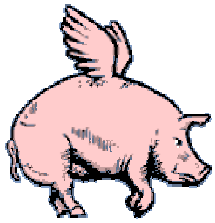
Australian Institute of Occupational Hygienists

Continuing Education Session

November 1997, Albury

Chemical Protective Clothing



- The first work with diffusion through membranes was done in 1829 using bladders, possibly from pigs.
- Pigskin has been used as a surrogate for human skin in permeation testing.
- Complete protection by Chemical Protective Clothing and the sighting of Flying Pigs are equally common.

(apologies to http://www.randi.com)

David Bromwich, Griffith University

Sue Reed, University of Western Sydney

Contents

Figures

Tables

1. Biographical note

The authors met at the London School of Hygiene and Tropical Medicine in 1985, where they had both gone to undertake a Master's degree in Occupational Hygiene. David already had a Masters in Medical Physics and was a health physicist in the uranium mines in the Northern Territory. Sue had a Masters in Engineering Science, specialising in acoustics, and was a hygienist in the defence industry in New South Wales. The year in London must have had the same effect on them as they independently moved to academia and are both pursuing research relating to Chemical Protective Clothing.

1.1. Author details

David Bromwich, BScHons (*Adel*). MAppSc(MedPhys,*QUT*), MSc(OccHyg,*Lond*), COC(BERBOH), CIH, MARPS, MAIOH
Lecturer in Occupational Hygiene
School of Environmental Engineering
Griffith University
Nathan Q 4111
Tel +61 7 3875 7487
Fax +61 7 3875 7459
E-mail D.Bromwich@mailbox.gu.edu.au
Home Page http://wilbur.gu.edu.au/hygiene/db.htm

Research

- Industrial Ventilation
- Chemical Protective Clothing

Sue Reed BSc(*NSW*), MEngSc(*NSW*), MSc(OccHyg,*Lond*), CIH, MAIOH
Senior Lecturer
School of Applied and Environmental Sciences
University of Western Sydney Hawkesbury
Locked Box 1, Richmond NSW 2753
Tel +61 45 701492
Fax +61 45 701267
E-mail S.Reed@uws.edu.au
Home Page http://www.hawkesbury.uws.edu.au/faculties/scitechag/REED.htm

Research

- Occupational and environmental noise
- Permeation of chemicals through protective clothing
- Skin contact and exposure to chemicals

2. Glossary and Terms

ACGIH	**American Conference of Governmental Industrial Hygienists**. A US hygiene organisation formed over 50 years ago. Full voting membership is not available to people from industry to try to keep their TLV's free from commercial influences. They publish "Applied Occupational and Environmental Hygiene" which now contains notices of intended change to TLV's, and "Industrial Ventilation", which is the "bible" of ventilation. Their Web site is http://www.acgih.org, which also contains their publications catalogue.
AIHA	**American Industrial Hygiene Association.** The largest Industrial Hygiene organisation in the world with over 13,000members. They publish various books and the leading hygiene journal, the "American Industrial Hygiene Association Journal". Their web page is http://www.aiha.org .
AIOH	**Australian Institute of Occupational Hygienists**. The professional body for occupational hygienists in Australia.
BT	**Breakthrough Time** (minutes). Time until the first appearance of the chemical on the inside of the CPC. BT is dependent on analytical method and sensitivity.
Carrier Solvent	The solvent used to make the chemical dissolve in a formulation
Closed Loop	Closed Loop testing of CPC involves the Collecting Flow past the "inside" surface of a CPC test sample. While it does allow the buildup of chemical on the inside of the sample, which may reduce the permeation rate of the test chemical, it does offer much greater sensitivity, particularly if the detector (eg PID, IR) does not affect the permeant. It is possible to change form Closed Loop until Breakthrough is detected, then switch to Open Loop. The test you will perform with a stain tube will give similar results to Closed Loop testing.
CPC	**Chemical Protective Clothing**. This includes gloves, splash suits, chemical suits, boots and aprons. Most commonly gloves and chemical suits
Diffusion	The random movement of molecules. There will be an overall movement of molecules down a concentration gradient. The rate at which they move is characterised by their diffusion coefficient **D** (cm^2/min). [Don't confuse it with D for dispersive forces, also used in this paper.]
Lag Time (LT)	The intercept of the straight part of the integral or Closed Loop permeation curve with the time axis. This actually has a mathematical basis and is less dependent on analytical detection limits than Breakthrough Time.
nBT	**Normalised Breakthrough Time** (usually 0.1 µg/cm^2/min for open loop testing). Developed to make testing independent of analytic sensitivity by specifying a detection limit. The toxicity of the chemical is not considered.
Open Loop	**Open Loop** testing of CPC involves the single pass of the Collecting Flow past the "inside" surface of a CPC test sample to a detector.. This approach is less likely to inhibit permeation by allowing a the concentration on the "inside" surface of the test sample to rise. Compare with Closed Loop testing. Most solvent testing is Open Loop testing.
Penetration	The bulk movement of chemical through CPC through holes, tears, zips and other openings.
Permeant	The chemical you are testing
Permeation	The molecular process of a chemical transported through CPC. The chemical dissolves into the CPC, diffuses through it and then evaporates on the other side.
Permeation Rate	The rate of permeation though a membrane. The units are mass per unit area per unit time, usually µg/cm^2/min
SSPR	**Steady State Permeation Rate** (µg/cm^2/min). Test sample permeation rate rarely reach a true steady state, but it is an indicator of the permeation rate under continuous exposure to a chemical.
STEL	**Short Term Exposure Limit**. For chemicals that have acute effects, a STEL of 15 minutes is sometimes given, to protect workers from these effects.
TLV	**Threshold Limit Values**. Occupational exposure limits for physical and chemical agents in the workplace that are thought to protect most workers, for a lifetime exposure to that agent. Some agents have a "skin" notation to indicate that the skin may be a significant route of entry.
TWA	**Time Weighted Average**. The average concentration of a chemical in air, calculated over a working day.

3. Aim

This workshop seeks to give you a sound understanding of the permeation of chemicals through Chemical Protective Clothing (CPC) so that you can understand the application and limitations of CPC.

4. Historical

Since World War II, inhalation exposure standards have dropped by a factor of 100, increasing the relative importance of the skin as a route for chemical exposure [(1)]. This, and a greater awareness of skin exposure are the impetus behind this workshop.

The first observation of permeation of a chemical through a membrane was by Graham in 1829 [(2)], when wet bladders that were exposed to an atmosphere of carbon dioxide became inflated. The carbon dioxide dissolved in the water in the membrane and diffused through the water in the membrane, driven by the carbon dioxide gradient. We are all familiar with gases permeating intact membranes as children, when we see helium balloons gradually sink to the floor as the helium diffuses through the balloon. Another paper by Graham in 1866 [(3)] developed many of the concepts we use today in membrane science, including the further development of the concept of diffusion and the idea that the process is molecular. He measured permeation rates, the permeation rates of mixtures and the quantified of permeation in terms of amount per unit area per unit time. This knowledge was to remain hidden from CPC users for over 100 years.

Protective clothing was not new, and the discovery of rubber lead to coated waterproof fabrics for use in the workplace. Getting noticeably wet with contaminants was probably the real concern for the person in Figure 1[(4)].

Figure 1 Nineteeth century sewerman in a waterproof suit

In 1925 Alice Hamilton [(5)], the founder of occupational medicine in the US, noted that

> *" Gloves make the hands sweat and the skin soft and hot and in excellent condition for the absorption of poisons, and if there is even a small rip or tear in the glove letting the dust or liquid in, it will form what is practically a poultice of poison around the hand"*

Hamilton had noticed the obvious, that holes in gloves let chemicals in and keep it in. She also recognised that the glove itself reduced the effectiveness of the natural protective barrier of the skin my making it soggy. An understanding of the more subtle role of diffusion was to wait another 45 years.

In 1970, a British orthopaedic surgeon, Pegum [(6)] correlated dermatitis on his hand with the pattern of use of bone cement. A number of tests were performed, including taping to the skin the ingredients of the bone cement in the fingers of surgical gloves to patch test the chemicals. The discovery that chemicals can pass through intact gloves was a major advance and is behind much of the content of this workshop.

Pegum's paper lead to a steady flow of published work in the area, principally in the American Industrial Hygiene Association Journal. More recently the American Society for Testing and Materials (see http://www.astm.org) has published six seminar proceedings "Performance of Protective Clothing". This intense interest has lead to the development and standardisation of the testing technology. Standards are still developing and papers are still being published on the performance of individual items of CPC, particular chemicals, the technology of testing and of the theory of permeation and how to predict the performance of CPC under workplace conditions. There is also a deal of work being done in specialised areas, like CPC for firefighters and meat workers.

In the US, 1974 OSHA standards for 14 carcinogens required "workers…shall be required to wear clean, impervious clothing". This lead to a NIOSH study of these chemicals and gloves and ignited the interest in testing of CPC testing, particularly as no threshold was set for exposure to carcinogens [(7)].

With some 12,000,000 chemicals in the workplace and endless permutation to them in formulations and further impurities in industrial grade chemicals, and an increasing array of glove materials and brands, a pragmatic combination of laboratory testing and predictive models is beginning to emerge. Hygienists will be increasingly asked to give professional judgements on CPC based on a firm theoretical foundation and a practical knowledge of how test results can be applied in the workplace. This workshop will attempt to give some of both.

4.1. Penetration and Permeation

Penetration is the direct passage of a chemical though holes, tears and fissure in CPC. This includes pinholes, seams and zips. The greater the pressure, the faster the chemical will penetrate. Holding and inflated glove under water to test for holes tests for absence of penetration.

Permeation is a molecular process, driven by concentration gradients. The driving mechanism is diffusion, a random movement of molecules from a high concentration outside the CPC to a initial zero inside the CPC. The process occurs in three stages. The chemical first has to dissolve in the CPC polymer. The maxim "like dissolves like" can be applied here. Once inside the polymer, it tends to move across the thickness of the CPC and then evaporate on the inside

For a chemical to reach you through the CPC material, it must:

1. **dissolve** into the glove or suit material.
2. **diffuse** through the material.
3. **evaporate** from the inner side of the material

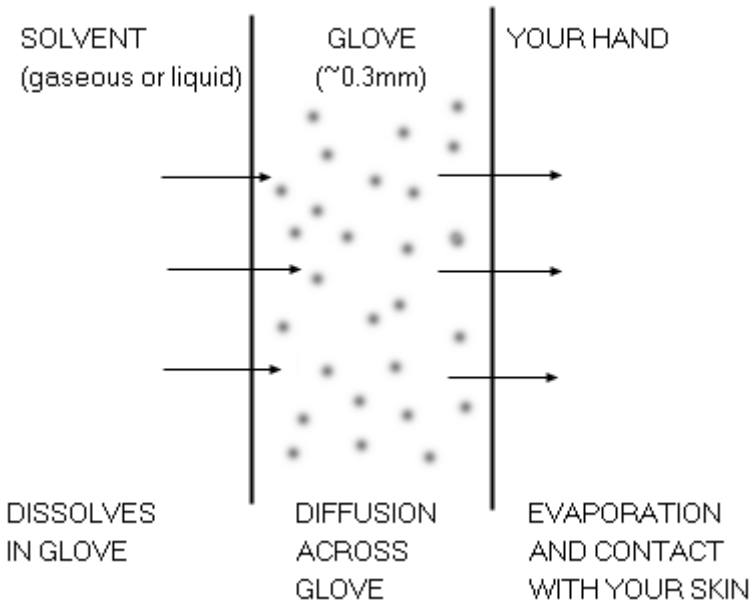


Figure 2The Permeation Process

A similar process then occurs with the skin, a complex bio-polymer, for the chemical to enter the bloodstream.

Any chemicals can permeate any material. Its just a question of how quickly and how much. It doesn't matter if it is hydrogen and steel or acetone and PVC. In hygiene terms, what we are usually concerned about is the total amount permeating while the wearer is using the item of CPC.

4.2. Theories

There are a number of theories used to understand permeation though polymer membranes. The underlying theory is that for diffusion.

4.3. Diffusion

The equations for diffusion were developed in direct analogy to corresponding equations for heat transfer. Diffusion through a material is often described by **Ficks's First law**.

$$F = -D\frac{\partial C}{\partial x} \quad \text{.....Equation 1}$$

This means that the amount of chemical "F" diffusing through a membrane is proportional to the concentration gradient (the rate of change of concentration "C" with distance "x"). The constant is the diffusion coefficient "D". Note that the diffusion coefficient has a negative sign as the chemical is moving from a high concentration to a low concentration. The Diffusion coefficient has the units of area per unit time. eg **cm^2/min**

The way that the concentration changes with time is described by **Fick's Second Law**.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad \text{.....Equation 2·}$$

Both equations are solved my various means using calculus and algebra (often using expansions of series or Laplace Transforms). These are relatively easy to solve on a personal computer. An example is given using a spreadsheet in Appendix B and is shown graphically Figure 3. Note that an estimate of Breakthrough Time is less definite than that of Lag Time.

