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Glove permeation of chemicals: The state of the art of current practice—Part 2. Research emphases on high boiling point compounds and simulating the donned glove environment

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ABSTRACT

This second part of the review of the 21st century literature on glove permeation is divided into the following major themes; permeation data and mathematical models, exposure/risk assessment, and manufacturer data. The major issues in the literature were the demonstrations that increasing temperature and applying forces increased permeation; and that glove manufacturer data were sometimes not reproducible. Double gloving of disposable gloves was found to be effective in resisting chemical permeation for short periods of time. Harmonization of standards and commercial glove classifications were called for at conditions that were closer to the temperature and applied forces actually present in the workplace, including whole glove testing and quantitative rather than just qualitative criteria. More research was recommended in each section and subsection with particular emphasis on defining the efficiency of solid phase collection devices, and more data in areas like exposure to cosmetics, household products, liquid foods, drinks, and cleaning liquids. More research in exposure assessment for permeated chemicals with sensors on the inner glove surface and on the skin was called for. Finally, it was decided that the state of the art of current practice was in a situation that needed the permeation standards, research, and the permeation charts of glove manufacturers to be at conditions that better reflected those encountered by workers with donned gloves.

KEYWORDS

Commercial permeation classifications; glove permeation review; mathematical models; risk assessment

Introduction

This is the second part of the review on chemical permeation through gloves. The first part considered the basics, the permeation standards, and whole glove alternatives (Banaee and Que Hee 2019).

The previous comprehensive reviews of the glove permeation scientific literature came in the late 20th and early 21st centuries (Boeniger and Klingner 2002; Brouwer et al. 2005; Klingner and Boeniger 2002; Mellstrom and Boman 1994; Schwoppe et al. 1988). The ASTM and the International Program on Chemical Safety (IPCS) Symposia were also very important from 1984 onward. So were the publications of a book edited by Mellstrom et al., (1994) a 1999 book edited by Forsberg and Keith (1999b), the most recent 2014 glove selection quick guide handbook of Forsberg et al. (2014), and a glove permeation computer data base still being updated by Forsberg

and Keith (1999a) from 1999. There have been reviews in specialty areas for permeation of wood preservatives by Garrod et al. (1999), of mineral oils by Irzmanska and Dynska-Kukulska (2012), and of chemotherapy drugs by Landeck et al. (2015). Many reviewed general glove selection and properties (Blayney 2001; Cherrie et al. 2004; Zuther and Marschner 2004, 2005; Packham 2006, 2009; Cieslik et al. 2013; Forsberg et al. 2014).

The aims were the following:

- Detail the major research areas with attention on challenge chemical types, permeation cell conditions, workplaces, issues, and needs for future research
- Assess the impact of these data on glove selection for industrial hygienists and environmental professionals who recommend gloves for their workers in terms of worker exposure, risk assessment, and manufacturer chemical resistance charts.

Table 1. Review reference totals through time for the review portions with references.

Portion	Subportion	Reference Totals by Year			
		<2000	2000–10	2010–18	All
Introduction		6	9	5	20
Low ... Mixtures		1	23	19	43
	General ... Studies	1	10	3	14
	Temperature Effects	0	1	1	2
	Glove Reuse	0	1	1	2
	Tensile ... Forces	0	3	10	13
	Double Gloving	0	2	1	3
	Solid Collection	0	6	2	8
	Gas-Vapor Permeation	0	0	1	1
High ... Mixtures		19	49	31	99
	Que Hee ... Team	13	16	7	36
	Other ... Studies	1	5	5	11
	Petroleum	0	6	3	9
	Glycol Ethers	0	1	0	1
	Isocyanates	0	1	3	4
	Chemotherapy Compounds	1	7	7	15
	Dental Compounds	1	6	1	8
	Hairdressing Compounds	0	2	1	3
	Miscellaneous Liquids	0	2	1	3
	Organic Solids	3	3	3	9
Mathematical ... Law		3	12	2	17
Exposure/Risk Assessment		3	20	17	40
	Glove Toxins	0	5	5	10
	Permeant Toxins	3	14	10	27
	Epidemiology Studies	0	1	2	3
Glove ... Classifications		4	11	16	31
	Introduction	1	4	8	13
	Permeation Classifications	3	7	8	18
Totals		36	124	90	250

The current review is subdivided into three major themes: permeation data and mathematical models; exposure/risk assessments; and glove manufacturer permeation classifications.

Table 1 summarizes the number of references cited. Though there were 190 references in this review, there were multiple citations that contributed to the total of 250.

Unless specifically indicated otherwise, all gloves investigated are chemically protective clothing (CPC). The collection flow rates of open-loop and recirculating closed-loop systems for permeation cells, temperatures and determinant analytical techniques are specified. The references in each distinct section and subsection are in chronological order to allow the reader to assess change over time. Each subsection ends with a summary: the first paragraph provides the major points in the literature cited; the second paragraph contains the major future research needs for information gaps.

Permeation data and mathematical models

Low boiling point solvents, gases/vapors, and their mixtures

General liquid studies

Acetone, 1-butanol, chloroform, 1,2-dichloroethane, methyl chloroform, and toluene were studied singly

and in admixture at 21 °C relative to butyl rubber, natural rubber, nitrile, and neoprene in an ISO-CEN type stainless steel permeation cell of diameter 2.54 cm at an open-loop collection air flow rate of 100 mL/min (Park and Zellers 2000a). The breakthrough times (BTs) at 1 µg/cm²/min from a portable microsensor array were within ±3 min of those from gas sampling valve gas chromatograph-flame ionization detection (GC-FID). Further studies with this microsensor array using vapors of benzene, 2-butanone, *n*-butyl acetate, perchloroethylene, 2-propanol, toluene, trichloroethylene, *m*-xylene, and water unsuccessfully attempted to deal with relative humidity (RH) interferences; there were also selectivity issues with mixtures containing more than four components and isomers (Cai et al. 2000; Park and Zellers 2000b). A concentrator/thermal desorption variant of this instrument to increase selectivity with 3 microsensors was then successfully tested against the vapors of 16 single solvents and their binary mixtures in the 10–300 ppm range for acetone, benzene, 2-butanone, *n*-butylacetate, dichloromethane, 1,4-dioxane, *n*-hexane, isoamyl acetate, isooctane, 2-methoxyethanol, perchloroethylene, 2-propanol, tetrahydrofuran, toluene, trichloroethylene, and *m*-xylene (Hsieh and Zellers 2004; Park et al. 2000). As the

number of components increased and the more dilute the mixture became, the less accurate were the responses compared with GC-FID data, and the greater the complexity of the pattern recognition computer process to assign the concentration of each component. Nevertheless, for glove permeation purposes for single and up to three-component mixtures, the system had promise to yield semiquantitative direct reading screening data. The field monitoring of air between the skin and the glove or detecting breakthrough within the inner air space of just doffed gloves at shift breaks for up to three-component mixtures is possible if relative humidity interference does not occur.

Ethanol and methanol singly and their precursor tri- and tetra-alkoxy silanes and siloxanes were tested on nitrile, neoprene, butyl, PVC, and 4H-laminate gloves using the open-loop ASTM F739-96 with a 2.54 cm permeation cell operated at 150–500 mL/min of collection air at 22 °C and with GC-FID (Nelson et al. 2000). The laminate protected over 8 hr against all chemicals. The permeation behavior of the hydrolysis alcohol was correlated with its parent silane or siloxane. Ten compounds produced ethanol and three generated methanol as hydrolysis products. PVC always had the shortest BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ if permeation occurred. PVC generally also showed the biggest SSPR.

