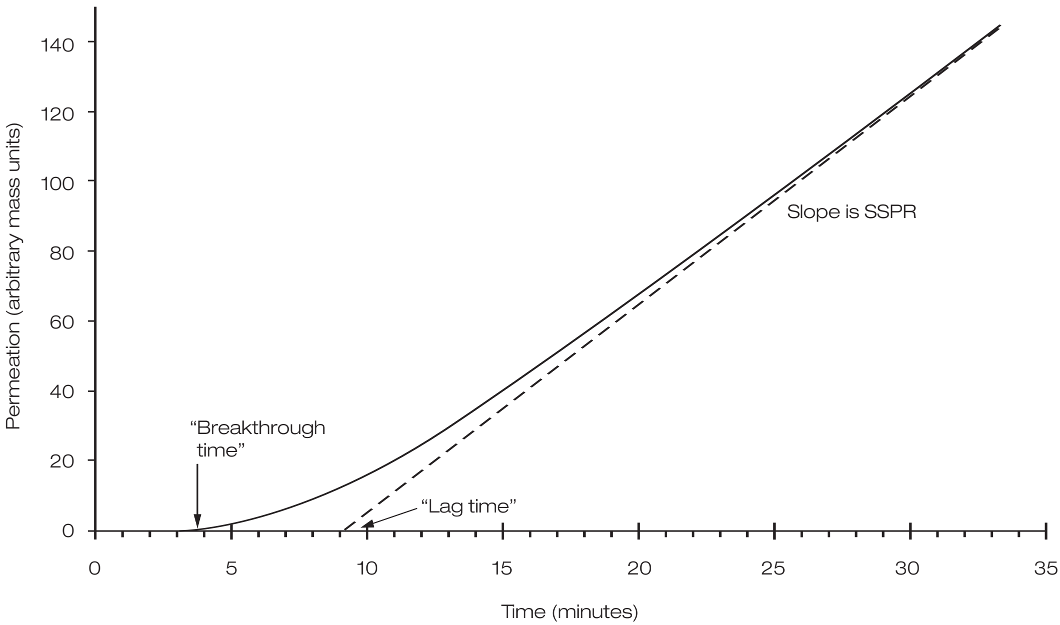
For a breathing hose that is stored in a contaminated state, there is the possibility of significant amounts of vapour pooling inside the hose. Blowing out the hose before use will remove the pooled vapour, but the contamination in the walls of the hose will be a persistent problem for the life of the hose, even if the outside surface is cleaned.

Where used hose is exposed to chemicals, a significant reduction in BT and an increase in SSPR can be expected, even if it appears to be in a good condition.[3]

Resolving the problem

Keeping the hose out of contact with chemicals is the best solution, but if the hose does become contaminated, even with slowly evaporating chemicals, then prompt decontamination of the surface would lessen permeation during storage. Perkins found that warm, soapy water was one of the best approaches to decontaminate chemicals on the surface of gloves and the approach should also be applicable to hoses.[15] Thermal decontamination and Freon have also been used with gloves, but thermal decontamination would require special equipment and Freon was found to be only partially effective.[16,17]

FIGURE 8
Theoretical shape of permeation curve for a hose



The future

While there is a huge range of polymers and blends of polymers for different glove applications, there is a very limited range of polymers for breathing hoses. It appears that most hoses are made from PVC, with plasticisers, fillers and colourants. Often a different formulation of polymer is used for the outside, but the composition of the polymer blends is proprietary. By its nature, PVC is polar, and many strong solvents (like MEK) are also polar, so particular care is needed to avoid even short-term breathing hose exposure to polar solvents. The importance of avoiding long-term contamination of chemicals like aviation fuel and diesel has now also been demonstrated.

There is considerable scope for the development of chemical-resistant polymers that are suitable for breathing hoses, particularly ones where a polar layer is oil and fuel-resistant, with a second layer that is less polar which would limit the permeation of polar solvents.

Conclusion

This study suggests that there is a limited life for even mechanically sound hose when it has extended contact with chemicals.

All chemicals permeate all polymers — be it a glove, chemical suit or breathing hose. Slowly evaporating chemicals like diesel and kerosene-type fuels took weeks to permeate the Arbin Rinba hose, but even short periods of chemical contact could be significant if residual contamination on the hose surface is not removed (as the permeation of the film will continue between uses). Longer periods of continual immersion will result in significant contamination of the hose wall that cannot be removed by surface decontamination.

Preventing chemical contact with a hose is the best preventative policy, but prompt removal of surface contamination with warm, soapy water is likely to be the best method of limiting permeation during storage. There are opportunities for manufacturers to develop chemical-resistant breathing hoses.

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