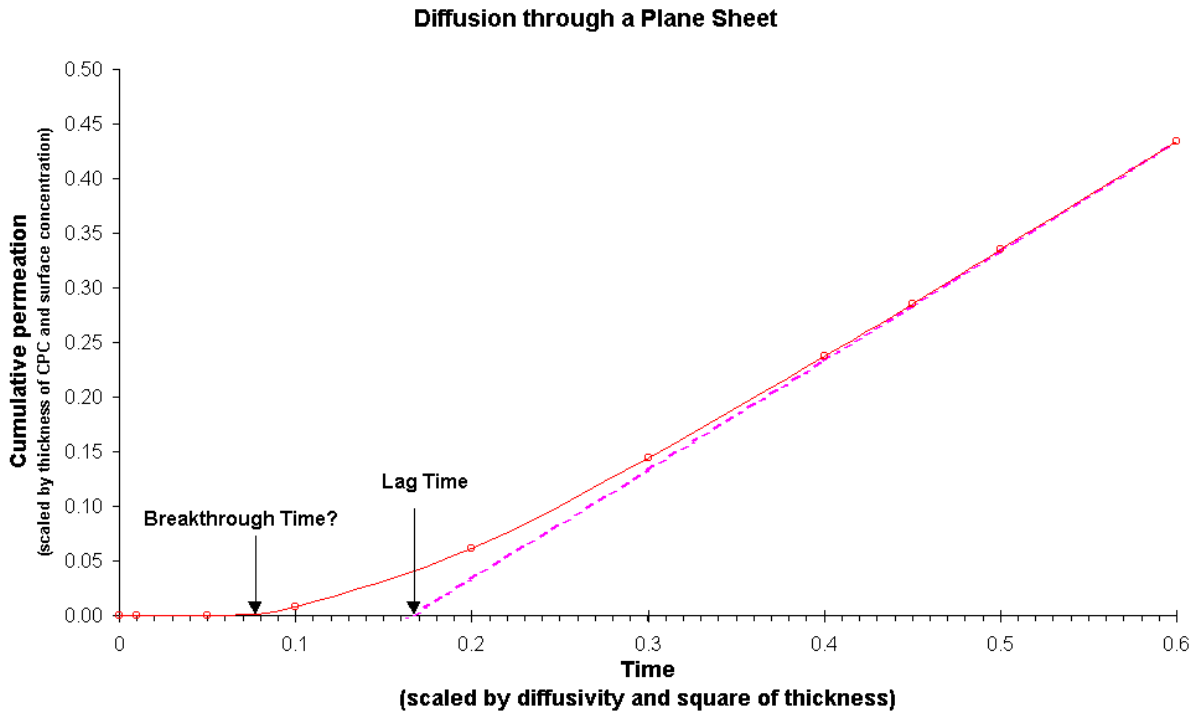


Figure 3 Simple Diffusion Model

All models have to make assumptions, and the most common ones are that the diffusion coefficient is a constant with distance, time, temperature and chemical concentration. Complexities arising from crystalinity and bonds between polymer chains are not addressed by simple diffusion models.

4.4. Free Volume Theory

We have all played with the puzzle games which requires moving of squares held in a frame, until a patten if formed. A square cannot move unless the space is next to it. Free Volume Theory is the same, except in three dimensions and a larger scale. Originally developed to describe liquids as solid spheres, it has found its application in polymer chains and (small) solvent molecules. Each diffusion step is characterised by a molecule vacating a position and the "free volume" being filled by another molecule. A translation occurs if the hole is big enough to accommodate a molecule. The mathematics become quite complex, but several books review the theory in depth. A review of Free Volume theory in Crank and Park's classic, "Diffusion in Polymers"(1968) [8] has recently been supplanted by a chapter [9] in more recent book by Neogi (1996) of the same title.

The application of the theory to CPC is in its ability to describe the effects of crystalinity and cross linkages between polymer chains, two of the confounding factors in predicting the barrier performance of CPC.

4.5. Solubility Parameters

Solubility parameters have been applied to select the most appropriate solvent for inks and resins. In a similar way a CPC polymer could be selected to give least solubility by a given chemical. The power of the use of solubility parameters is its potential to eliminate the worst selections of CPC polymers for a given mixture of chemicals. In practice, the solubility parameters for any particular CPC are not published and the best it can do is to allow ranking of CPC. The approach still has potential. In the form of the **Three Dimensional Solubility Parameter (3DSP)**, a set of three numbers that can characterise any chemical, including those that make up CPC. Any chemical mix or polymer (or blend, as CPC are a proprietary mix of polymers, plasticisers, fillers and dyes) or can be characterised by three molecular forces -

- **Dispersive D**, from momentary imbalances in the electron distribution in a molecule (or temporary dipole)
- **Hydrogen bonding H**, between a proton (hydrogen atom) and unshared electrons on another molecule.
- **Polar P**, between permanent dipoles of "polar" molecules - usually with O, F or N and another molecule

Figure 4 is adapted from Hansen (1992) [10] and shows these three components for a Challenge 5100 chemical suit. The surface of the sphere is determined by breakthrough detected within in 3 hours. Note the contracted scale for the Dispersive forces.

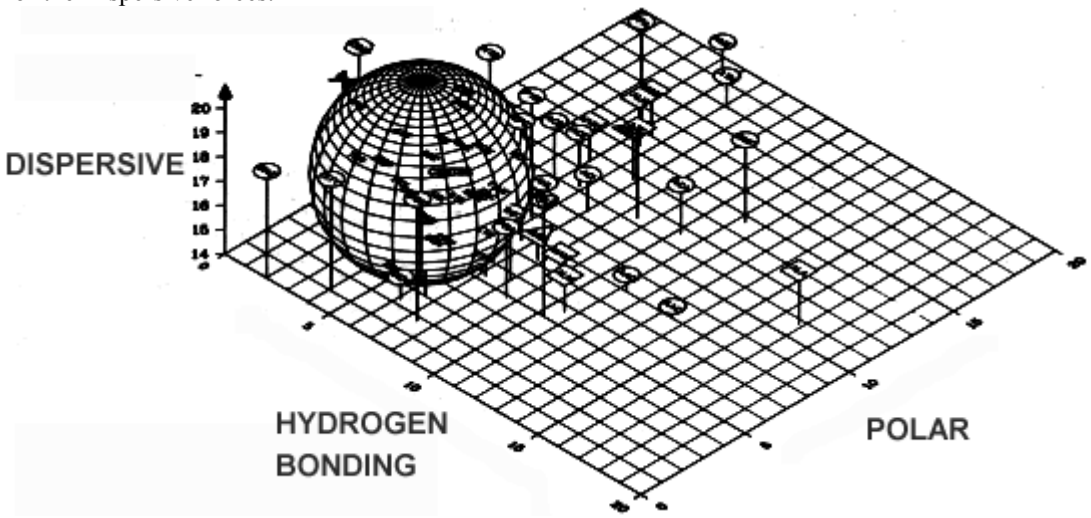


Figure 4 3DSP plot, showing Dispersive, Hydrogen bonding and Polar forces

The total energy binding the solvent to the polymer is given by the sum of these forces.

This total cohesive force is given by S

$$S^2 = D^2 + P^2 + H^2 \text{ in J/cm}^3 \quad \text{..... Equation 3}$$

Hansen [11] found that if the Dispersive forces were plotted on a stretched axis, then the volumeof influence - where "like dissolves like" on a plot of D P and H for both polymer and solvent, became nearly spherical, instead of like a pill.

This "Three Dimensional Solubility Parameter", which weights the cohesive forces is given by

$$3DSP^2 = 4D^2 + P^2 + H^2 \quad \text{..... Equation 4}$$

or

$$3DSP = \sqrt{4D^2 + P^2 + H^2} \quad \text{..... Equation 5}$$

A sphere is constructed, centred on values of 2D, P and H for the polymer, so that the chemicals that affect the polymer are inside the sphere. The **radius** of the sphere it determined by the estimation of no-effect on the CPC. This may be 10% of the maximum weight gain when a samples of the CPC are immersed in a range of test chemicals until they are saturated. It is somewhat subjective. Other methods of determning the radius, like degree of swelling or visible changes are less reliable [12]. Figure 4 uses Breakthrough Time.

Application of 3DSP

Imagine you have (the manufacturers have decided to publish!) the 3DSP parameter for a number of gloves and wish to use this data to select the best glove for a task. The task involves the use of a mixture of chemicals (say methylene chloride, methanol, toluene and a glycol ether) in a paint stripper. The 3DSP for each chemical in this mix is known and a weighted 3DSP for the formulation can be calculated by a weighted average of the 3DSP for each component. If this 3DSP for the mix of chemicals is inside the 3DSP sphere for the glove - where "like dissolves like ", then the glove would be a poor choice. The poor choices can be reasonably rejected and permeation testing can be done on the remaining gloves.

The book Industrial Solvents Handbook by Archer (1996) [13] contains a disk with a number of spreadsheets of solubility parameter for solvents and resins, with the ability to show the two dimensional projection of a plot like Figure 4. It refers to commercial versions of the program aimed at inks and resins and allows mixtures to be calculated. (Unfortunately, the spreadsheet was programmed for Lotus 123, and the full implementation of the graphic output cannot be shown). A print-out of the form of the plots is shown in Figure 5.

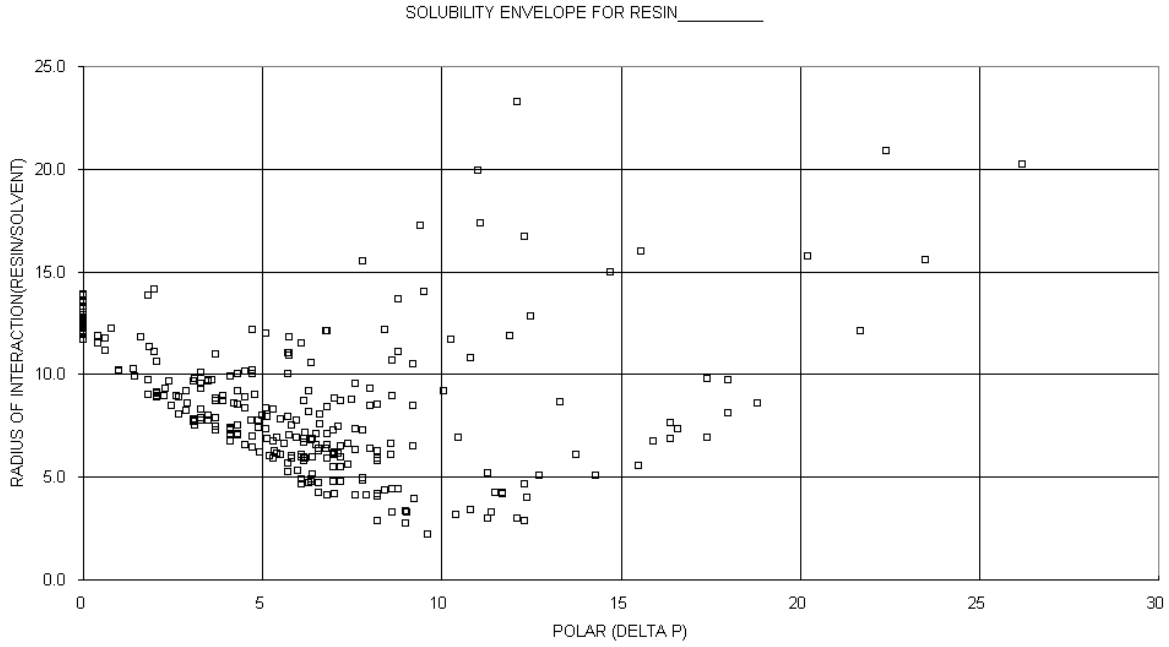


Figure 5 Solubility Parameter plot from Archer 1996

A crude but effective alternative

A crude, but reasonably effective screen for CPC is to cut small pieces (a 20 mm wad punch will do) of CPC, weight them (to 1 mg) and put them in test tubes with 10 ml of the test chemicals overnight, preferably with some agitation.. The next day, re-weight the CPC samples. The technique is to lightly dry the sample between two tissues and then quickly weigh it. The CPC samples with the greatest percentage weight gains can be rejected This at least narrows the selection, but does not allow the prediction of which chemicals will be most likely to affect the CPC.

Limitations of 3DSP

The model is a crude one and does not take into account the size of the molecules or tight binding forces between polymer molecules in some gloves. This may reduce the weight gain during immersion, but have less effect on the amount of chemical permeating the glove. Like all models, a crude one is relatively easy to use,but always has significant limitations.

However, given there are some 12,000,000 chemicals available in endless combinations in formulations, the approach has merit in selecting gloves and chemical suits by rejecting the worst choices. There is also the potential to estimate Breakthrough Times and Steady State Permeation Rates[14].

Manufacturers do not publish 3DSP for their CPC, and as their formulations are secret and it is not easy to derive them [15]. The approach is still not a substitute for (expensive) permeation testing.

4.6. Polymers

The range of polymers used in CPC is huge. It is further complicated by differences between manufacturers, different additives (including fillers, plasticisers and dyes; PVC gloves may contain 50% plasticiser), polymer blends and laminates and the quality of manufacture.

Some of the more common polymers are given in Table 1. The table has been adapted from Appendix A in Perkins 1990 [16] in the AIHA book "Chemical Protective Clothing".

Table 1 Polymers used in CPC

Name	Comment
Butyl	97% isobutylene, 3% isoprene copolymer
Chlorobutyl	butyl rubber with chlorine atoms substituted randomly for hydrogens
Chlorinated polyethylene	Polyethylene with 36% to 45% by weight chlorine atoms substituted randomly for hydrogen atoms
EVA/PE	Blend of 14% ethylene/ vinyl acetate copolymer; 86% polyethylene
EVOH	ethylene/vinyl alcohol copolymer
Fluorine/Chloroprene	Viton, chloroprene laminate
FEP	fluorinated ethylene propylene resin. A hexafluoropropylene/ tetrafluoroethylene copolymer
FEP/TFE	FEP/ tetrafluroethylene blend
Natural rubber	Isoprene
NBR	Nitrile, random or alternating acrylonitrile/butadiene copolymer
Neoprene	Chloroprene
Polyethylene	Ethylene
PVA	vinyl alcohol
PVC	vinyl chloride
PVC/Nitrile	Blend
Saran	85% vinylidene chloride, 15% vinyl chloride copolymer
Saranex	laminate of polyethylene and saran
SBR	25% styrene, 75% butadiene random copolymer
Silver Shield or 4H	laminates of polyethylene and EVOH
Viton	Hexafluoropropylene, vinylidene fluoride random copolymer
Vitrile	Viton, nitrile blend
Troionic	Natural rubber, neoprene carboxylated nitrile blend
Urethane	Condensation product of a polyisocyanate and a polyol

A number of coated fabrics are used, particularly in chemical suits. Table 2 is adapted from the same source as Table 1.

Table 2 Coated Fabrics

Material	Comment
Cellulose or cotton	Polysaccharide or polyalcohol
Disposaguard	Cellulose reinforced with nylon (scrim reinforced)
Fibreglass	Fibres of glass, usually coated with silicon or silanes
Gore-Tex	TFE, polyester or Nomex laminate
Nomex	Aramid fibre, polyamide
Nylon	Polyamide, condensation product of diamine and dicarboxylic acid, eg Nylon 66
Polyester	Condensation product of ethylene glycol and terepthalic acid, eg Dacron, Sonata
Rayon	Regenerated cellulose fibre
Safeguard	Three layers of polypropylene
Tyvek	Non-woven polyethylene fibres

5. Factors Affecting Permeation

5.1. Predicting permeation

There have been many attempts to model the performance of CPC. Even the simple modelling of pure polymers with pure solvents under laboratory conditions is difficult. A good introduction to the mathematics is in Crank Chapter 4 "The Mathematics of Diffusion" [(17)]. The simplest model is to take an infinite block of polymer, with a thin plane of chemical in it. The chemical spreads out away from the plane with time, in both directions. This symmetry allows a slightly more realistic model, with a semi-infinite (extending in one direction) block of polymer with an infinitely thin layer of chemical on its surface. In reality, the surface layer is finitely thick and the polymer itself has a finite thickness. Bringing even the simplest model into the real world rapidly escalates the complexity.