Closed-loop studies included: sulfuric, hydrochloric, and nitric acids through neoprene, nitrile, and PVC in a EN 374 cell with water collection at 23 °C and measuring the BT at pH 3.5 (Liwkowicz and Kowalska 2000); toluene and acetone through neoprene, butyl, and nitrile in a 2.54 cm AMK cell (similar to the Franz cell) with air collection at 23 °C and MIRAN gas analysis to provide detection BTs (Gao et al. 2005); N,N-dimethylformamide and 2-butanone through neoprene in a 2.54 cm ASTM cell at 25 °C using various collection solvents of which methanol was optimal at 100 mL/min with GC-FID to provide BTs at 10 $\mu\text{g}/\text{cm}^2/\text{min}$ (Chao et al. 2010); aniline through CPC and disposable latex gloves in a Franz cell (Chien et al. 1983); International Organization of Standards (ISO) (2001); Permegear (2019) with aqueous collection medium and liquid chromatography/ultraviolet detection (LC-UV) at 12 hr of permeation, where the CPC material proved effective but not the disposable glove material against 0.01 and 0.102 mg aniline/mL aqueous solution, presumably at 37 °C (Feng et al. 2012); and up to 25% tetramethylammonium hydroxide in water through nitrile and natural rubber in a ASTM cell with water collection and an unspecified analytical technique, with nitrile

superior relative to the BT at 0.25 $\mu\text{g}/\text{cm}^2/\text{min}$ at the same temperature (23 °C and 35 °C) (Su et al. 2013).

Summary

These open- and closed-loop studies demonstrate the use of the permeation standards at many different conditions to obtain permeation parameters with six studies being at 21–25 °C, and the two studies of 2012 and 2013 using temperatures of 35–37 °C.

Development of microsensors to detect vapor breakthrough inside gloves at breaks or continuously during a work shift needs to be researched further. More permeation studies at 35–37 °C are needed.

Temperature effects

Butyl and nitrile gloves were challenged by acetone and ethyl acetate in open-loop testing with a EN 374 type permeation cell operated at 35/35 °C, 23/35 °C, and 23/23 °C, for temperatures outside/inside the glove using 1 $\mu\text{g}/\text{cm}^2/\text{min}$ BTs (Evans et al. 2001). The butyl glove showed no permeation at these conditions. The average acetone steady state permeation rate (SSPR) through the nitrile glove at 35/35 °C increased 36%, and at 23/35 °C, 22%, relative to the observed data at 23/23 °C, the latter also being 37% more than expected from manufacturer data at the same temperature. The respective average BTs decreased 27% and 14%, respectively, and the measured BT at 23/23 °C was 2.15 times longer than expected from manufacturer data at that temperature. For ethyl acetate, the respective data for the SSPR showed increases of 37% and 11%, respectively, relative to 23/23 °C data, with the observed rate of the latter being 63% less than expected from manufacturer data at that temperature. Similarly, the respective average BTs decreased 40% and 4%, relative to 23/23 °C data, the latter being 24% shorter than manufacturer data at that temperature.

Tetramethylammonium hydroxide in 25% aqueous solution that challenged natural rubber and nitrile in a closed-loop ASTM cell referred to in the previous section also showed similar behavior (Su et al. 2013). At 35 °C, the respective BTs at 0.25 $\mu\text{g}/\text{cm}^2/\text{min}$ were reduced by 24% and 43% compared to those at 23 °C, but the respective average SSPRs similarly decreased 35% and 16%.

These data imply a factor of about two might be used to convert 23 °C data to 35 °C for BTs for these CPC nitrile gloves. For example, a BT of 30 min at 23 °C is approximately equivalent to 15 min at 35 °C. The SSPR data are more complex. Not enough data

exist to make such approximations for other glove types, a data gap that needs filling.

Summary

BTs for acetone and ethyl acetate challenging nitrile gloves in an open-loop system were decreased 24 to 40% by increasing temperature from 23 °C to 35 °C, with SSPRs increased by 36–37%. A 23 °C challenge with 35 °C collection produced intermediate values. The irreproducibility of manufacturer permeation data at 23 °C for the nitrile gloves tested was also demonstrated, observed BTs for ethyl acetate and acetone being shorter, and the acetone SSPR being larger and the ethyl acetate SSPR being smaller. The tetramethylammonium hydroxide in 25% aqueous solution closed-loop system also showed shorter BTs but lower SSPRs at 35 °C compared with at 23 °C.

More research comparing BTs and SSPRs at realistic skin (35 °C) and room temperatures is needed, but it is clear increasing temperature generally decreases BTs if there is permeation at room temperature.

Glove reuse

Gao et al. (2005) investigated neoprene, butyl, and nitrile gloves in a ASTM closed loop system after each thermal decontamination (air dried for 3 hr followed by 100 °C for 16 hr per cycle) for up to 10 cycles. The changes in detection BTs and SSPRs for toluene and acetone were 12% and 14% after 7 cycles, and 27% and 16% after 10 cycles with the detection system described previously in General Liquid Studies. The only exception was for butyl/toluene where BT differed after one cycle, and the SSPR differed after five.

The reuse of neoprene gloves was not justified for a 1:1 (v/v) dimethyl formamide/2-butanone mixture after aeration at 25 °C or heating at 40 °C (Chao et al. 2011). A stainless steel ASTM permeation cell system was used with methanol collection solvent at 25 °C in a recirculating closed-loop system at 100 mL/min with a sampling point. Analytes were quantified by GC-FID. Reuse was possible after heating at 70 °C or 100 °C for 10 hr followed by aeration.

Summary

Both literature studies took advantage of the volatility of acetone, 2-butanone, dimethylformamide, and toluene as a removal/“cleaning” mechanism at elevated temperature and aeration to optimize the conditions for glove reuse. High boiling point solvents are not as amenable to such methods.

The costs of new gloves versus the costs of reuse have to be weighed.

Tensile strength and forces

The BT at 1 µg/cm²/min of cyclohexane through a stretching neoprene membrane (0.069 cm thickness) was not significantly affected by 200 N force every alternate 5 sec exerted by a piston (Krzeminska 2014). The force was administered in a modified stainless steel large EN 6529 gravity permeation cell with open-loop air collection at 265 mL/min at room temperature with in-line gas sampling valve GC-FID. The BT was shortened by 20% relative to no force for a fabric coated with butyl rubber (0.035-cm thickness) when subjected to a force of 200 newton for every alternate 5 sec ethyl acetate BTs through butyl rubber membranes (0.039-cm thickness) and a fabric coated with butyl rubber (0.35-mm thickness) decreased about 30% at 100 newton every alternate 5 sec relative to no force.

The BTs at 0.4 µg/cm² were determined (Phalen et al. 2014) with a 10.6 eV photoionization detector for disposable whole gloves (palm thicknesses 0.010–0.013 cm) subjected to forces and not, during ethanol challenge in a stainless steel-glass environmental chamber at 21.4 °C for latex (–23% relative to no forces) and nitrile (–31%) gloves. The forces were exerted by inflating and deflating the gloves with air at 0.1 inch of water pressure every 30 sec. The SSPR for nitrile was increased by 47%, but was not affected for latex. Only the nitrile glove showed enhanced cumulative permeation at 30 min (111%). Vinyl gloves showed no permeation. Tensile strength accounted for only 1% of the nitrile permeation dependence, the major factors accounting for 53–67% dependence being area density (glove weight per glove external surface area in g/cm²), acrylonitrile content, carboxylation of the base polymer, the amount of extractable oils and oily plasticizers, and polymer uniformity (Phalen and Wong 2015). The results were similar to those for nitrile leak penetration potential (Phalen and Wong 2012b). The mechanism of ethanol permeation through nitrile was also investigated by positron annihilation lifetime spectroscopy to define the factors that contributed to the nitrile material's free volume (Pham et al. 2015). The latter did not involve interaction with the nitrile chemical functional group.

Banaee and Que Hee (2019) have also discussed the effects of applied forces on permeation of solvents for whole gloves (Banaee and Que Hee 2017; Mathews and Que Hee 2017a,b; Phalen and Que Hee 2008; Phalen and Wong 2012a).

Summary

These two studies at room temperature indicated that the thinner the glove the more likely that BT will

decrease and SSPR will increase when force is applied. The interaction at the same temperature depends on chemical and glove type, glove thickness, and magnitude of the force.

Permeation behavior near the glove maximum critical tensile strength and force needs further investigation at 35 °C.

Double gloving

The permeation of 70% isopropyl alcohol through disposable natural rubber glove pieces using an EN 374 permeation cell with open-loop nitrogen collection at 474 mL/min showed that the BT at 1 $\mu\text{g}/\text{cm}^2/\text{min}$ and 23 °C with gas-sampling valve-GC-FID of the single 0.022-cm glove piece of 4.6 min increased to 80 min on double layering (Maekelae et al. 2003a). Formalin solutions permeated a single natural rubber disposable glove piece (BT of 17–67 min at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ at 23 °C and derivatization/LC-UVD), but did not through double layers (Maekelae et al. 2003b).

The BT at 0.25 $\mu\text{g}/\text{cm}^2/\text{min}$ of 25% tetramethyl ammonium hydroxide in water through double natural rubber glove pieces at 23 °C was 17 times longer than for a single layer, and with a SSPR 3.6 times lower (Su et al. 2013). The natural rubber outside/nitrile inside combination was 1.35 times more resistant relative to BT than the reverse. Thus, the more resistant glove should be on the inside when donning dissimilar whole gloves.

Summary

The cited double-layering results with glove pieces support the conventional wisdom that double gloving of the same glove type should be much more protective than a single glove, with BTs ranging from 17 times longer to no breakthrough at 23 °C for the layering data in permeation cells. The more resistant glove should be on the inside when donning dissimilar whole gloves.

More double layering studies need to be done with glove pieces but at 35 °C and compared with field data for donned whole gloves.

Solid collection

Investigations of solid collection devices for solvents at 20–25 °C in closed-loop static collection systems ranged from direct reading colorimetric badges for aniline (Vo et al. 2000), organic and inorganic acids (Vo 2002; Vo et al. 2003), aldehydes (Vo and Zhuang

2009), and isocyanates (Ceballos et al. 2011), to sorbent materials like 3 M Empore filters for acetone, methanol, toluene, and trichloroethylene (Vo et al. 2001), and carbon cloth for organic solvents like 2-butanone, ethyl benzene, 2-heptanone, styrene, toluene, and xylene isomers (Tran et al. 2012). The analytical aspects to define sensitivity/lower limit of quantitation and selectivity (confirmation of identity, particularly important in colorimetric devices) were generally provided in these studies.

Summary

The analytical aspects to define sensitivity and selectivity were generally provided for the many solid collection devices cited.

It was unclear from all these studies how efficient was analyte transfer from the glove to the solid collection medium, this being mediated by the degree of fit, contact area of the collection medium to the glove, analyte volatility, the absorptive capacity of the solid medium, and the desorption efficiency of the determinant compound for subsequent quantification for non-direct reading solid devices. The relative order of resistance is probably valid for each study at the same conditions. Every solid collection device needs its collection efficiency determined for quantitative results. The solid media that are not direct reading also need the desorption efficiency of the desorbed determinant compound to be measured. Therefore, most of the results from studies using solid media are semiquantitative at best.

Gas/vapor permeation

The mass transfer coefficient and BT (at 8 ppm[v/v] = 30 mg/m^3) of toluene vapor through butyl (0.0253 cm) and nitrile (0.0638 cm) gloves were investigated with an open-loop large ASTM F739 permeation cell with the glove piece horizontal exposed to the liquid headspace vapor, with the upper collection chamber filled with nitrogen flowing at 55 mL/min at 25 °C and 60% RH, the permeation cell being in a water bath at 25 °C inside a walk-in stainless steel chamber at 25 °C and 60% RH (Cheng et al. 2012). A Fourier transform infrared spectrophotometer in absorption mode was used to measure the toluene vapor concentration in the collection gas. The mass transfer coefficient and BT were dependent on challenge vapor concentrations. Thus, the diffusion process was non-Fickian. The higher the concentration the shorter the BT. As glove thickness for the same

material increased at the same vapor concentration challenge, so too did the BT. Permeation rate versus time curves were sigmoidal rather than flat-topped. Swelling of the glove materials occurred and caused more flexibility according to tension testing. At a toluene challenge concentration of 140 mg/L, butyl rubber was four times less resistant than nitrile relative to BT, 2.5 fold of this being accounted for by the greater thickness of the nitrile glove. The gloves aged by 50 cycles of 0.63 W/m^2 ultraviolet radiation at 60°C for 8 hr, followed by condensation at 50°C for 2 hr showed much shorter BT and higher diffusion coefficients. Toluene vapor permeation was characterized by longer BT than from liquid toluene challenges at 25°C , but even so, swelling occurred.

Summary

A toluene vapor challenge of butyl and nitrile gloves produces longer BT than the corresponding liquid at the same temperature but was non-Fickian in nature and BT and diffusion coefficients are dependent on toluene vapor concentration. Materials artificially aged show much shorter BTs and larger diffusion coefficients than “new” ones.

Although less important than liquid challenges of the same volatile solvent, more vapor challenges investigations are needed but at 35°C , especially for sensitizers, carcinogens, and reproductive toxins, and also for such gases. The effects of aging on CPC materials need more research and this would be helped if glove manufacturers would date-stamp on the glove container when the glove lot passed its quality assurance/quality control tests.

High boiling point compounds and their mixtures

Much of the recent research has focused on liquids with boiling points near or above 150°C , solids, and mixtures.

Que Hee research team

The Que Hee research team started with the 1984 moving tray water bath technique for the large glass ASTM permeation cell (Mikatavage et al. 1984; Que Hee 1989) with closed-loop collection without recirculation to simulate gentle forces on test materials. This also provided efficient mixing for the isopropanol collection solvent when the glove materials (supported and unsupported/unlined nitrile and unsupported/unlined Viton) were exposed to liquid mono- and dichlorobenzenes and mono-chlorotoluenes at 25°C .

These compounds have boiling points above 150°C except for chlorobenzene (131°C). Unsupported nitrile was more resistant than supported nitrile relative to BT at $177 \mu\text{g/cm}^2$ using GC-FID, the SSPP on a mole/area/time basis being equivalent. Viton did not allow breakthrough within 4 hr.