These simple models assume little interaction between the chemical and the polymer, and a constant rate of diffusion. Interactions do occur, and they are often characterised by degradation or swelling of the polymer. The diffusion rate varies with depth and with time, particularly if the chemical leaches out some of the additives or changes the structure of the polymer.

Any model is further complicated by a string of factors such as temperature gradients, mixtures of chemicals and intermittent and repeated exposures. Individual effects have been modelled with varying success, but there is no super- model that the hygienist can have on a computer to precisely predict the behaviour of an item of CPC.

5.2. Challenge chemical

The simplest maxim "like dissolves like" can be used to guide the selection of CPC to at least eliminate poor choices. PVA gloves dissolve in water, making them a poor choice for polar solvents like water.

5.3. Polymer

The polymer with its additives is the major determinant the barrier properties of the CPC. However, the name of the polymer is not sufficient to make a choice. There are variations of the polymer covered by the same generic brand, differences between manufacturers and between batches [(18)]. The method of manufacture and construction is also important. Fillers, plasticisers, dyes and support materials can also affect polymer performance, sometimes detrimentally. The most reliable performance data is on the brand and type of CPC with the chemical(s) of interest, and hopefully at the same temperature of use.

5.4. Thickness

The limiting factor affecting the ***range*** of CPC (particularly gloves) is the ability to do the task using the CPC. An absence of tactility can make a task impossible or quite slow [(19,20)]. Thicker gloves do give greater protection, but with reduced feel. To a good approximation, t*he Breakthrough Time is inversely proportional to the square of the thickness and the Permeation Rate is inversely proportional to the thickness.*

When CPC is made thicker, it is less likely to bend and will tend to break or delaminate, but thicker CPC will tend to reduce the effects of temperature, particularly heat from the hand or a hot chemical.

5.5. Pattern of Exposure

Most testing of CPC is done to the US standard ASTM F739 1996 [21] developed in 1981. This CPC test is for liquid or solid chemicals under continuous contact. This is directly applicable if you job is standing still with your gloved hands in a bucket of chemical, but probably conservative otherwise. In reality, most tasks involve intermittent exposure, and the diffusion rates may be concentration dependent to the extent of the difference between a snail and a jet aircraft. Confounding factors that makes any reliance continuous exposure data conservative are workplace factors such as actual performance of the chemical mix with the actual CPC polymer, the effects of mechanical stresses and temperature.

5.6. Duration

The longer an item of CPC is worn, the more chemical will permeate through it. The toxicology of the chemical will decide whether the exposure is likely to be toxic.

Only about 1% of chemicals listed in the NIOSH RTECS database have acute dermal toxicity figures. Fewer have any chronic toxicity data. There is relatively little data on which to judge unacceptable dermal exposure.

The US EPA has been reported as using cumulative exposure, estimated by assuming no exposure before Breakthrough is detected, then Steady State permeation thereon. This is a conservative approach for low to moderate toxicity materials with analytic detection limits than ensure that toxic amounts of chemical are detected. There is some move towards recording the cumulative permeation at intervals during testing, but the pool of existing test data does not include cumulative permeation data.

5.7. Temperature

The effects of temperature of CPC are difficult to estimate [22] [12,23,24]. Hot tasks may reduce the protective life of a glove from hours to minutes or seconds. Published test data is usually for tests performed between 21 and 25°C, though there is limited data for 37°C, 45 °C and higher for some CPC.

When a glove is put on, the temperature of the inside surface in contact with the hand rises within a few seconds to the skin temperature (around 33°C). The skin is insulated from normal evaporative, radiative and convective cooling and the temperature inside the glove climbs to around 36-37°C in the next 2 to 3 minutes. If the glove is removed, it takes something like 30 minutes to return to room temperature (25°C).

The warmth of a hand will quickly seep through a thin glove like a Silver Shield or 4H laminated glove, particularly if a more tear/cut resistant glove is worn over the top. In this case, the chemical resistance should be related to testing at 37°C. If the glove is thick and the workplace is cool, then the temperature of the workplace will largely determine rate and amount of chemical permeating the glove.

5.8. Mixtures

The testing of chemical mixtures until recently has been considered difficult due to limited availability of suitable analytical techniques. The first work published was by Mickelsen, Roder and Berardinelli [25] in 1986. Over the last five years a number of analytical technics have been developed due using either GC columns, such as Ke, Levine, Mouradian, and Berkeley [26] (1992), that can analyse samples with multiple components very quickly or in the last couple of years using new FTIR techniques. Unfortunately not many results have been published yet. These new analytical techniques will allow for better selection of protective gloves that will give longer protective life.

Examples of results of some experimental data under by Reed, Cook and Vaccaro[27] follow.

Experimental Permeation Data for Chemicals Mixtures

Case 1: Bayleton

Agricultural fungicide

Table 3 Breakthrough Times and Permeation Rates of Bayleton

Glove Material	Chemical	Breakthrough Time (min)	Permeation Rate ($\mu g\ min^{-1}\ cm^{-2}$)	Length of Test (min)
Butyl Rubber	Triadimefon	25	59.76	172
	Xylene	25	57.88	
Neoprene	Triadimefon	17	79.51	122
	Xylene	15	74.54	
Nitrile	Triadimefon	57	45.31	142
	Xylene	62	49.43	
PVC	Triadimefon	47	33.89	157
	Xylene	50	30.56	
Viton	Triadimefon	350	4.98	480
	Xylene	392	1.7	

The results of the testing shows that Viton gloves have the longest breakthrough time and lowest permeation rates. Generally the permeation rates for both components are similar. The gloves with the lowest breakthrough time and highest permeation rate are neoprene gloves.

Case 2: Folidol

Insecticide for the control of boll weevils and many biting sucking insects in crops

Table 4 Breakthrough Times and Permeation Rates of Folidol

Glove Material	Chemical	Breakthrough Time (min)	Permeation Rate ($\mu g\ min^{-1}\ cm^{-2}$)	Length of Test (min)
Butyl Rubber	Parathion-methyl	160	79.27	275
	Xylene	200	5.58	
Neoprene	Parathion-methyl	30	519.39	192
	Xylene	37	11.97	
Nitrile	Parathion-methyl	107	100.19	195
	Xylene	95	5.08	
PVC	Parathion-methyl	90	171.52	240
	Xylene	122	4.37	
Viton	Parathion-methyl	>480	<0.02	480
	Xylene	>480	<0.02	

The gloves offering the best protection for this mixture are the Viton gloves since neither of the ingredients broke through in under 8 hours (480 minutes). In regards to the other glove materials, which one of the ingredients permeated first varied but in all cases the permeation rate of the Parathion-methyl was significantly greater than xylene.

Case 3:Epoxy Resin Wash

Used to wash equipment used in spray painting

Table 5 Breakthrough Times and Permeation Rates of Epoxy Resin Wash

Glove Material	Chemical	Breakthrough Time (min)	Permeation Rate ($\mu g\ min^{-1}\ cm^{-2}$)	Length of Test (min)
Butyl Rubber	Toluene	20	53.76	122
	Methyl Ethyl Ketone	20	121.48	
	Ethanol	25	23.11	
Neoprene	Toluene	12	79.98	87
	Methyl Ethyl Ketone	10	313.43	
	Ethanol	12	100.37	
Nitrile	Toluene	15	62.33	102
	Methyl Ethyl Ketone	10	250.55	
	Ethanol	15	86.63	
PVC	Toluene	17	73.07	102
	Methyl Ethyl Ketone	12	208.82	
	Ethanol	17	52.83	
Viton	Toluene	115	10.65	460
	Methyl Ethyl Ketone	100	50.86	
	Ethanol	115	7.09	

It is interesting to note from the literature, Johnson & Anderson [28](1990), that the breakthrough times for each of the components of the epoxy resin wash when tested against each glove material varies greatly. The results indicate that once one component permeates through the glove sample the other components also permeate. The permeation rate for methyl ethyl ketone is much higher than toluene or ethanol in all mixture/glove material combinations even though it only comprises of 15% of the mixture. Also the ratio of ethanol/toluene breaking though varied with each glove material with respect to permeation rate. The ratio varied in respect to which component was the predominate permeate.

Viton gloves appear to provide the optimum protection when handling Epoxy Resin Wash but they should not be used for long periods without being replaced, as they don't have an unlimited life. The other glove materials would seem to offer reduced protection as they all have relatively short breakthrough times and high permeation rates.

Case 4: General Purpose Primer

Primer used in the construction industry for the priming of impervious floors before the application of floor levelling compounds.

Table 6 Breakthrough Times and Permeation Rates of General Purpose Primer

Glove Material	Chemical	Breakthrough Time (min)	Permeation Rate ($\mu g\ min^{-1}\ cm^{-2}$)	Length of Test (min)
Butyl Rubber	Toluene	7	394.51	67
	Methyl Ethyl Ketone	7	2515.67	
	Iso-Hexane	7	2730.95	
Neoprene	Toluene	10	235.74	70
	Methyl Ethyl Ketone	7	6762.46	
	Iso-Hexane	7	2440.27	
Nitrile	Toluene	17	448.73	92
	Methyl Ethyl Ketone	12	3683.54	
	Iso-Hexane	15	818.12	
PVC	Toluene	17	324.40	82
	Methyl Ethyl Ketone	17	1560.29	
	Iso-Hexane	17	1747.88	
Viton	Toluene	65	71.27	480
	Methyl Ethyl Ketone	87	25.83	
	Iso-Hexane	75	28.52	

With this mixture Viton has the longest breakthrough time and lowest permeation rates of the glove materials tested. The interesting point with this chemical mixture/glove material combination is that the relationship of each of the components of the General Purpose Primer differed between each combination. For Viton gloves, toluene has the highest permeation rate, whereas for nitrile and neoprene methyl ethyl ketone the highest permeation rate and for butyl rubber and PVC iso-hexane the highest permeation rate.

These results reflect the care that must be taken when selecting gloves on only one ingredient of a chemical mixture.

6. Standards

6.1. Australian

Currently Australia does not have a standard for the testing of gloves against the permeation or penetration of chemicals. A draft standard has been considered and was not considered suitable so that a new draft standard is currently being prepared and should be available for comment in 1998.

6.2. US(ASTM)

The US standard for the permeation of chemicals is F 739-96 and is published by ASTM [(29)]. This method specifies the design of the permeation cell (a mechanism exists for validating alternate cells), which will measure the resistance of a protective glove material to permeation by a test chemical. This is measured by assessing the Breakthrough Time, Normalised Breakthrough Detection Time, and subsequent Permeation Rate through replicate specimens of the glove material.

The CPC testing standards set by the American Society for Testing and Materials, particularly ASTM F739 in its 1981,1985 and 1996 versions for continuous contact has been very influential in setting the standards for permeation testing. As most testing on CPC has been done using the F739 standard, any future data will have to show some equivalence to be accepted. Another paper at this conference [(30)] reviews the design of the cells, particularly the ASTM cell.

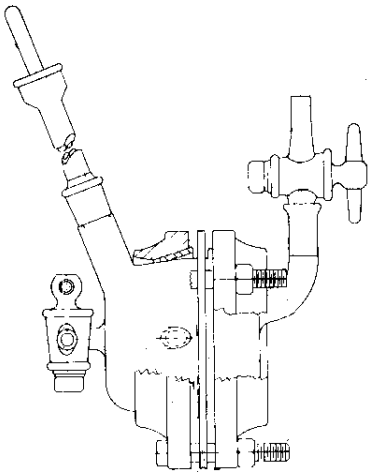


Figure 6 ASTM F739 1981 Cell for continuous contact

More recently a standard for intermittent chemical contact ASTM F1383 1996 [31] has been developed, with a more complex version of the F739 cell, to allow the cell to be more readily filled and drained.

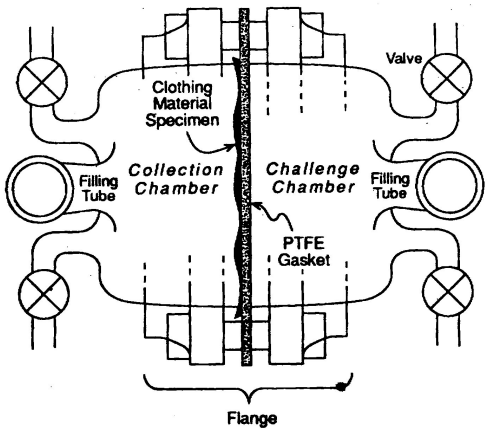


Figure 7 ASTM F1383 Cell for Intermittent Contact

In order to make various testing methodologies equivalent, particularly for the measurement of Breakthrough Times, a set Permeation Rate has been set to give a Normalised Breakthrough Time at 0.1µg/cm^2/min for Open Loop testing and 0.25 µg/cm^2/min for Closed Loop testing. It still does not overcome the problem of Breakthrough Times having little physical or toxicological significance.

The permeation curve from the ASTM intermittent cell is shown in Figure 8, derived from Figure 5 in ASTM F1383-96. The neoprene sample is wet with acetone every 15 minutes for 1 minute. It takes almost 15 minutes for the permeation peak to travel through the specimen, by which time the sample is dry and about to be wet again. Different wet-dry regimes produce very different curves, but the maximum permeation rate is a fraction of the steady state rate with continuous chemical contact.