The second permeation publication in 1989 featured a pesticide emulsifiable concentrate and its highest recommended aqueous emulsion spraying concentration for Esteron 99 containing the isooctyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) as active ingredient (Que Hee, 1989; Harville and Hee 1989). The 2.54-cm glass ASTM-type cell in the moving tray water bath technique at 30°C was used with hexane collection solvent in a closed-loop system without recirculation to test supported/unsupported and lined/unlined neoprene and nitrile gloves as well as Tyvek with collected samples analyzed by gas chromatograph-electron capture detection. Tyvek and the unsupported/unlined nitrile glove were the most resistant (at least 100 min for both), based on the time to permeate $10 \mu\text{g}$ of 2,4-D ester for both the emulsion concentrate and aqueous emulsion. The neoprene gloves degraded. The emulsion concentrate always permeated faster than the aqueous emulsion.

The third publication was a theoretical paper on glove permeation models based on consideration of solubility parameter, chromatographic theory, polarity, and liquid partition theory discussed in Mathematical Models Not Related to Fick's Law (Que Hee 1996).

The publication of a series of permeation studies at 30°C then occurred involving the 2.54-cm glass ASTM permeation cell with closed-loop hexane collection solvent without recirculation in the moving tray water bath technique and gas chromatograph-mass spectrometry (GC-MS) of moderately volatile single solvents through nitrile that were in pesticide formulations as “inert components”: alkylbenzenes of molecular weight 120 (Tsai and Que Hee 1996), and xylenes (Tsai and Que Hee 1997). These studies led to the conclusion that the physical properties of pure solvents did not correlate with the SSPP and BT when in mixtures for the same material. Similar experiments for the same system and conditions then followed for the active ingredient of pesticide emulsifiable concentrates and the highest recommended pesticide spray concentration in aqueous emulsion for chlorpyrifos and endosulfan (Khan et al. 1997); methomyl (Lu and Que Hee 1998); malathion (Lin and Que Hee 1998a,b,c,d); 2,4-D derivatives (Lin and Que Hee 1999); captan (Phalen et al. 2007); Phalen and Que Hee 2003, 2005, 2007, 2008; folpet (Zainal and Que

Hee 2003); telone (Zainal and Que Hee 2005); telone-chloropicrin (Zainal and Que Hee 2006a); benomyl (Zainal and Que Hee 2006b); comite (Zainal and Que Hee 2006c); dichlobenil (Que Hee and Zainal 2010a); and chlorothalonil (Que Hee and Zainal 2010b). The investigations also demonstrated the utility of Fourier transform infrared attenuated total reflectance as a direct reading technique to detect pesticides on glove surfaces after permeation and to measure glove surface integrity. The malathion formulation studies (Lin and Que Hee 1998a,b,c) resulted in a kinetic model for the permeation of all liquid components in a malathion emulsifiable concentrate based on mass fraction, the logarithm of the octanol/water coefficient, and the molar volume of each component. For the solid pesticides studied, the “inert component” solvents, their composition, and their interaction with the material determined the pesticide permeation. The Captan studies also assessed nitrile disposable glove properties like acrylonitrile content (Phalen et al. 2007), and variation of glove quality control and assurance among manufacturers (Phalen et al. 2007; Phalen and Que Hee 2005, 2007).

Metalworking fluid permeation was also similarly investigated for disposable and CPC gloves at 35 °C using the 2.54-cm glass ASTM permeation cell in the moving tray water bath technique and GC-MS to investigate glove swelling behavior, permeation in the field, and the best collection solvent for nitrile disposable gloves challenged by non-polar solvents since hexane degraded them (Xu and Que Hee 2006a,b; 2007, 2008a,b; 2010). The optimum collection solvent for nonpolar analytes was perfluorohexane.

More recent work since 2008 (Banaee and Que Hee 2017; Mathews and Que Hee 2017a,b; Phalen and Que Hee 2008) resulted in the developments of the first recirculating closed-loop system using water at 35 °C as collection solvent for a whole glove dextrous robot hand in 2017, and of the first quantitative leak test for whole glove and glove piece chemical penetration (Mathews and Que Hee 2016). The dextrous robot hand results were discussed in part one of this review (Banaee and Que Hee 2019).

Summary

The moving tray water bath technique was used to simulate gentle forces on pieces of the CPC and disposable glove materials as well as to provide efficient mixing for the collection and challenge solvents at various temperatures for an ASTM permeation cell with a closed-loop collection system without recirculation. The challenges evaluated included xylenes,

molecular weight 120 aromatic hydrocarbons, pesticide formulations, and their aqueous emulsions at highest field use concentrations, liquid and solid pesticides, and metal working fluids. Many collection solvents were also evaluated with water the best for polar organics challenges, and perfluorohexane good for nonpolar ones. Dextrous robot hand systems were developed for a solid pesticide employing solid glove collection and for water soluble nonvolatile organic solvents that involved closed-loop collection systems with water recirculation. Mathematical models of permeation were also developed and compared for single solvents and mixtures.

Dextrous robot hand systems need to be developed for volatile and moderately volatile non-polar challenge solvents to study permeation through the thinnest gloves.

Other pesticide permeation studies

The permeation cell studies involving pesticide exposure to glove pieces used a closed-loop collection without recirculation configuration unless stated otherwise.

A sampling patch technique sensitive to the picogram level using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that reused coveralls still allowed about 10% of the previously applied dose of copper-chromium-arsenic, solvent- and water- based wood preservatives to be sampled by inside patches (Garrod et al. 1999). The insides of reused gloves always showed some residual permeation/penetration. Wearing fresh gloves each time decreased exposures to arsenic by 71% and to permethrin by 37% relative to reused gloves as also confirmed by the results of biological monitoring of worker urinary arsenic, chromium, and permethrin metabolites. Resistance to permethrin was also tested by intercepting the skin-bound fraction with an inner prewashed cotton glove underneath the protecting glove and extracting the pesticide for final GC-MS analysis. Geometric mean protection factors (the protection factor is defined as the pesticide skin coverage in pesticide weight/skin area units without the glove divided by that with the donned glove in the same units) of 96, 470, and 200 were determined for PVC (0.12 cm thickness), and for two nitrile gloves (0.044 and 0.048 cm thickness), respectively. These gloves were rated not to permeate within 8 hr. Most of the exposures occurred when the pressure sprayer malfunctioned. When gloves were used for nonagricultural purposes, pesticide was almost always detected on the inner cotton glove especially for reused CPC

gloves, mostly by contact with contaminated surfaces during donning and doffing (Garrod et al. 2001).

Granular Terbufos breakthrough as assessed by gas chromatography-nitrogen-phosphorus detection was dependent on the degree of contact of the solid collection patches with the inner side of the glove, alpha-cellulose being superior to cotton gauze (Guo et al. 2001).

The permeation of 2-methyl-4-chlorophenoxyacetic acid (MCPA) herbicide emulsifiable concentrates through nitrile (0.0301 cm thickness), neoprene (0.0790 cm), viton-coated neoprene (0.1877 cm), and natural rubber (0.1750 cm) glove pieces, took more than 24 hr for the salt formulation and 8 hr for the ester formulation using an ASTM cell and liquid collection with 0.01 M sodium hydroxide solution and LC-UVD with a BT based on 10 µg accumulated (Purdham et al. 2001). Nitrile was most resistant and also swelled the most.

The permeation of a paraquat formulation Contact 280 (9.35%) through 12 households, CPC, and medical (disposable) glove materials in an ASTM cell with water collection solvent revealed no detected permeation of paraquat through the nitrile gloves within 5 hr with LC-UVD quantitation (Saad et al. 2004). An ASTM cell with water collection solvent evaluation of 2,4-D in D-Amine 720 formulation showed that nitrile gloves (disposable and CPC) resisted permeation up to 8 hr relative to other CPC, household, and disposable types, using LC-UVD quantitation (Saad et al. 2006).

Six types of glove pieces (natural rubber latex (0.0099 cm thickness), vinyl (0.0121 cm), nitrile (0.0125 cm), neoprene-latex (two: 0.0600 and 0.0707 cm), and butyl (0.0354 cm) were evaluated over 8 hr at 35 °C with EN-374-3 and ASTM F739-12 cells with the membranes horizontal rather than vertical (Berankova et al. 2017). The challenges were with aqueous emulsions of emulsifiable concentrates of Mospilan 20SP (acetamiprid; 1.00 µg/cm²), Pirimor WG50 (pirimicarb; 18.8 µg/cm²), and Reldan 22 (chlorpyrifos methyl; 24.8 µg/cm²) with a collection fluid of stirred artificial sweat supplemented by PEG-20 oleyl ether surfactant for the last pesticide. Natural rubber latex was permeated as detected by LC-UVD by chlorpyrifos methyl in 10–15 min at 0.84 µg/cm², by acetamiprid in 50–60 min at 0.10 µg/cm², and by pirimicarb in 20–30 min at 0.42 µg/cm². The respective vinyl glove BTs were 35–40 min, 120–150 min, and 40–50 min at a unspecified BT criterion. Butyl rubber was impervious. The two neoprene gloves did not permeate before 270 min for chlorpyrifos-methyl and beyond 8 hr for the other formulations. Disposable nitrile permeated at 150–180 min for the first two formulations and at 45–60 min for chlorpyrifos-methyl.

Glove pieces kept on permeating after being removed from exposure.

Two types of PVC glove pieces challenged by technical grade dichlorvos and a diazinon formulation were evaluated for 8 hr with 2.54 cm ASTM cells at 23 °C and 45 °C (Ismail et al. 2018). Application strength aqueous dichlorvos broke through (1 µg/cm²/min) only at 45 °C (≥180 min) whereas the undiluted form broke through at both temperatures (180 and 60 min, respectively). The BT at 45 °C was one-third that at 23 °C. Diazinon did not break through except for the undiluted form at 45 °C (≥120 min). Gloves pre-exposed to ultraviolet light for undiluted dichlorvos and abrasion (over double the cumulated permeation relative to unabraded for both undiluted pesticides) were much less resistant. Thus, increasing temperature increases permeation.

A solid-state collection technique within a Teflon permeation cell with solid disk collection was approved for nonvolatile pesticide active ingredients as part of an ISO 19918 standard in 2017 (International Organization of Standards (ISO) 2013, 2017). A pendamethalin emulsifiable concentrate was used for developmental work at room temperature (Shaw et al. 2017). The efficiency of transfer of the pesticide to the solid collection element was not provided but the collection material was chosen on the basis of cumulated mass at a designated time. Penetration also occurred for many solid collection elements and it was unclear whether one shaking of the aqueous emulsion was adequate to have a constant challenge concentration for and during every trial.

Elbow-length PVC gloves are often recommended for protection against organophosphorus pesticide exposure in agriculture. Glove permeation tests were conducted (Ismail et al. 2018) using ASTM cells with pieces from two PVC elbow glove brands at 23 °C and 45 °C for up to 8 hr. Technical grade dichlorvos and formulated diazinon were used undiluted and at application strength in water. Breakthrough at 1 µg/cm²/min of undiluted dichlorvos occurred at both 23 °C and 45 °C, but only at 45 °C for application strength as detected with LC-UVD. Breakthrough of diazinon did not occur, except when undiluted at 45 °C. UV-exposed and abraded glove pieces showed reduced performance, with the effect being approximately 2-fold for dichlorvos. Only small differences were noted between glove brands.

Summary

CPC gloves exposed to high boiling point nonpolar liquids or nonpolar solid pesticides in solvents were often not reusable since the gloves were difficult to

clean. Increasing temperature increased pesticide permeation in two studies when the glove was not impervious, emulsion concentrates always permeating more than aqueous emulsions simulating field spraying conditions. The active ingredient BT at $1.0 \mu\text{g}/\text{cm}^2/\text{min}$ and 45°C was one-third that at 23°C for a dichlorvos formulation. Including the Que Hee team pesticide studies, the permeations of at least 19/26 pesticides reviewed were studied at temperatures $\geq 30^\circ\text{C}$ to simulate skin surface temperatures rather than room temperature.

The new ISO 19918 standard with solid collection should be compared with the 2.54 cm ASTM-type cell in the moving tray water bath technique at 35°C with a collection solvent that solubilizes the permeant but is inert to the glove for water-insoluble organics, or water collection for water soluble organics.

Petroleum

Petroleum fractions and blends, often used in pesticide emulsifiable concentrates, were also examined. Thus, the permeation of gasoline, diesel, bioethanol (E-85), and biodiesel (B20) fuels through CPC neoprene (0.051 cm thickness), nitrile (about 0.061 cm), and Viton (about 0.041 cm), and through disposable latex (0.014 cm), nitrile (0.011 cm), and vinyl (0.014 cm) in an ASTM F739 open-loop configuration at 25°C at 130 mL/min collection showed that gasoline had the shortest breakthrough times at $0.1 \mu\text{g}/\text{cm}^2/\text{min}$ as detected by a 10.6 eV PID, and that Viton was the most protective glove (Chin and Batterman 2010). The composition of the permeated vapors differed from that of the original liquids, being enriched in the high vapor pressure components.

Three oils were collected in a permeation cell by solid Whatman GF/C and GF/A glass fiber filters to a sensitivity of $3 \mu\text{g}/\text{mL}$ as detected by ultraviolet absorption spectrophotometry (Irzmanska et al. 2010).

The contributions of the Que Hee group for metal-working fluids have already been noted (Xu and Que Hee 2006a,b; 2007, 2008a,b; 2010). The permeation of mineral oils has been reviewed and the authors' solid sorbent collection methods included (Irzmanska and Dynska-Kakulska 2012).

Summary

The permeation of complex liquid mixtures in an open-loop permeation system with gas collection may lead to unexpected changes in the composition of the gas collection vapor relative to the original liquid.

The efficiencies of any solid collection media need to be determined.

Glycol ethers

Glycol ethers are often used in pesticide emulsifiable concentrate formulations as adjuvants to promote water solubility, surface tension optimization, or as antifreezes.

The permeation of four glycol ethers (2-propylene glycol-1-methyl ether, ethylene glycol n-butyl ether, diethylene glycol ethyl ether, and diethylene glycol butyl ether) using EN 374 and EN 369 testing conditions revealed that 0.45-mm and 0.65-mm-thick butyl gloves had BTs at $1 \mu\text{g}/\text{cm}^2/\text{min}$ greater than 8 hr (Martin et al. 2006).

Summary

Butyl gloves had the longest BTs against the small set of low molecular weight glycol ethers tested. More glycol ethers should be evaluated for CPC and disposable gloves at 35°C .