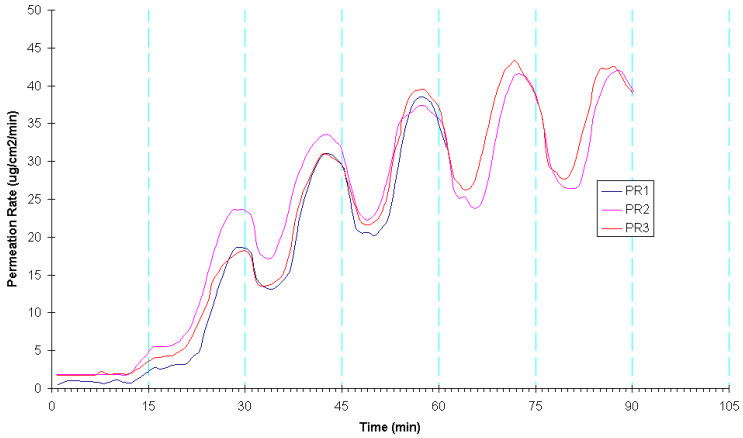


Figure 8 Intermittent Exposure permeation curve

There is still a great need for further standards development and an international convergence of standards, but it could be expected that these will follow developments in the US standards.

6.3. European/ British

The European/British standard has been developed which looks at both penetration and permeation of chemicals through protective cloth material. The section on assessment of permeation is limited because it only requires that breakthrough time to be measured and recorded. Permeation rate is not required to be measured, this means that insufficient information is generated in regards which protective glove material will be most effective. The method uses the same cell as the ASTM F739 method.

6.4. International

Currently the international standard calls for the use of a cell that was developed by the BOHS in the mid 1980's but this is currently being replaced by a redrafted standards which should be available for comment in 1998 and may use the ASTM cell. The sketch of the BOHS/ISO cell in Figure 9 is adapted form Leinster [32].

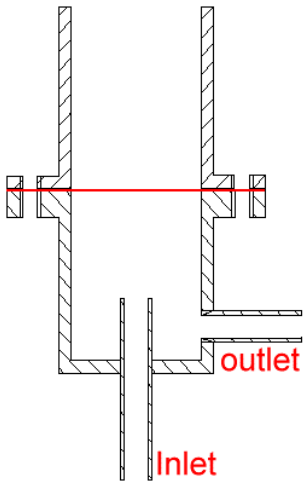


Figure 9 The original BOHS/ISO cell

It is expected that the standards on testing of permeation for glove materials will be similar to the draft standard, ISO 6529 (New Working Draft), for testing of CPC. This draft standard includes provisions for both continuous and intermittent testing of CPC.

7. Indices

7.1. Detection Limits and Toxicology

The testing and interpretation of testing of CPC is still not a fully developed science. Cautions should be taken in interpreting permeation data, particularly when a challenge chemical is not detected within a certain time. There is some confusion as to what constitutes detection of a chemical. To say that a chemical has been detected, is to say that the chemical has been detected above the background level detected by the instrument. This limit of detection does require that the statistical distribution of the background signal above the background level be known [(33)]. In the absence of any information about this distribution, three standard deviations of the background signal above the background mean is the detection limit. If the background signal is normally distributed about the background mean, then two standard deviations rather than three may be used, with a corresponding decrease in the limit of detection. These statistical matters have not been properly addressed by either CPC researchers or standards.

With testing of CPC, some researchers run the system without the addition of the challenge chemical for considerable periods to ensure a stable background level. Whatever the analytic detection limit, it should not be forgotten that the real question of toxic exposure has to be answered and if the detection system is inadequate to prevent toxic amounts of a chemical coming in contact with the skin, then we delude ourselves that adequate protection is present. Conversely, a low detection limit of a low toxicity chemical may produce unnecessary alarm that inadequate protection is given by an item of CPC. The latter would be a rare event.

7.2. Breakthrough Time

Breakthrough Time has been defined many ways. The best definition to use is the time that has elapsed since the test chemicals has come in contact with the CPC under test, until the chemical is detected on the inside of the CPC. It will be dependent on the sensitivity of the analytical technique. The current thought is that breakthrough time should be defined as the elapsed time since the permeation test has been commenced until the analytical technique being used can detect a permeation rate of the given amount. Currently two amounts are being considered, ie 1 µg/cm^2/min and 0.1 µg/cm^2/min. Sometimes a lagged breakthrough time or Lag Time used. This term is used when the cumulative permeation rate has been calculated and is the point where the slope of the slope intersects the time axes. See Lag Time below.

7.3. Steady State Permeation Rate -

Steady State Permeation Rate is the permeation rate at which permeation becomes steady state as is best reflected by the graph produced from an open permeation test setup. A curve approaching steady state permeation is illustrated in Figure 10.

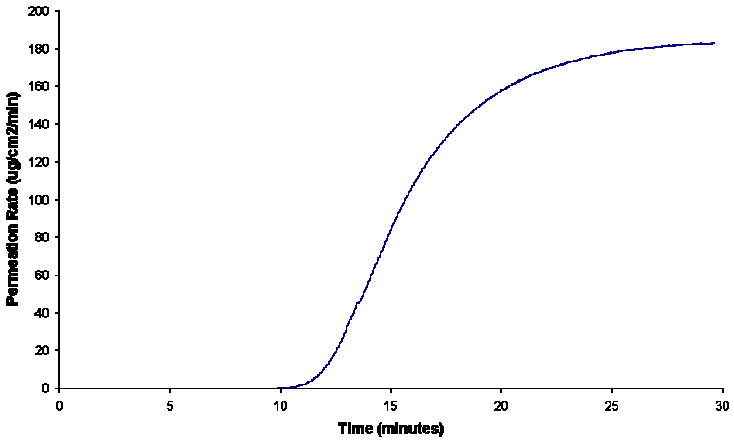


Figure 10 Open Loop Permeation Curve (acetone with neoprene)

7.4. Cumulative Permeation Indices

Cumulative Permeation Indices is a term used to define the amount of the test chemical that has permeated through in a given time. The times are usually 30 minutes and 60 minutes after breakthrough has occurred. A

cumulative permeation curve derived from integrating the curve in Figure 10 with the Trapezoidal Rule, is shown in Figure 11. Note that when the curve in Figure 10 flattens out to steady state permeation, the curve in Figure 11 becomes straight.

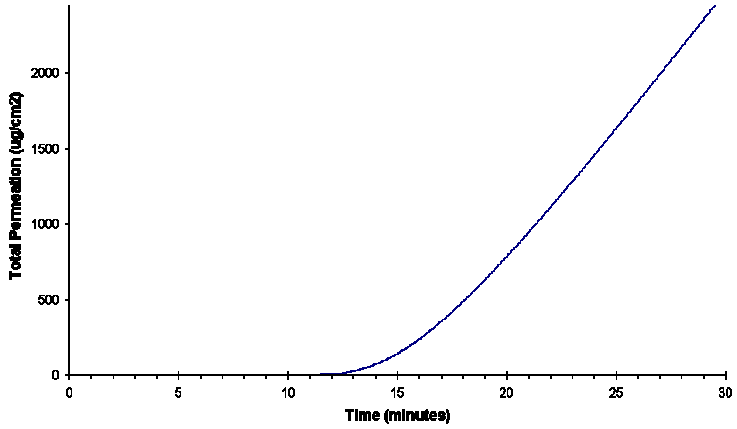


Figure 11 Cumulative Permeation (acetone with neoprene)

7.5. Lag Time

Lag Time has been various defined and is sometimes used interchangeably with Breakthrough Time. It is probably more useful to link it to the concept of time lag which has a mathematical meaning (see Appendix B: Permeation Models - Lag Time). This approach gives the Lag Time as the time intercept of the straight part of the cumulative permeation curve.

In Figure 12, the cumulative permeation curve for acetone and neoprene has had a best fit line fitted between 20 and 30 minutes and the time intercept extrapolated. The data used to calculate the Lag Time in this case is only that after 20 minutes, allowing for a very insensitive detector and the averaging effect of many data points. The Lag Time can be seen to be around 15.5 minutes.

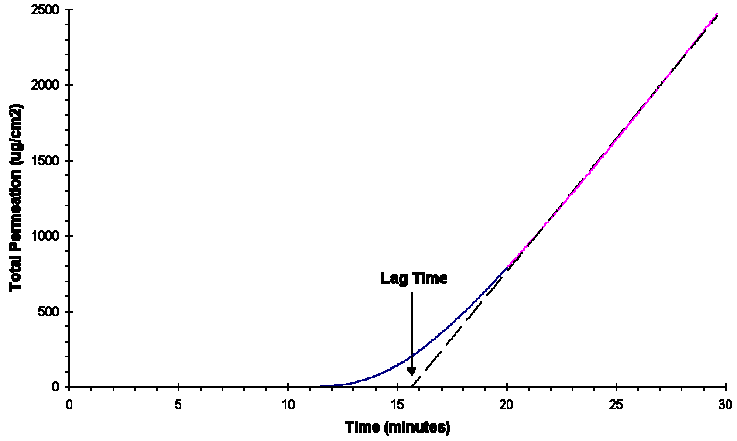


Figure 12 Lag Time (acetone with neoprene)

The difference in estimating total exposure at a given time between taking the straight line intercepting the time axis at the Lag Time, and the more complex integral curve, is quite small in practice. It can be ignored for most chemicals.

8. Hands on Testing

8.1. Selection of gloves

You are provided with a number of scenarios involving exposure to chemicals to the hands and forearms. You have a variety of gloves, glove catalogues and a computer expert system called **GlovES** in order to aid your selection of glove. The GlovES program is discussed later with other programs.

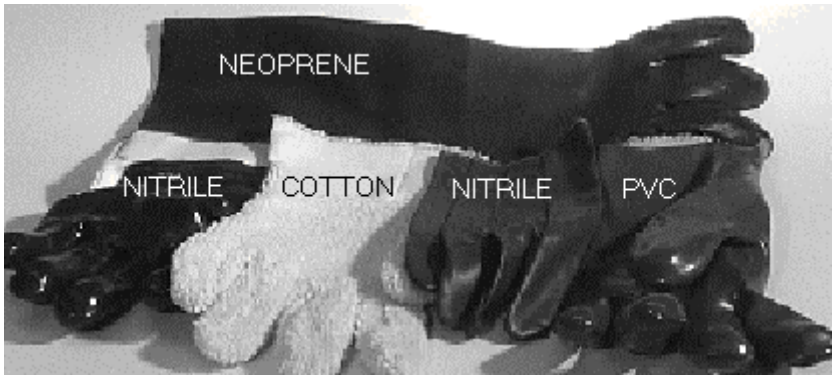


Figure 13 Gloves

8.2. Glove Selection

What type of glove would you use?
Fill in your glove selection for the scenarios in the boxes below:

1. Handling xylene all day. Splashes to forearms likely

Glove Selection .....

Reason.....

.....

2. Industrial food preparation. Contact with natural food acids and animal fats. Lots of overtime -> 10 hours/day.

Glove Selection .....

Reason.....

.....

3. Cleaning glassware and other tasks in 50% chromic acid for 2 hours day

Glove Selection .....

Reason.....

.....

4. Using chloroform 3 hours a day to "digest" liver. Little tactility is needed.

Glove Selection .....

Reason.....

.....

5. Adding phenol in a process for 1 hour a day. Immersion to mid forearm; splashes likely. Moderate tactility desirable

Glove Selection .....

Reason.....

.....

6. Fast food operation. Handling sandwiches. Health Department requires use of gloves.

Glove Selection .....

Reason.....

.....

7. Handling bottles of fuming nitric acid. Chance of splashes and spills. All day.

Glove Selection.....

Reason.....

.....

8. Moving greasy and oily heavy engineering parts. High tear and abrasion resistance required.

Glove Selection.....

Reason.....

.....

9. Clean-up kit for extremely toxic chemicals. Unknown properties and possibility of sharp edges. Expect 2 hours of contact.

Glove Selection.....

Reason.....

.....

8.3. Chemical splash suit

Chemical splash suits provide a much greater degree of chemical protection and other protection.

Figure 14 Splash Suit

♦ Why are chemical suits not used regularly?

.....

.....

.....

.....

.....

.....

8.4. Permeation rates and breakthrough times

This experiment shows two of the characteristics of chemical protective clothing.

You are going to produce a graph like the one below, and estimate the Breakthrough Time and Lag Time and calculate the Steady State Permeation Rate.

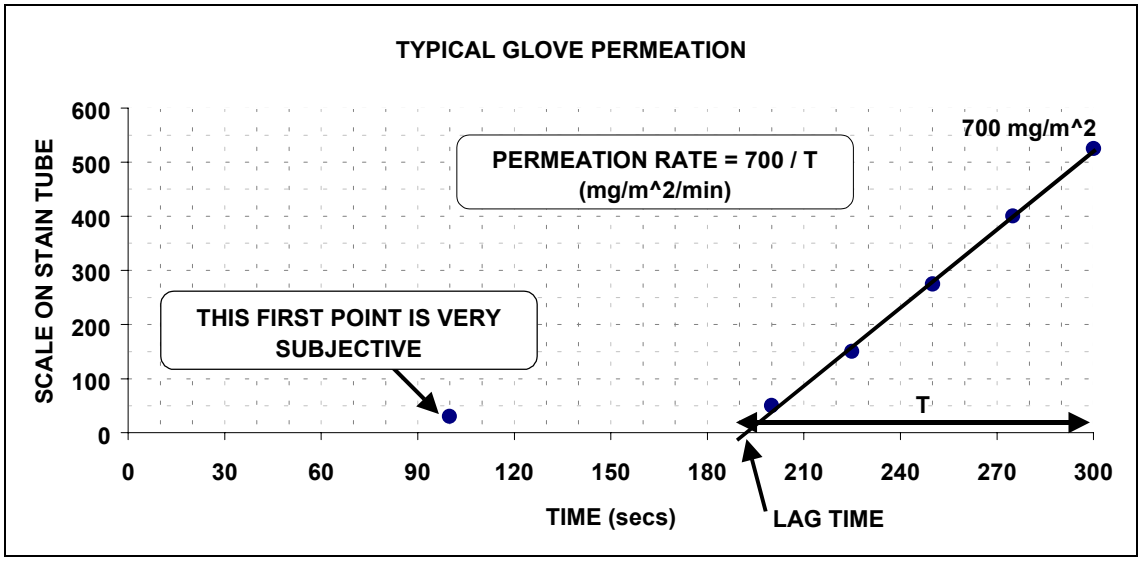


Figure 15 Using stain tubes to estimate glove performance

The **PERMEATION RATE** is just a measure of the amount of chemical passing through the protective material. So that we can compare tests, it is given in milligrams per square centimetre per second or (mg cm^{-2} s^{-1}). When the permeation rate levels off, it is called the **STEADY STATE PERMEATION RATE** (SSPR). In this workshop, the detector integrates the amount of permeant, and constant permeation is indicated by the permeation curve becoming a sloped straight line.