Isocyanates

A novel permeation panel was developed (Ceballos et al. 2011, 2014a) to test the permeation of sprayed monomers and oligomers of 1,6-hexamethylene diisocyanate and isophorone diisocyanate against 0.010–0.013 cm latex gloves. Monomers but not oligomers permeated immediately at $0.0029 \mu\text{g}/\text{cm}^2/\text{min}$ as shown by direct indicating Swypes and fiberglass filters impregnated with 1-(2-pyridyl)-piperazine whose derivatization products were analyzed by LC-UVD with a sensitivity of $0.1 \mu\text{g}$. Butyl gloves (0.033 cm) showed no permeation unlike nitrile (0.013 cm) and natural rubber latex (0.013 cm), with latex permeating fastest.

Minimal glove permeation for health care personnel through 0.013-cm-thick nitrile gloves occurred for diphenyldiisocyanate emitted during the application of orthopedic casts as evinced by biological monitoring, environmental measurements, and direct glove testing with Permea-Tec direct reading Swypes of sensitivity $5 \mu\text{g}$ (Pearson et al. 2013).

Diisocyanates (isocyanates), including methylene diphenyl diisocyanate (MDI), are the primary reactive components of spray polyurethane foam (SPF) insulation. Five common disposable garment materials (disposable latex gloves [0.07 mm thickness], nitrile gloves [0.07 mm], vinyl gloves [0.07 mm], polypropylene coveralls [0.13 mm], and Tyvek coveralls [0.13 mm]) were tested by Mellette et al. (2018). These materials were cut into small pieces and assembled into a permeation test cell system and coated with a two-part slow-rise SPF insulation. Glass fiber filters (GFF) pretreated with 1-(9-anthracenylmethyl)piperazine were used underneath the garment to collect permeating

isocyanates. GFF filters were collected at specific time intervals between 0.75 and 20.00 min and subsequently analyzed using liquid chromatography-mass spectrometry (LC-MS). The cumulative permeated concentration of total isocyanate, including phenyl isocyanate and three MDI isomers, was measured over the test time. The estimated BT, average permeation rate, and standardized breakthrough time (SBT) at the estimated $0.1 \mu\text{g}/\text{cm}^2/\text{min}$ permeation rate were also determined. Typical isocyanate loadings were in the range of $0.900\text{--}15 \mu\text{g}$ MDI/ cm^2 . Each type of glove material had an observed average permeation rate well below the ASTM F739 SBT. Disposable latex gloves displayed the greatest total isocyanate permeation rate ($4.11 \text{ ng}/\text{cm}^2/\text{min}$), followed by the vinyl and nitrile gloves, respectively. Nitrile gloves also showed the lowest cumulative permeation.

Summary

A butyl glove that does not allow detectable permeation $<0.1 \mu\text{g}/\text{cm}^2/\text{min}$ in permeation cell experiments is the most resistant one to wear against 1,6-hexamethylene diisocyanate and isophorone diisocyanate.

It was unclear whether the low permeation rates for the MDI and the 1,6-hexamethylene diisocyanate and isophorone diisocyanate studies reflected material chemical resistance, poor solid collection efficiency, low challenge concentrations, or all factors, though the relative order of glove resistance is probably valid. More research is needed in determining the importance of such factors.

Chemotherapy compounds

The June 8, 1997 mercury poisoning death of a healthcare researcher handling dimethyl mercury that she spilled on August 14, 1996, within a fume hood on her latex glove which did not protect her, brought public and scientific attention to glove permeation in healthcare work settings (Blayney 2001; Nierenberg et al. 1998).

The healthcare workplace has been the area of greatest growth in the 21st century in the assessment of permeation of glove materials. Healthcare gloves are usually disposable, most drugs are nonvolatile, and formulations are often used. Most of the analytical chemistry techniques to detect permeated drugs involve LC-appropriate detector hyphenated methods, immunoassays, or bioassays. Unless stated otherwise, the permeation cell systems discussed are closed-loop collection without recirculation.

Antineoplastic, cytotoxic, chemotherapeutic, chemotherapy drugs are nonvolatile solids that are usually dissolved in or diluted with isotonic solutions before intravenous injection. The permeation potential is largely determined by the solvent, glove quality, and injector expertise.

Latex gloves (0.018–0.022 cm thickness) hydrated between 2–30 min in isotonic saline and by 30 min of surgical usage lost their electrical and mechanical resistance with the rupture load decreasing by 24% (Hentz et al. 2000).

The effect of 70% isopropyl alcohol pretreatment (to simulate cleaning/disinfection work practices before injection) was investigated (Connor and Xiang 2000) on disposable 0.025-cm-thick natural rubber latex and 0.017 cm nitrile glove finger-tip permeation of the antineoplastic agents carmustine, cyclophosphamide, 5-fluorouracil, doxorubicin (adriamycin), thiotepa, and cisplatin at standard administration concentrations at 23°C using a *Salmonella typhimurium* reverse mutation bioassay for mutagens and LC-UVD for non-mutagens. Pretreated latex for 1 min and 5 min caused detection of camustine by a *Salmonella* reverse mutation assay. The pretreatment did not appear to change glove permeation of the drug.

Carmustine solution permeated a single-layer latex glove piece of unspecified thickness from the cuff after 180 min with breakthrough at about 45 min in a EN 374-3 permeation cell with water as collection solvent at 20°C and LC-UVD detection, but did not reach the $1.0 \mu\text{g}/\text{cm}^2/\text{min}$ EN critical level (Klein et al. 2003). Double layered latex did not allow carmustine permeation.

A study on the inside-out middle finger of neoprene, natural rubber latex, nitrile, and vinyl gloves of thicknesses 0.012–0.033 cm involved challenges with solutions of thirteen cytotoxic agents with water collection at 25°C and quantitation by LC-MS-MS (Wallemacq et al. 2006). Vinyl, the thinnest glove, permeated the most. Carmustine permeated most of the materials by 60 min. The same research group (Capron et al. 2012) 17 antineoplastic drug solutions evaluated with LC-UVD analysis under conditions of dynamic contact with neoprene, natural rubber latex, nitrile, or synthetic polyisoprene at 37°C with and without pretreatment with 70% isopropyl alcohol or ethanol. None of the permeations exceeded EN 374-3 or ASTM F739 critical limits but carmustine exposure for 60 min exceeded the ASTM D-6978 limit of $0.010 \mu\text{g}/\text{cm}^2/\text{min}$ at 35°C for two single natural rubber gloves (one of thickness 0.0230 cm and another 0.0180 cm thick). Double layering resulted in no

observed permeation in all instances even at 43 °C. The permeation of 70% isopropyl alcohol through surgical gloves of natural rubber and chloroprene rubber using the ASTM F739 and EN 374 methods has been referred to above (Maekelae et al. 2003a), but these single surgical glove layers also resisted aqueous solutions of 45% potassium hydroxide, 13% sodium hypochlorite, 30% hydrogen peroxide, 2% glutaraldehyde, and 0.35% chlorhexidine digluconate.