The **BREAKTHROUGH TIME** is a more difficult concept. On contact with a chemical, some will immediately dissolve in it. In an instant some molecules will diffuse straight through the glove and evaporate on the other side. This rapid diffusion is seen with strong smells - it only takes seconds to smell something across a room. Thus the actual Breakthrough Time reported is largely dependent on the **sensitivity of the detector**. However, the time does have some meaning in that it shows how long it takes for significant amounts to be detectable.

You have a special permeation test cell (which has been validated against the standard ASTM test cell), a pump to move air through the cell and a stain tube as a detector.

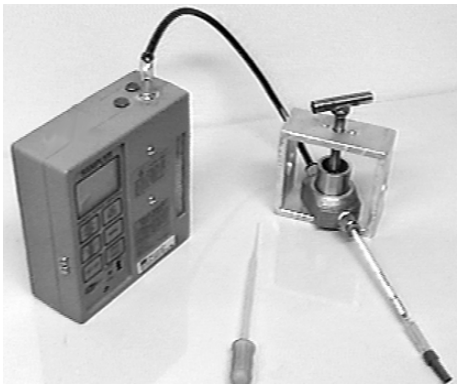


Figure 16 Using a personal sampling pump to measure glove permeation

You will be shown how to assemble the cell and inject the toluene into it.

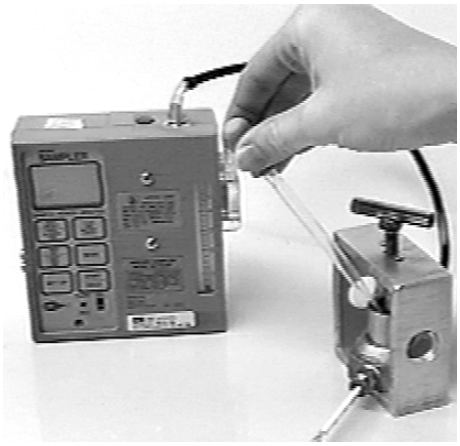


Figure 17 Charging the cell with solvent

At the instant you inject the toluene into the cell, start your stopwatch. In about 1 to 3 minutes you should see a slight discolouration of the stain tube. Record this time..

Initial stain tube discolouration time ..... minutes (Breakthrough Time)

Record the times as the stain moves to the 100, 200, 300, 400 and 500 ppm marks on the stain tube.

100 ppm .....seconds

200 ppm .....seconds

300 ppm .....seconds

400 ppm .....seconds

500 ppm .....seconds

Graph your findings below:

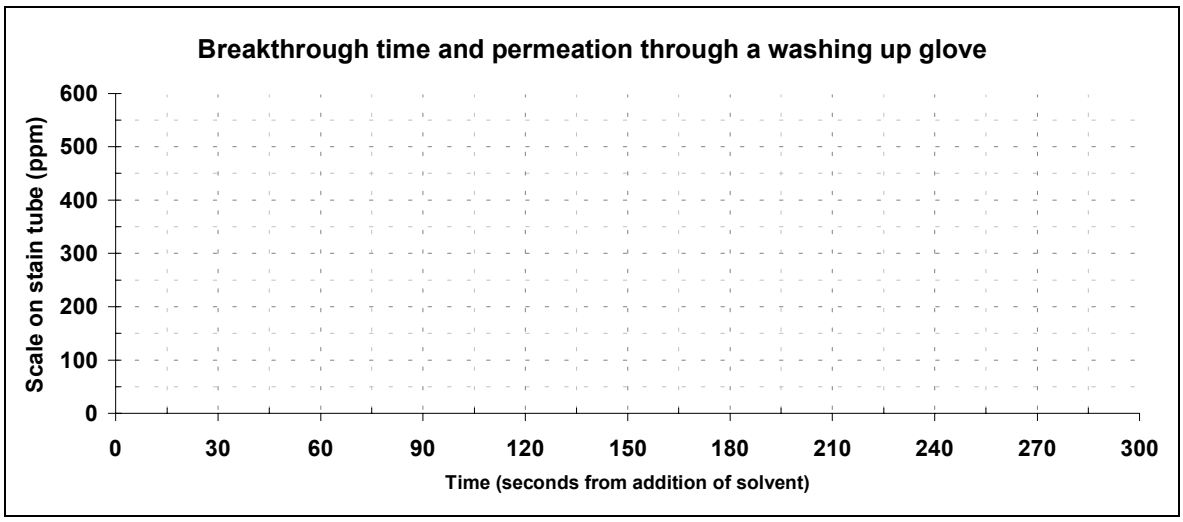


Figure 18 Your permeation results

The 500 ppm stain tube reading is equivalent to **700 mg/cm^2** (this may vary with stain tube brand) toluene permeating the glove, taking into account flow rates and test cell area. To turn this into a rate you need to get the actual rate ie the slope of the line and convert from seconds to minutes. Fill in the breakthrough times and permeation rates for toluene

Breakthrough time ..... (seconds)

Permeation rate ..... (mg/cm^2/minute)

Lag Time..... (seconds)

9. Technology of Testing

Note that testing o samples is not testing of whole garment

9.1. Cells

Dozens of different cells have been used for testing CPC. Few have design features which are explicitly explained and fewer have been tested to demonstrate equivalence to the ASTM F739 cell which is accepted as the standard cell and has been used to create the pool of permeation data.

9.2. Collection Media

Once a chemical has permeated a sample of CPC, the simplest way to take sequential samples of the permeant is to pass a collecting fluid past in inside surface, and convey the permeant and fluid to a detector. The permeant must not saturate the fluid and the fluid must not interfere with the CPC sample or the detector. The fluid can be a **liquid** (distilled water and isotonic saline and various sweat substitutes have been tried, but water is the most common), or a **gas** (nitrogen, helium and air are the most common). The fluid is collected for re-use or disposal. Solid collection media have also been tried with pesticides [(34)], overcoming the problem of low vapour pressure and low water solubility.

9.3. Detectors

Most detectors used to measure permeation through CPC are used with either a gaseous or liquid collecting medium. As most testing is performed in chemical laboratories, gas chromatography features in many research papers with both gaseous or liquid collection media. A range of sensors - Flame Ionisation Detectors (FID) and Photoionisation Detectors (PID) are the most common. The portable HNU 101(with a 10.2 eV lamp) photoionisation detector, familiar to many hygienists, is also often used - but only with gases, as it is fast and sensitive to many organic chemicals

9.4. Systems

A number of automated testing systems have been developed, as recording lists of numbers from an instrument or analysing a chart recorder is tedious and time consuming. Most of the systems have concentrated on data logging, using software attached to a gas chromatograph. Some systems also monitor flows, temperatures, pressure and may control flows and test temperatures. Very few attempt to automate the analysis of data and calculation of permeation indices. If multiple cells are tested at once, with a shared detector (one system has three Miran analysers), then the detector has to have a fast response, particularly if there is to be a flushing stage or calibration check between the cell measurements.

There has been a surprising lack of statistical analysis of the sensitivity of permeation indices. This should be done to indicate the number of samples that is required, and thus drive the development of systems and standards.

9.5. Mixtures

Most work with mixtures of chemicals has been done with gas chromatography, but it is tedious unless an automatic sampler is used. Some work has been done with dispersive infra red (like the Miran), but there is great potential to use Fourier Transform Infra Red (FTIR) in a variety of modes,

as multi-component mixtures can be analysed in seconds. A Miran in scan mode to give a complete spectra, takes some 20 minutes to perform a single scan.

9.6. Immersion Testing

It is possible to get figures for the Solubility and Diffusion rate of chemicals in CPC by immersing samples in the chemical. If the chemical is in a liquid state, then immersing the sample in the liquid from 1 to 3 days is sufficient with most chemical/ CPC combinations to give a measurable weight gain. It would also indicate other changes that would occur with heavy exposure. Similar experiments can be done with gases or vapours, but over a longer period, perhaps a month. If gases and vapours are used, then the process is more gentle, and the weight can be recorded continuously without having to dry the sample. Care must be taken to ensure the temperature remains very constant.

10. Sample Variation

Little work has been done on batch variation and variation between manufacturers. Some work has been done on the variation over the surface of a glove. It can be expected that the variation over the surface of a new dipped glove would be greater than effect of workplace use [35].

11. Seams, zips and other opening

Seams zippers and nay openings are the weakest link in a protective garment including gloves. It is important that these are tested in addition to the material by itself. Currently very little has been written in this area but new methods of testing whole garments is being investigated which will also include splash testing and the effect on permeation rates. It is important to note that current and proposed test methods call for seam and zipper section to be tested if they are included in the glove or garment.

12. Decontamination of CPC

12.1. Issues

Some of the issues surrounding decontamination involve cost and knowledge. A chemical suit that has been used once with a toxic chemical and where the surface could be expected to on the surface of the suit, is a candidate for decontamination and re-use. A cheap PVC glove that is obviously affected by exposure to a chemical, would be disposed of after limited use. That glove should be treated as toxic waste, making the cost of disposal significant and changing the real cost of choice of glove.

Between the lightly contaminated suit and the single use glove there is a spectrum of choices, but relatively little data on which to base decisions. One of the impediments to re-use is social [35], if a glove has not been laundered between use, as the smell of old sweat lingers, making re-use unacceptable. If the chemical does not have a strong, offensive smell, then it is possible that chemical exposure from use of a contaminated glove will not be an issue to the user. It is up to the hygienist to increase the concern about chemical exposure in this case.

The technical issues of whether various methods of decontamination affect the barrier properties of the CPC will now be discussed in detail.

12.2. Decontamination

A good review of decontamination of CPC has been done by Perkins [36]. Surface contamination is best removed with warm, soapy water. Simple water rinsing was found to be only of use with water soluble chemicals that permeated slowly and were not volatile [37].

Laughlin [38] has a good review (108 references) of decontaminating pesticide contaminated CPC.

Much of the mathematics and understanding of permeation can be applied to decontamination, with factors that enhance permeation being the same as those that increase permeation.

12.3. Matrix contamination

The removal of matrix contamination is contentious, particularly as chemical suits are expensive and are not considered single use items. There is some thought that "innocuous" solvents can be used, but the user should be aware that molecular damage may occur and affect the barrier properties of the CPC. Air drying at elevated temperatures (between 50°C and 60 °C may have merits), and some research does indicate that satisfactory removal of contamination can occur, but the polymer may be damaged at higher temperatures [39]. Some research has been done with moderate temperatures and a vacuum, but this approach remains largely unexplored.

The use of dishwashers and strong detergents can remove some contamination, but the net effect is to redistribute contamination. Perkins [36]summarises the laundering of agricultural clothing:

> *"Hot water (60°C) is better than cold water. To some extent, bleach will aid in degradation of pesticides. Cotton fabrics are easier to launder than polyester. Fluorocarbon fabric finishes decrease the absorption of pesticides. Laundry prewashes aid in the removal of pesticides."*

For chemicals that readily permeate CPC or are very toxic, the CPC should be seen more like a blotter or a layer of sponge cake than a thin, impervious barrier. Continued use of contaminated CPC will ensure continued exposure.

13. Heat Stress

The heat balance equation is sometimes given as

$$S = \pm C \pm R \pm K - E \quad \text{..... Equation 6}$$

Where

S = stored heat (does not change if the average temperature of the body is constant)
C = conductive heat transfer (from contact with surfaces, including the ground)
R = radiative heat transfer (infra red radiation, especially from the skin and hot objects)
K = convective heat transfer (from air movement)
E = evaporative heat transfer (from sweat)

For most Australian workplaces, heat lost on the breath can be ignored. When CPC is worn, the CPC acts as an insulator and a minor decrease in convective heat transfer can be expected. Convective heat transfer is slowed, as there is negligible air movement in a suit or glove. Radiative heat transfer can also be expected to decrease, though the colour in the infra red of a suit would affect the amount of heat absorbed or emitted. The factor that is most affected is evaporative heat losses. As convection has been reduced to remove moist air, the relative humidity in a suit or glove climbs rapidly, effectively blocking evaporative cooling. Note that only evaporative heat loss (E) has a negative sign. All the other components have either a (+) or (-) sign.

A free computer program is available that evaluates heat stress and thermal comfort interactively, varying the insulation level of clothing, air velocity, radiant heat, humidity and air temperature from one of the presenter's (DB) FTP site as ftp://plato.ens.gu.edu/au/sys/xfers/hygiene/hot.zip . This may help understand the complex interaction between these factors.

A quick search of MEDLINE (http://www.ncbi.nlm.nih.gov/PubMed) which is now available *free* on the Internet, courtesy of US Vice President Al Gore, revealed dozens of articles on heat and CPC. The military has a considerable interest, as the microclimate inside a chemical warfare suit limits its usage to something like 20 to 30 minutes.

Impervious CPC is not too different and a correction in the order of +10°C [40]has to be made to a WBGT estimate of heat stress. Breathable fabrics have a lesser effect as moisture can evaporate, taking with it the latent heat of evaporation. The effect is about that of wearing two overalls [41]. An Australian study with chemical suits [42]may have limited application as the study was performed in a climate chamber. This study did not appear to reproduce radiant heat loadings found in outdoor workplaces, but it did find that for 30 minute tasks, core temperatures did not exceed 38°C.

Care should be taken in estimating core temperatures in workers using CPC. A 1996 study [43]of oral and tympanic (ear drum) temperature measurements showed oral temperatures not be a reliable

indicator of core temperature. Cheap tympanic thermometers are available and could be used in the workplace to determine physiological limits.

14. The skin, creams, and other skin coatings

The skin is made of a number of layers. The outer layer, the stratum corneum, is of most interest to users of CPC as it is the major barrier to chemicals entering the skin.

Table 7 Structure of skin

Skin layer	Thickness (μm)	Structure or function	Blood flow (% of cardiac output)
Epidermis	10 (dead) and 40 (live)	Diffusion barrier, flat cells and lipids	
Dermis	1250	Protein, blood vessels	3.3
Hypodermis	1000-6000	Connective tissue, fat	2.2

A good review of the toxicology of the skin by Professor Emmett (ex Worksafe) contains Figure 19, illustrating the various layers of the skin.

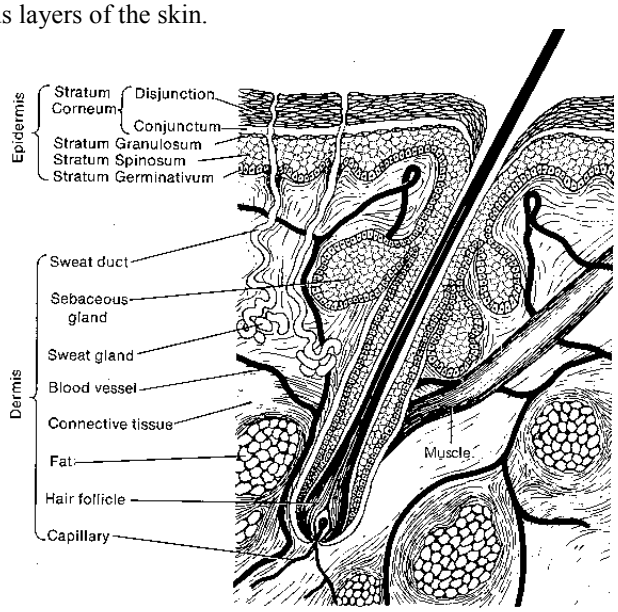


Figure 19 Structure of the skin

Of most interest to hygienists is the outer 20 μm thick horny layer (Stratum Corneum or SC) which can be seen as a brick wall, with bricks of flat keratin-filled corneocytes and mortar of lamellar lipids. Near the surface, there are more lipids from sebaceous secretions and this intercellular lipid. Deeper in the SC the bricks of keratin are closer together.

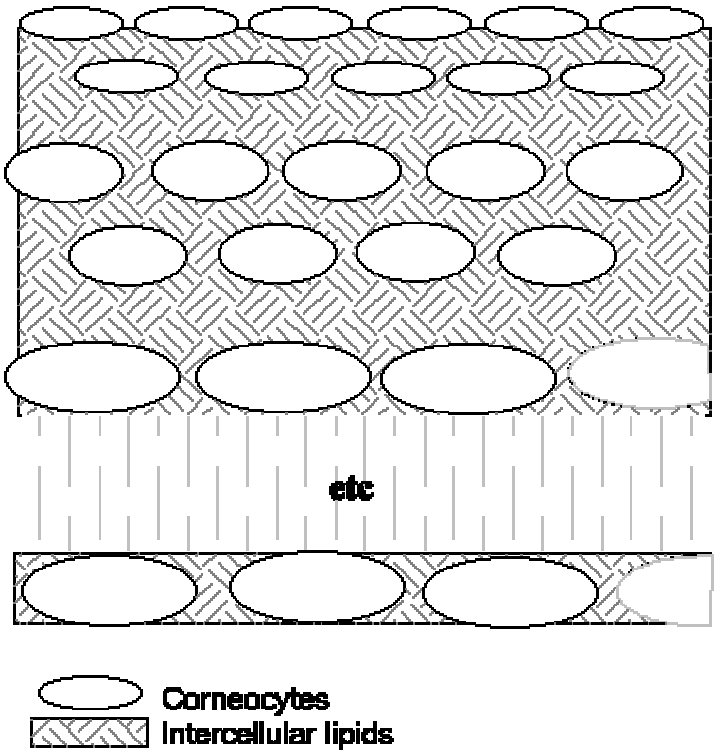


Figure 20 Structure of the Stratum Corneum after Bommannan 1990

Chemicals that dissolve fat pass through the lipids and water tends to pass through the keratin. Damaging the outer layers with a solvent removes the lipid and allows more rapid water loss from the skin. The skin becomes cracked and more susceptible to chemicals and infection. Figure 20 shows keratin plates floating in a sea of intercellular lipid. This structure was derived by Bommannan [(44)], using infra red analysis of successive layers of skin stripped off with sticky tape.

The ground rules for determining the effects of chemicals on the skin may change with research into the effect chemicals have on the ability of DNA in the skin to replicate. Living skin replicates - like any other tissue, so the slowing down of the process gradually kills the skin. If these cellular changes are considered significant, then we will be forced to review our regulatory approaches to skin contact with chemicals. Ursin (1995) [(45)] reported that DNA from the epidermis of breast skin. The permeation of octyl acetate through the skin was less than 1 ug/m^2 in 2 hrs or 0.8 pg/cm^2/min, by itself and in mixtures with DMSO (dimethylsulphoxide). This minute amount produced around 50% decrease in DNA activity. Ursin concluded

> *"even extremely small amounts of particularly toxic solvents can affect DNA synthesis".*

Creams and skin coatings could be expected to reduce the dehydration of the skin by replacing the lipid. However, the creams themselves may act as a pathway for chemicals to enter the skin. If the cream or skin coating increases the hydration of the skin, then the keratin becomes soggy and less of a barrier to chemicals. The net effect, if the skin hydration is not controlled within tight limits, is to increase the permeation of the skin. Healthy, normal skin gives the best barrier.

It is interesting to note that creams were well advertised in the American Industrial Hygiene Association Journal in the 1950's, with quite extravagant claims to protect the skin. The basic action of creams has not changed.

While creams and skin coatings may not do much to directly prevent chemicals contacting the skin, skin coatings may have a role in preventing large molecules interacting with skin, such as molecules associated with latex allergies. A recent editorial in the Medical Journal of Australia indicates that spray on films may be of use for preventing latex allergies [(46)].

15. Guidelines

15.1. General

Testing of chemical protective clothing is commonly performed at 25 °C for 8 hours with gloves and 3-4 hours with protective suits and other apparel, giving a wide range of safety as chemical exposure tends to be intermittent [47]. This assumes that the use is not at an elevated temperature and mechanical stresses are unimportant.

The ACGIH published annual lists of TLV's, some that have a "skin" notation to indicate that entry through the skin should be considered. This may underestimate the chemicals of importance [1,48] but these chemicals must be given particular attention when selecting chemical protective clothing.

A number of Guidelines have been published. The largest is by Schwope [49,50] in two loose-leaf folders. Guidelines published by the US National Safety Council appeared in the appendix of Hassler's PhD thesis [51] and are reproduced in Appendix A. Guidelines for specific CPC include Forsberg and Mansdorf's pocket guide [52] and commercial guides from Ansell Edmont [53].

15.2. Computer Programs on the Internet

Best Gloves

Several manufactures have produced computer programs to aid selection of CPC. Best Gloves has a DOS program which can be obtained from the Internet at http://www.bestglove.com . The information is specific to Best brand gloves. It would be unwise to use this data to choose gloves from another brand, as considerable difference in the formulations of the same type of polymer between manufacturers.

Ansell Edmont

Ansell Edmont also have a program and it may be purchased. A demonstration version of their SpecWare program is available at http://www.industry.net/c/mn/08h6jsd001/. It claims to be the "ultimate reference tool" for selecting CPC, with 200 chemicals and 80 glove types.

Oaklahoma State University

A free spreadsheet with over 380 chemicals is available from Okalahoma State University at http://www.pp.okstate.edu/ehs/hazmat/gloves.htm as an Excel file or a large on-line table (rename the *.exe file to *.xls to make the spreadsheet work - the file is not compressed). A section of the spreadsheet is shown below. The data appears to be conservative and has a colour code for various chemical types. There are also other resources on CPC on the Internet of varying quality and reliability.

Table 8 Oklahoma State University CPC Spreadsheet

Oklahoma State University Chemical Guide

Chemical	NFPA 704				DOT Class	Waste Codes	Category	breakthrough time, totally immersed at room temp in minutes					
								Gloves				Suits	
	Fire	Health	Reactivity	Other				Nitrile	4-H / Silver Shield	Neoprene	Latex	Tychem (TM) 9400	Saranex
Acetaldehyde	4	2	2	N	3	U001, D001	A	<0.6	>360	10.2	7		
Acetic Acid	2	2	0	N	8	D002	Co-Ac	5	>480	360	21	180	>4000.2
Acetic Anhydride	2	2	1	N	8	D002	Co		>480	210	3	>480	
Acetone	3	1	0		3	U002, F003, D001	A	3	>1440	2.4	2.4	>480	33
Acetonitrile (Methyl Cyanide)	3	3	0	N	3	D001	B	<5	>1440	<10.8	<0.6	>480	>480
Acetophenone	2	1	0	N		U004	A		>480				
Acetyl Chloride	3	3	2	WR	3	U006, D001, D002, D003	FI					160	37.2

GlovES

The GlovES+ program was developed from published data and contains about 15,000 test data. The "ES" in the name means Expert System, but it is really a sophisticated "look-up" table, not artificial intelligence. Within a few years there may be computer programs that will predict glove performance, based on theory and experiment. This program appears to have the greatest acceptance with hygienists and it is available through the ACGIH (http://www.acgih.org)

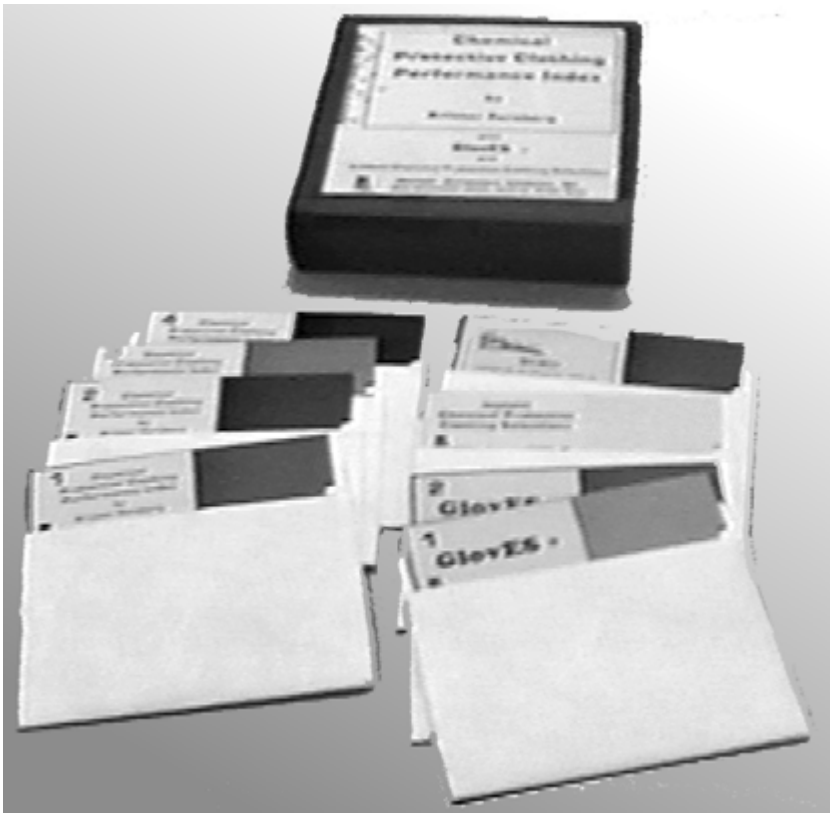


Figure 21 GlovES "Expert" system for glove selection

16. References

1. **Fiserova-Bergerova, V.**: Relevance of Occupational Skin Exposure. *Annals of Occupational Hygiene* ,(6): 673-685 (1993).

2. **Graham, T.**. Notice of the Singular Inflation of a Bladder. *Royal Institute Journal*,: 88-89 (1829).

3. **Graham, T.**: On the Absorption and Dialytic Separation of Gases by Colloid Septa. *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science* Series 4: 401-420 (1866).

4. **Smart, J., and J. Griffiths**. *Covering Up*. London: Science Museum, London, 1982.

5. **Hamilton, A.**. *Industrial Poisons in the United States*. New York: The Macmillan Company, 1925.

6. **Pegum, J.S., and F.A. Medhurst**.: Contact Dermatitis From Penetration of Rubber Gloves by Acrylic Monomer. *BMJ* 2: 141-143 (1971).

7. **Perkins, J.L.**: Chemical Protective Clothing: I. Selection and Use. *Applied Industrial Hygiene* 2,(6): 222-230 (1987).

8. **Kumins, C.A., and T.K. Kwei**.: Free Volume and Other Theories. *Diffusion in Polymers.*,eds J. Crank, and G.S. Park, pp. 107-40. London: Academic Press, 1968.

9. **Duda, J.L., and J.M. Zielinski**.: Free-Volume Theory. *Diffusion in Polymers.*,Editor P. Neogi, pp. 143-72. Vol. Chapter 3. New York: Marcel Dekker, 1996.

10. **Hansen, C.M., C.B. Billing Jr, and A.P. Bentz**. "Selection and Use of Molecular Parameters to Predict Permeation Through Fluoropolymer-Based Protective Clothing Material." *Performance of Protective Clothing*, Editors J.P. McBriarty, and N.W. Henry, 894-907. Fourth Volume ed. Philadelphia: American Society for Testing and Materials, 1992.

11. **Hansen, C.M., and K.M. Hansen**. "Solubility Parameter Prediction of the Barrier Properties of Chemical Protective Clothing." *Performance of Protective Clothing*, Editors S.Z. Mansdorf, R. Sager, and A.P. Nielsen, 197-208. Second Symposium ed. Philadelphia: American Society for Testing and Materials, 1988.

12. **Bentz, A.P., and C.B. Billing Jr**. "Determination of Solubility Parameters of New Suit Materials." *Performance of Protective Clothing*, Editors S.Z. Mansdorf, R. Sager, and A.P. Nielsen, 209-18. Second Symposium ed. Philadelphia: American Society for Testing and Materials, 1988.

13. **Archer, W.L.** "Industrial Solvents Handbook.". New York: Marcel Dekker Inc, 1996.

14. **Perkins, J.L., and A.D. Tippit** .: Use of Three-Dimensional Solubility Parameter to Predict Glove Permeation. *Am Ind Hyg Assoc J* 46,(8): 455-459 (1985).

15. **Perkins, J.L., M.C. Ridge, A.B. Holcombe, M.K. Wang, and W.E. Nonidez**.: Skin Protection, Viton, and Solubility Parameters. *Am Ind Hyg Assoc J* 47,(12): 803-808 (1986).

16. **Perkins, J.L.**: Chemistry of Chemical Protective Clothing Formulations. *Chemical Protective Clothing.*,Editors J.S. Johnson, and K.J. Anderson, pp. 25-36. Vol. Chapter 3. Fairfax, Virginia: American Industrial Hygiene Association, 1990.