To assess if low-level permeation could be biologically important to the skin was examined by using doxorubicin solution (2 mg/mL in isotonic sodium chloride solution or in 0.05 M formic acid pH 2.0) to challenge two disposable natural rubber gloves and one disposable nitrile glove of thickness 0.01–0.03 cm (Boccellino et al. 2010). The inner and outer exposed surfaces were wiped with gauze soaked in 0.05 M formic acid at 0, 30, 60, and 480 min and analyzed by LC-fluorescence detection. Natural rubber and nitrile did not permeate at neutral pH apparently at room temperature. At acid pH, nitrile (but not natural rubber) permeated to the extent of 0.56% in 480 min. Concentrations above 0.0025 mg/mL caused effects on human keratinocyte cell line DNA, this being below the equivalent concentration observed on the glove inside for the acid challenge of the nitrile glove at 480 min. The same research group did a similar study with the same gloves on epirubicin with similar results (Pieri et al. 2013).

Five antineoplastic agents (cyclophosphamide, doxorubicin hydrochloride, etoposide, fluorouracil, and paclitaxel) at their maximum administration concentrations were evaluated against three disposable glove types (chlorinated latex, non-chlorinated latex, and nitrile of thickness about 0.01 cm) in a ILC14 continuous flow in-line permeation cell with LC-MS-MS analysis (Oriyama et al. 2017). Only cyclophosphamide and fluorouracil permeated through latex at 0.010 $\mu\text{g}/\text{cm}^2/\text{min}$, the chlorinated type being more resistant. The five drugs did not permeate nitrile. Double layering with chlorinated latex caused shorter BTs (at least a factor of 2) than a single layer.

Isotonic saline solutions of docetaxel (10 mg/mL with 25.1% [w/w] ethanol), 5-fluorouracil (50 mg/mL) and doxorubicin (1 mg/mL) were evaluated at 27 °C in a modified closed-loop (175 mL/min) EN ISO 6529:2001 permeation cell with LC-UVD (Krzeminska et al. 2018). Fluorouracil and doxorubicin did not permeate by 480 min for the 2.5 $\mu\text{g}/\text{cm}^2$ threshold through natural rubber latex (0.021 cm), nitrile (0.010 cm), neoprene, (0.017 cm), and layered materials Latex, nitrile, and neoprene resisted all three

cytostatic agents but the layered material did not block docetaxel, probably because of the presence of ethanol.

Summary

These healthcare glove studies with chemotherapy compounds and disposable gloves demonstrated that the thicker the glove piece the more drug resistant it was, and thus double layering to simulate double gloving, lowered permeation compared with a single layer. Some investigators used temperatures 35–45 °C to better mimic skin contact temperatures. A temperature of 37 °C caused carmustine isotonic solution to permeate a natural rubber latex glove >0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ in 60 min compared with 180 min at 20 °C.

The advent of ASTM D-6978 that standardized the permeation temperature at 35 °C (Banaee and Que Hee, 2019) will provide more realistic permeation data for disposable health care gloves exposed to antineoplastic agents. Other anticancer drugs not included in the ASTM D-6978 list also need testing.

Dental chemicals

Disposable gloves are commonly used in dental clinics. As with chemotherapy agent permeation, most dental chemical agents used for teeth are nonvolatile, and formulations are often used. Most of the analytical chemistry techniques involve LC-appropriate detector hyphenated methods. Unless stated otherwise, the permeation cell systems discussed are closed-loop collection without recirculation.

Nonvolatile acrylic compounds used as bonding agents in tooth repair and replacement have received scientific attention because of their contact sensitization effects. A mixture of 50% (w/w) 2-hydroxyethyl methacrylate (HEMA) and triethylene glycol dimethacrylate (TEGDMA) that challenged natural rubber and PVC disposable glove pieces resulted in breakthrough for both within 10 min in a EN 374 permeation cell (Maekelae et al. 1999). Natural rubber was more resistant. Double gloving of natural rubber with polyethylene gloves lengthened BTs to greater than n hr.

Mixtures of 1:1 (w/w) HEMA and TEGDMA were compared undiluted, diluted in ethanol, and diluted in acetone for the third inside-out finger of five types of disposable natural rubber latex and of five types of nitrile gloves with water collection without recirculation (Munksgaard 2000). The respective mean lag times extrapolated at the time axis from the steady state periods for all HEMA and TEGDMA data for latex were 4.9, 4.8, and 2.8 min at 37 °C as detected by

LC-UVD. For the disposable nitrile gloves, the respective lag times were 15.7, 9.9, and 2.8 min. Acetone decreased lag times, and ethanol also did for nitrile.

Further studies on disposable nitrile gloves showed that 0.01-cm-thick gloves resisted permeation for 30 min for low viscosity acrylates, 0.045 cm thickness resisted for 4 hr, and 0.056 cm thickness resisted for at least 8 hr (Zwanenburg 2000).

A study with pure methyl methacrylate, HEMA, and TEGDMA and 30% solutions in ethanol and acetone evaluated 9 different glove types at 21 °C using a Franz-type permeation cell with the outcome that all the gloves did not resist adequately (lag times <3 min) against methyl methacrylate at an nitrogen collection flow rate of 120 mL/min with gas sampling valve-GC-FID (Andreasson et al. 2003). Neoprene material resisted most relative to lag time for HEMA and TEGDMA using water collection and GC-FID analysis. The organic solvents decreased lag times and increased SSPRs, particularly acetone.

Loennroth and Ruyter (2002) evaluated two methacrylate mixtures (HEMA, TEGDMA, bisphenol-A dimethacrylate (BIS-GMA), ethoxylated bisphenol-A dimethacrylate (BIS-EMA), urethane dimethacrylate (UEDMA), 2-methoxyethyl methacrylate, 2-(N,N-dimethylamino) ethyl methacrylate, and 4-methacryloxyethyl trimellitic anhydride (4-META)) of 3 (3:4:3 HEMA, TEGDMA, BIS-GMA) to five monomers (the rest in respective proportions of 3:3:3:5:5) against 14 types of disposable natural rubber, synthetic rubber, and synthetic polymer material in a EN 374 permeation cell at 20 °C with water collection that was stirred and with samples analyzed by LC-UVD. The most resistant gloves relative to BTs at 1 µg/cm²/min were Nitra Touch (nitrile) that protected against all monomers for at least 120 min but swelled; Tactylon (synthetic rubber); and Metin (polyvinylchloride). This research team similarly (Loennroth and Ruyter (2003) extended their observations to methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), and 1,4-butanediol dimethacrylate (1,4-BDMA), all chemicals causing substantial swelling and degradation.

Nakamura et al. (2003) confirmed that HEMA, TEGDMA, and MMA permeated the fingers of all 5 glove types (latex, powder-free latex, coated latex, chloroprene, and PVC) within 10 min at 37 °C with ethanol collection and UVD. EGDMA permeated in 60 min. Two monomers (UEDMA and bis-glycidyl methacrylate) did not permeate.

The glove finger permeability of methyl methacrylate relative to non-powdered latex and non-latex

(polyisoprene) gloves (each with three different thickness) was examined at different time intervals up to 60 min at 37 °C using ethanol as collection solvent and UVD (Rajan et al. 2017). An equal number of latex (n=90) and non-latex (n=90) gloves were included. In both the groups, three subsets were made based on different thickness, each containing 30 samples. The permeability of these non-latex gloves was found to be higher than that of latex gloves.

Summary

Many of the permeation studies involved acrylate contact sensitizers with evaluation in closed-loop collection systems. The thicker the glove the more resistance was achieved, and double gloving of disposable gloves was also effective. Three dental glove permeation studies were done at 37 °C.

The studies with acrylic agents in organic solvent challenges and with organic solvent collection may be suspect because of solvent-facilitated transport. As different acrylate bonding agents appear, they too will need to be tested.