17. **Crank, J.**: The Mathematics of Diffusion. second ed. pp. 414. Oxford: Clarendon Press, 1975.

18. **Perkins, J.L., and B. Pool**.: Batch Lot Variability in Permeation Through Nitrile Gloves. *Am Ind Hyg Assoc J* 58,(7): 474-479 (1997).

19. **Bellingar, T.A.**: Effect of Protective Gloves on Hand Movement: an Exploratory Study. *Applied Ergonomics* 24,(4): 244-250 .

20. **Bensel, C.K.**: The Effects of Various Thicknesses of Chemical Protective Gloves on Manual Dexterity. *Ergonomics* 36,(6): 678-696 (1993).

21. **British Standards Institute**.: *BS EN 22286:1994 BS 3424: Part 1:1994 ISO 2286:1986 Methods for the Determination of Length and Width of a Roll, Net Mass and Mean Mass Per Unit Area of a Piece, Cut, Roll or Sample and the Determination of Thickness of Coated Fabrics*, British Standards Institute, 1994.

22. **Perkins, J.L., and M.-J. You**.: Predicting Temperature Effects on Chemical Protective Clothing Permeation. *Am Ind Hyg Assoc J* 53,(2): 77-83 (1992).

23. **Alexy, B., and R.M. Buchan**.: Temperature As a Variable in Evaluating the Permeability of 1,1,1 - Trichloroethane Through Four Types of Chemical Protective Clothing. *Am Ind Hyg Assoc J* 48,(2): A104-A109 (1987).

24. **Zellers, E.T., and R. Sulewski** .: Modelling the Temperature Dependence of N-Methylpyrrolidone Permeation Through Butyl - and Natural - Rubber Gloves. *Am Ind Hyg Assoc J* 54,(9): 465-479 (1993).

25. **Mickelsen, R.L., M.M. Roder, and S.P. Berardinelli**.: Permeation of Chemical Protective Clothing by Three Binary Solvent Mixtures. *Am Ind Hyg Assoc J* 47,(4): 236-240 (1986).

26. **Ke, H., S.P. Levine, R.F. Mouradian, and Berkeley**.: Fast Gas Chromatography for Air Monitoring Limits of Detection and Quantitation. *Am Ind Hyg Assoc J* 53,(2): 130-137 (1992).

27. **Reed, S., D. Cook, and A. Vaccaro**.: *Study of the Protective Life of Gloves*, Research Report for the WorkCover Authority, NSW. 1995.

28. **Johnson, J.S., and K.J. Anderson:** Eds. *Chemical Protective Clothing*, Vol. Volume 1. Fairfax, Virginia: American Industrial Hygiene Association, 1990.

29. **American Society for Testing and Materials**.: *ASTM F739-85 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases*, American Society for Testing and Materials, 1986.

30. **Bromwich, D.W.**: The Design of Permeation Cells for Testing Chemical Protective Clothing. *Proceedings of the Sixteenth Annual Conference of Australian Institute of Occupational Hygienists* .Melbourne: Australian Institute of Occupational Hygienists , 1997.

31. **American Society for Testing and Materials**.: *ASTM F1383-96 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact*, American Society for Testing and Materials, PA, 1996.

32. **Leinster, P.**: The Development of a Standard Test Method for Determining Permeation of Liquid Chemicals Through Protective Clothing Materials. *Annals of Occupational Hygiene* 30,(4): 381-395 (1986).

33. **Long, G.L., and J.D. Winefordner.**. Limit of Detection. A Closer Look at the UIPAC Definition. *Anal Chem* 55,(7),: 712A-724A (1983).

34. **Ehntholt, D.J., D.L. Cerundolo, I. Bodek, A.D. Schwope, M.D. Royer, and A.P. Nielsen**.: A Test Method for the Evaluation of Protective Glove Materials Used in Agricultural

Pesticide Operations. *Am Ind Hyg Assoc J* 51,(9): 462-468 (1990).

35. **Bromwich, D.W., F. Smith, and J. Yu**. *The Use of Gloves to Control Chemical Exposure in the Workplace*. Brisbane: Griffith University, 1997.

36. **Perkins, J.L.**: Decontamination of Protective Clothing. *Applied Occupational and Environmental Hygiene* 6,(1): 29-35 (1991).

37. **Schlatter, C.N.**: Effects of Water Rinsing on Subsequent Permeation of Rubber Chemical-Protective Gloves. *Performance of Protective Clothing.* Second Symposium ed. Editors S.Z. Mansdorf, R. Sager, and A.P. Nielsen, pp. 376-85. Vol. ASTM STP 989. Philadelphia: American Society for Testing and Materials, 1988.

38. **Laughlin**.: Refurbishing Pesticide-Contaminated Clothing. *Protective Clothing Systems and Materials.*,Editor M. Raheel, pp. 97-135. Vol. Chapter 5. New York: Marcel Dekker, 1994.

39. **Perkins, J.L., J.S. Johnson, P.M. Swearengen, C.P. Sackett, and S.C. Weaver**.: Residual Spilled Solvents in Butyl Protective Clothing and Usefulness of Decontamination Procedures. *Applied Industrial Hygiene* 2,(5): 179-182 (1987).

40. **Paull, J.M., and F.S. Rosenthal**.: Heat Strain and Heat Stress for Workers Wearing Protective Suits at a Hazardous Waste Site. *Am Ind Hyg Assoc J* 45,(5): 458-463 (1987).

41. **Kenney, W.L., D.E. Hyde, and T.E. Bernard**.: Physiological Evaluation of Liquid-Barrier, Vapor-Permeable Protective Clothing Ensembles for Work in Hot Environments. *Am Ind Hyg Assoc J* 54,(7): 397-402 (1993).

42. **Payne, W.R., B. Portier, I. Fairweather, S. Zhou, and R. Snow**.: Thermoregulatory Response to Wearing Encapulated Protective Clothing During Simulated Work in Various Thermal Environments. *Am Ind Hyg Assoc J* 55,(6): 529-536 (1994).

43. **Beaird, J.S., T.R. Bauman, and J.D. Leeper**.: Oral and Tympanic Temperatures As Heat Strain Indicators for Workers Wearing Chemcial Protective Clothing. *Am Ind Hyg Assoc J* 57: 344-347 (1996).

44. **Bommannan, D., R.O. Potts, and R.H. Guy.**. Examination of Stratum Corneum Barrier Function *In Vivo* by Infrared Spectroscopy. *J Invest Dermatol* 95,(4),: 403-408 (1990).

45. **Ursin, C., C.M. Hansen, J.W. Van Dyk, P.O. Jensen, I.J. Christensen, and J. Ebbehoej**.: Permeability of Commercial Solvents Through Living Human Skin. *Am Ind Hyg Assoc J* 56: 651-660 (1995).

46. **Walls, R.S.**: Latex Allergy: a Real Problem. *Med J Aust* 164: 707 (1996).

47. **Stull, J.O., and B. Herring**.: Selection and Testing of a Glove Combination for Use With the U.S. Coast Guard's Chemical Reponse Suit. *Am Ind Hyg Assoc J* 51,(7): 378-383 (1990).

48. **Potts, R.O., and R.H. Guy.**. Predicting Skin Permeability. *Pharm Res* 9,(5),: 663-669 (1992).

49. **Schwope, A.D., P.P. Costas, J.O. Jackson, J.O. Stull, and D.J. Weitzman**. "Guidelines for the Selection of Chemical Protective Clothing, Volume II: Technical and Reference Manual.". 3rd ed. Cincinnati: American Conference of Governmental Industrial Hygienists, 1987.

50. **Schwope, A.D., P. Costas, J.O. Jackson, J.O. Stull, and Welzman D J**. "Guidelines for the Selection of Chemical Protective Clothing, Volume 1: Field Guide.". 3rd ed. Cincinnati: American Conference of Governmental Industrial Hygienists, 1987.

51. **Hassler, K.D.** "Factors Affecting Breakthrough Time of Commercial Pesticide Formulations Through Butyl Glove Material." Ph.D. diss., University of North Carolina at Greensboro, 1989.

52. **Forsberg, K., and S.Z. Mansdorf**. "Quick Selection Guide to Chemical Protective Clothing.". 2nd ed. New York: Van Nostrand Reinhold, 1993.

53. **Ansell Edmont**.: *Ansell Edmont Chemical Resistance Guide*, Ansell Edmont , 1990.

54. **Ursin, C., and I. Drabaek**. "Carbon-14 Tracers in Permeation Studies: Feasibility Demonstration." *Performance of Protective Clothing*, Editors S.Z. Mansdorf, R. Sager, and A.P. Nielsen, 266-94. Second Symposium ed. Philadelphia: American Society for Testing and Materials, 1988.

17. CPC Workshop Further Reading

17.1. Journals

Most papers (over 70) on CPC are published in the **American Industrial Hygiene Association Journal**. Another 20 or so are published in **Applied Occupational and Environmental Hygiene** and the **Annals of Occupational Hygiene**. There is a scattering of CPC articles in safety, ergonomics, environmental and toxicology journals. There is also an increasing number of articles on latex allergies, particularly in the medical and allied health journals, of variable quality.

17.2. Books

Forsberg, K., and L.H. Keith. "Chemical Protective Clothing. Permeation and Degradation Compendium",. Boca Raton: Lewis, 1995.

Forsberg, K., and S.Z. Mansdorf. "Quick Selection Guide to Chemical Protective Clothing.". 2nd ed. New York: Van Nostrand Reinhold, 1993.

Grandjean, P.. *Skin Penetration: Hazardous Chemicals at Work*. London: Taylor & Francis, 1990.

Johnson J.S., K.J. Anderson *(eds) Chemical Protective Clothing*,. Fairfax, Virginia: American Industrial Hygiene Association, 1990.

Mellstrom, G.A., J.E. Wahlberg, and H.I. Maibach: (eds). *Protective Gloves for Occupational Use*. Dermatology: Clinical and Basic Science. Boca Raton: CRC Press, 1994.

Schwope, A.D., P. Costas, J.O. Jackson, J.O. Stull, and Welzman D J. "Guidelines for the Selection of Chemical Protective Clothing, Volume 1: Field Guide.". 3rd ed. Cincinnati: American Conference of Governmental Industrial Hygienists, 1987.

Schwope, A.D., P.P. Costas, J.O. Jackson, J.O. Stull, and D.J. Weitzman. "Guidelines for the Selection of Chemical Protective Clothing, Volume II: Technical and Reference Manual.". 3rd ed. Cincinnati: American Conference of Governmental Industrial Hygienists, 1987.

17.3. Conference Proceedings

The **American Society for Testing and Materials** has published 6 proceedings of seminars with the title **"Performance of Protective Clothing"**. The two most recent are available from ASTM (http://www/astm.org). Various versions except the 1997 proceedings (too recent) are available in some Australian libraries.

The **American Industrial Hygiene Association** annual conference has papers, but apparently no published proceedings of these conferences.

The **Australian Institute of Occupational Hygienists** annual conference has occasional papers on CPC. These are available in some libraries on the ACEL OH&S microfiche.

17.4. Reference Books

Barton, A.F.M.. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*. Boca Raton: CRC Press, 1983.

Crank, J., and G.S. Park *Diffusion in Polymers.* London: Academic Press, 1968.

Crank, J.: The Mathematics of Diffusion. second ed. pp. 414. Oxford: Clarendon Press, 1975.

Cussler, E.L.. *Diffusion, Mass Transfer in Fluid Systems* Cambridge University Press, 1984.

Hamilton, A.. *Industrial Poisons in the United States*. New York: The Macmillan Company, 1925.

Hildebrand, J.H.. *Viscosity and Diffusion, A Predictive Treatment*. New York: John Wiley & Sons, 1977.

Neogi, P.: Transport Phenomena in Polymer Membranes. *Diffusion in Polymers.*, Editor P. Neogi, pp. 173-210. Vol. Chapter 4. New York: Marcel Dekker, 1996.

Stastna, J., and D. De Kee. "Transport Properties in Polymers.". Lancaster: Technomic Publishing Company, 1995.

Veith, W.R. "Diffusion In and Through Polymers: Principles and Applications.". Munich: Carl Hanser Verlag, 1991.

17.5. Standards (incomplete list)

American Society for Testing and Materials.: *ASTM F1383-96 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Intermittent Contact*, American Society for Testing and Materials, PA, 1996.

American Society for Testing and Materials.: *ASTM F739-85 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases*, American Society for Testing and Materials, 1986.

American Society for Testing and Materials.: *ASTM F739-96 Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact*, American Society for Testing and Materials, 1996.

American Society for Testing and Materials.: *D 543-95 Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.*, pp. 25-31. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

American Society for Testing and Materials.: *F 1001-89 Standard Guide for Selection of Chemicals to Evaluate Protective Clothing Materials.*, pp. 790-792. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

American Society for Testing and Materials.: *F 1407 -96 Standard Test Method for Resistance of Chemical Protective Clothing Materials to Liquid Permeation - Permeation Cup Method.*, pp. 849-54. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

American Society for Testing and Materials: *ASTM F903-87 Standard Test Method for Resistance of Protective Clothing Materials to Penetration by Liquids.*, pp. 477-86 . American Society for Testing and Materials, 1987.

American Society for Testing and Materials: *D 471-95 Standard Test Method for Rubber*

Property - Effect on Liquids., pp. 86-96. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

American Society for Testing and Materials: *E 171-94 Standard Specification for Standard Atmospheres for Conditioning and Testing Flexible Barrier Materials.*, pp. 887. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

American Society for Testing and Materials: *E122 -89 Standard Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process.*, pp. 31-35. Vol. Annual Book of ASTM Standards. PA: American Society for Testing and Materials, 1996.

British Standards Institute.: *BS 2471:1978 Textiles - Woven Fabrics - Determination of Mass Per Unit Length and Mass Per Unit Area*, British Standards Institute, 1978.

British Standards Institute.: *BS 7184:1989 Selection, Use and Maintenance of Chemical Protective Clothing*, British Standards Institute, 1989.

British Standards Institute.: *BS EN 20139:1992 ISO 139:1973 Textiles - Standard Atmospheres for Conditioning and Testing*, British Standards Institute, 1992.

British Standards Institute.: *BS EN 22286:1994 BS 3424: Part 1:1994 ISO 2286:1986 Methods for the Determination of Length and Width of a Roll, Net Mass and Mean Mass Per Unit Area of a Piece, Cut, Roll or Sample and the Determination of Thickness of Coated Fabrics*, British Standards Institute, 1994.

British Standards Institute.: *BS EN 374-1:1994 Protective Gloves Against Chemicals and Micro-Organisms Part1. Terminology and Performance Requirements*, British Standards Institute, 1994.

British Standards Institute.: *BS EN 374-2:1994 Protective Gloves Against Chemicals and Micro-Organisms Part3. Determination of Resistance to Penetration*, British Standards Institute, 1994.

British Standards Institute.: *BS EN 374-3:1994 Protective Gloves Against Chemicals and Micro-Organisms Part3. Determination of Resistance to Permeation by Chemicals*, British Standards Institute, 1994.

British Standards Institute.: *BS EN 511:1994 Protective Gloves Against Cold*, British Standards Institute, 1994.

Standards Australia.: *Australian Standard AS 3765.1-1990 Clothing for Protection Against Hazardous Chemicals. Part 1: Protection Against General or Specific Chemicals*, Standards Australia, Sydney, 1990.

Standards Australia.: *DR 93127. Draft Australian/New Zealand Standard for Comment Industrial Gloves and Mittens*, Standards Australia, Sydney, 1993.

18. Appendix A: US National Safety Council Guidelines

This appendix is reproduced from Hassler's 1989 PhD thesis [51]. It is one of the more useful guidelines. Hassler states

> *" These guidelines for glove selection appeared in the June 1988 issue of **Safety and Health** which is published by the National Safety Council. This is the only published list of official rules which guide selection and use of gloves."*

National Safety Council Guidelines

Preliminary Information Before Glove Selection

1. Review processes, work practices and engineering controls for ways to eliminate the need for gloves. Glove controls for ways to eliminate the need for gloves. Glove use should be the last approach considered to provide employees with protection against skin contact with chemicals.
2. List all the chemicals against which protection is sought and estimate the wearing time requirement for gloves (e.g. all day, few hours, periodically for minutes).
3. Determine from MSDS and other sources the known consequences of skin contact with chemicals to be used (e.g. sensitisation, dermatitis, systemic poisoning, skin absorbable).
4. Single Agents. Find the chemical against which skin contact protection is sought from among those listed in various sources of permeation data (see manufacturer's published literature e.g. Edmont, North, Dow, DuPont, Pioneer, AIHA Monograph). Choose gloves which provide the best performance based on breakthrough time.
5. Mixtures. For protection against chemical mixtures where component permeability data exist and components are known not be skin absorbable, systemic poisons, corrosives or sensitisers, select gloves which maximise protection against the component(s) likely to be present in greatest quantity (see Appendix Note 1).
6. Gloves should not be selected for protection against mixtures based on component permeability data if a mixture component is skin absorbable, a systemic poison, corrosive or sensitiser.

Glove Selection: Permeability Data not available.

7. When protection is sought against single agents or mixture component for which there is consistent toxicological evidence of high systemic toxicity, skin absorbability or irreversible effects, experimental determination of chemical permeability through gloves should be made. Gloves selected should have at least a 30 minute breakthrough time.
8. When seeking protection against chemicals for which toxicological evidence suggests a less serious hazard and there are no permeability data available, use the following selection procedure:
9. Use any two glove pairs of different composition from the permeation guide and treat the outer glove as disposable and discard it frequently, or
10. Use any single glove as disposable to be discarded after completing the operation for which protection was needed or 15 minutes, whichever is sooner.

Other Selection Factors

11. After selection of gloves based on permeability data, or after selecting suitable double glove system, the following additional factors should be considered. Durability; dexterity; tactile sensitivity; friction' wearing schedule (all day, short term/frequent); cost.
12. Gloves chosen based on best permeability may not always be the best for other selection factors, but should reflect a best effort to optimise factors which are often at cross purposes (e.g. glove

thickness favours reduced permeability and improved durability, but may compromise dexterity and touch).

Glove Use

13. Gloves are not intended to permit contact with chemicals, but are intended to prevent contact when accidental encounter occur. Gloves should be kept as clean as possible during use.
14. Gloves should only be used as protection against the agent considered during the selection process. Do not use gloves work to protect skin from chemicals to clean-up broken glass or to handle unusually hot or cold objects. Gloves in contact with chemicals substantially above ambient temperatures may not provide the protection predicted by permeability data developed at another temperature.
15. The loss of tactile sensitivity during glove use may result in glove contamination without the wearer's knowledge. This increase the risk of (1) area contamination and (2) personal exposure and enhanced health effects.
16. Minimise the spread of contamination throughout the work area and beyond by making the location where gloves are to be used clearly known to all area personnel.
17. Rinse gloves frequently to minimise the spread of contamination within a designated glove-use area or to the face and mouth of the wearer. Frequent rinsing will also eliminate continued chemical challenge to gloves contaminated without the wearer's knowledge. Rinsing is recommended every half-hour and after high-potential contact operations. Even well-selected gloves will fail with continued chemical contact. The consequences could be patching of a permeated chemical on the skin and enhanced skin or systemic effects.

Glove Reuse, Disposal and Storage

18. When evidence of glove contact with chemicals other than those known to be skin absorbable, systemic poisons, or corrosives or sensitisers is visible or otherwise known or suspected, the contaminant(s) may be washed from the glove and the glove continued in service or reused.
19. When evidence of glove contact with chemicals known to be skin absorbable, systemic poisons, corrosives or skin sensitisers, is visible, otherwise known or suspected the glove should be discarded (see Appendix Note 2).
20. Do not reuse gloves at the end of the work-week unless chemical contact is known not to have occurred.
21. If gloves are washed or otherwise cleaned with a specialised decontamination solution before disposal, contain any washings not permitted in the sewers.
22. Gloves removed for disposal need not be decontaminated. In general one contaminated glove should be peeled or stripped almost entirely off by turning the glove inside-out. Before removing it completely, use the partially removed glove as protection while similarly removing the second glove. A container should be ready to receive contaminated gloves for proper water disposal.
23. Before reusing gloves, (1) wash the outside with soap and water, (2) remove the glove from the hand without mechanically stressing the glove, (3) rinse the glove inside and out, (4) dry the glove thoroughly and store it in a clean place. The washing procedure should not be used for water soluble gloves (e.g. PVA).
24. Gloves known or assumed to be contaminated to the extent that their washings would not be permitted in the sewer should be discarded in accordance with proper disposal procedures.
25. Washing gloves with solvent (e.g. acetone) may have unpredictable effects on the elastomer's ability to protect when gloves are reused, so reuse of solvent washed gloves is not recommended.

Note 1 - Protection against mixtures

The limitation discussed below concerns direct application of single agent permeability data on mixtures of these chemicals. Research indicted that for mixtures which show no component adverse synergism towards glove material (mixture permeability no worse than predicted component permeability) the permeation rate of these mixtures will be directly proportional to volumetric concentration of each solvent. This behaviour cannot be predicted without conducting permeability studies but may be assumed without serious consequences for less hazardous chemicals. For protection against mixtures which do not contain hazardous chemicals you may select gloves which maximise protection against the component present in greatest concentration.

When protection is required against mixtures containing at least one of the hazardous materials (skin absorbable, systemic poison, corrosive or sensitiser), it is not reasonable to assume that there are no component adverse synergistic effects making mixtures more permeable than expected based on known component permeability. In this case a glove should not be selected until the permeability of the mixture has been determined experimentally and found acceptable.

Note 2 - Effect of Glove Washing
Most glove permeability data has been developed for single agents in continuous contact with glove material. When a glove is contaminated and then washed, some of the chemical which began to permeate the glove will continue toward and may reach the hand. For less hazardous chemicals continued use of a contaminated but washed glove is not expected to pose a serious hazard. For materials known to be skin or systemically hazardous continued use of a contaminated but washed glove could pose a more serious hazard and is not recommended.

As stated in paragraphs 15 and 16, frequent rinsing of gloves worn for extended periods will minimise area contamination, glove permeation, and skin contact resulting from glove contamination which occurs without the workers' knowledge. This work practice is strongly recommended because (1) area contamination e.g. workbench, equipment, desk, telephone etc.) can have serious consequences to the unprotected worker who is exposed later and (2) chemical breakthrough while the glove is in long term use can lead to enhanced absorption and a more serious health problem than the same exposure to even the ungloved hand (patch effect).

19. Appendix B: Permeation Models - Lag Time

Chapter 4 of Crank "The Mathematics of Diffusion" [17] is universally quoted as the starting point for calculations of diffusion through CPC (or any other membrane).

The code below was written in Visual Basic for Applications (VBA), the macro language residing beneath Microsoft applications like Excel97. You don't have to calculate it this way - you can do it all on the spreadsheet, but its quicker and neater this way. Its really only a couple of lines of code.

```
Function CrankCumm(N As Integer, W As Double) As Double
' see Crank "The Mathematics of Diffusion"
' page 51 equation 4.24 and Fig 4.2
' November 14 1997 by David Bromwich
  Dim DUMMY As Double
  Dim j As Integer
  Dim pi As Double
  pi = 3.14159265358979
'W is D * T/ L^2
  DUMMY = 0
For j = 1 To N
  DUMMY = DUMMY + (((-1) ^ j) / (j ^ 2)) * Exp(-(j * pi) ^ 2 * W)
Next j
  CrankCumm = W - 1 / 6 - 2 / (pi ^ 2) * DUMMY
End Function
```

The code solves this equation for a finite number of terms "N", as the series converges rapidly.

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) \quad \text{Equation 7}$$

Where

Q_t	= total amount of chemical diffusing until time t
l	= thickness of the membrane
$C1$	= initial concentration on the exposed surface
D	= diffusivity of the chemical through the membrane
t	= time from addition of the chemical

As t approaches infinity, the exponent disappears, and the curve becomes the straight line

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} \quad \text{Equation 8}$$

This line has an intercept on the time axis, L

$$L = \frac{l^2}{6D} \quad \text{Equation 9}$$

This time, L is the "time lag", or **Lag Time**

Note that the **Diffusion Coefficient** "D" can be directly estimated from this Lag Time.

Table 9 Effect of terms in diffusion equation

N	2	0	999	
D/tL^2	2 terms	Linear (zero terms)	999 terms	Difference between 999 and 2 terms
0	-0.01	-0.16666667	0.00000010	0.014684992625664500000
0.01	-0.01	-0.15666667	0.00000000	0.007205419182549990000
0.05	0.00	-0.11666667	0.00026934	0.000260563944752347000
0.1	0.01	-0.06666667	0.00788529	0.000003122916574282990
0.2	0.06	0.03333333	0.06146375	0.000000004433631665298
0.3	0.14	0.13333333	0.14382443	0.000000000000060174088
0.4	0.24	0.23333333	0.23724357	0.000000000000000000000
0.45	0.29	0.28333333	0.28572053	0.000000000000000000000
0.5	0.33	0.33333333	0.33479071	0.000000000000000000000
0.6	0.43	0.43333333	0.43387651	0.000000000000000000000

Even with two terms, the equation has converged very quickly and for D/tL2 = 0.1, the difference is less than 1% when compared to 999 terms (rounding errors would affect the calculation).

At small times, the curve does not become zero, but just gets smaller. This means Breakthrough Times can be whatever you want - just choose an insensitive detector and you will get great looking numbers. Lag Time, however is dependent on the straight line and the intercept is calculated. This almost immediate Breakthrough has actually been demonstrated with radioactive tracers and their exquisite sensitivity [54].

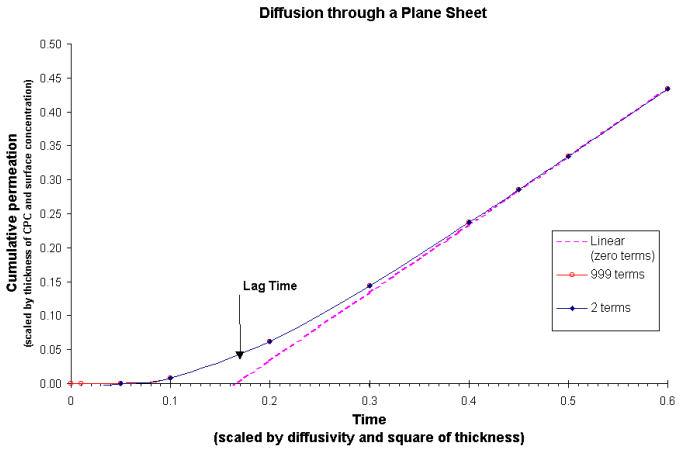


Figure 22 Calculation of terms in Equation 6

Another way to visualise the way that diffusion behaves is to plot the Cumulative Permeation on a Log scale. This has been done in Figure 23 and it shows the Cumulative Permeation rising steeply.

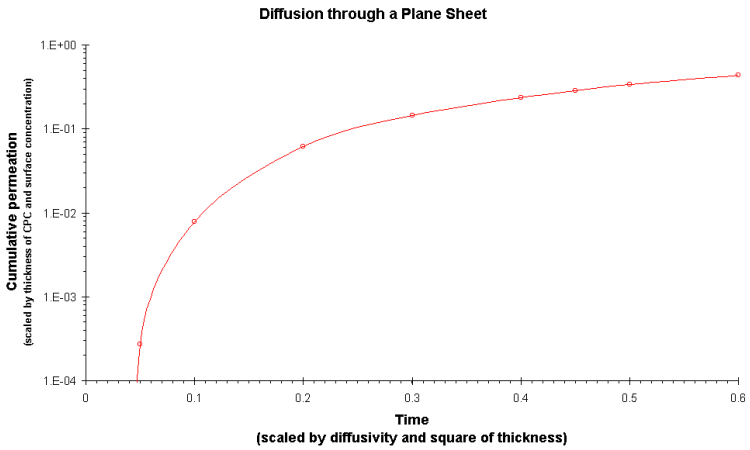


Figure 23 Cumulative Permeation, log scale

In this form, the curve looks very different from Figure 22, but it is the same data. The Log scale emphasises the low values and it can be seen that if a detector is sensitive enough, Breakthrough could be detected almost immediately with ANY chemical – CPC combination.

That's why the cover states that.

> *"Complete protection by Chemical Protective Clothing and the sighting of Flying Pigs are equally common"*

It is up to the hygienist to determine whether the amount of chemical is significant.