Hairdressing compounds

Research attention in hairdressing since 2007 has been on hair dye allergens like *p*-phenylene diamine, and acidic compounds like resorcinol. These two chemicals (5% w/v *p*-phenylene diamine and 10% resorcinol) and 0.75% toluene-2,5-diaminesulfate, all in borate buffer with 0.2 M ascorbic acid, were separately tested (Lind et al. 2007) in the ASTM F739 2.54 cm cell at 24 °C in borate buffer with 0.2 M ascorbic acid collection fluid in a closed-loop configuration at 5 mL/min and LC-UVD analysis against powder-free disposable gloves (0.020-cm-thick natural rubber latex, 0.012 cm PVC, 0.011 cm nitrile, and 0.002 cm polyethylene (polythene)). Nitrile resisted permeation except for resorcinol that had a lag-BT of 183 min. The thinnest glove, polyethylene, allowed *p*-phenylene diamine to have a lag-BT of 32 min and resorcinol of 119 min, but the PVC glove offered the least protection with both resorcinol and *p*-phenylene diamine having lag-BT at about 90 min. Toluene-2,5-diaminesulfate did not permeate any gloves. The natural rubber glove did not allow any permeation. In a further similar study by the same research group (Lind et al. 2015), the effect of pretreatment of gloves with hydrogen peroxide on the permeation of resorcinol on the same gloves above was adjudged to be minimal.

A Taiwanese group (Lee and Lin 2009) performed the permeation of the three aminophenol isomers (2–3%) and *p*-phenylene diamine (4%) singly in

ethanol, in the presence of 12% hydrogen peroxide, and in admixture in an ASTM cell with ethanol liquid collection at 21 °C and GC-FID analysis. No permeation at 0.25 µg/cm² was observed for disposable neoprene gloves up to 8 hr. At 40 min for the disposable PVC gloves, both *p*-phenylene diamine and *o*-aminophenol broke through, and SSPRs were the highest for all the gloves. Hydrogen peroxide appeared to inhibit breakthrough for all gloves that showed permeation without it, all BTs being greater than 240 min. The chemical composition was the key predictive factor for natural rubber, with molar volume and log *K*_{ow} important for PVC breakthrough times. The latter two factors and chemical composition were also important for SSPR.

Summary

The order of decreasing resistance using lag-BT to *p*-phenylene diamine and resorcinol in aqueous borate buffer against disposable gloves was latex, nitrile, polyethylene, and PVC. Toluene-2,5-diaminesulfate did not permeate any of these gloves. For aminophenols and *p*-phenylene diamine in ethanol, disposable neoprene allowed no permeation at 0.25 µg/cm² unlike disposable PVC gloves.

BTs at 35 °C would have decreased relative to the room temperature conditions used for these studies. More research needs to be done in this area and in the allied areas of permeation of cosmetics, nail polishes, household products, liquid foods, drinks, and liquid items in shops.

Miscellaneous liquids

Some miscellaneous studies of other nonvolatile compounds included with γ -butyrolactone, tetralin, nitrobenzene, N-methyl-2-pyrrolidinone, and m-cresol for the ASTM F739 cell at 22.5 °C with PID quantitation and comparing permeation results with swelling and compound solubility for neoprene (0.43 and 0.48 cm thickness), nitrile (0.40 cm), and butyl (0.78 cm) (Perron et al. 2000). The ASTM SSPRs for low volatile solvents at a gas carrier flow of 100 mL/min were always much lower than SSPRs from the solubility results for neoprene. BTs from neoprene swelling data (when swelling stopped) were also shorter than literature open-loop data with BTs defined at 0.1 µg/cm²/min. In contrast, all techniques on neoprene agreed for the volatile solvents cyclohexane and acetone.

The permeations at 25 °C of nonvolatile paint stripping solvents like N-methyl-2-pyrrolidinone and dibasic esters using GC-MS analysis were compared (Stull et al. 2002) with those of the conventional low

boiling paint strippers methylene chloride, methanol, isopropyl alcohol, acetone, and toluene using open-loop collection and GC-FID. Degradation, solubility (>25% was the rejection threshold) and thickness (>25% was the swelling rejection threshold) screening reduced the initial 20 glove types chosen for the comparison. Nitrile, PVC, and neoprene gloves were unsuitable. These nonvolatile solvents were resisted best by 4H plastic laminate (resisted all strippers tested except those with high methylene chloride concentration) and butyl rubber (less resistant to methylene chloride) in ASTM F739 (BTs at 0.1 µg/cm²/min) and ASTM F1383 (BTs at 0.05 µg/cm² cumulated) tests using ethoxyethanol or methanol solvents and also detection BTs. Artificial solvent mixtures were not good surrogates for commercial paint stripping formulations which are complex mixtures.

Cleaning workers use disposable gloves when handling chemicals including those with extreme pH-values (pH < 2; pH > 11.5). Latex, PVC, neoprene, and nitrile were tested against complex cleaning formulations based on 10–25% phosphoric acid (pH ≤ 0.50) and on sodium (30–60%) and potassium hydroxides (10–30%) of pH 14 (Suleiman 2019). The glove surface area was estimated from density and weight data. Acid/alkali-reserves of the cleaning products were determined by titrating the products accordingly with 0.1 M NaOH and 0.1 M HCl. The BTs of materials were determined where inside-out inverted glove cuttings of the middle fingers filled with 10 mL of cleaning products were immersed in pH-adjusted water with added pH-indicator at 23 °C, and at 35 °C. Permeation through the gloves was indicated by the color change of pH-indicator in the water. The time for the color change was noted as the material BT. Latex had generally the shortest BT in minutes (shortest >1; longest >11), while nitrile had the longest times (shortest >27; longest >57). Breakthrough times at 35 °C were shorter than at 23 °C, the effect being indistinguishable when short BTs at 23 °C occurred. The BT shortening for nitrile varied between factors of 3 to 14. Latex and PVC, though used by cleaners, are the least suitable for handling chemicals with extreme pH-values. Nitrile with its longer BTs is a better choice, but is also limited.

Summary

The compounds γ -butyrolactone, tetralin, nitrobenzene, N-methyl-2-pyrrolidinone, dibasic esters, and m-cresol were best resisted by laminated and butyl gloves. Closed-loop collection resulted in shorter BTs than did the analogous open-loop systems at the same

temperature. Disposable nitrile was more protective against cleaning solutions based on dilute phosphoric acid of $\text{pH} \leq 2$ and on sodium and potassium hydroxide ($\text{pH} 14$) than disposable latex, PVC, and neoprene. The BTs at 35°C were shorter than at 23°C , the effect being indistinguishable when short BTs at 23°C occurred. The BT shortening for nitrile varied between factors of 3–14.

Permeation experiments need to be performed at the appropriate temperature and with the appropriate permeation cell collection system. More complex mixtures need to be studied.

Organic solids

Benzoic acid (4 and 40 mg/mL in 45% (v/v) ethanol in water) was shown to permeate disposable latex and nitrile gloves and was transferred to human skin via an isotonic receptor medium in a system that combined the ASTM cell with the Franz cell at 32°C (Nielsen and Sorenson 2012). Nitrile gloves were superior at the low concentration. Benzoic acid was found within the glove materials after permeation and the authors recommended that disposable gloves not be reused. Ethanol was clearly responsible for the permeation of the solid benzoic acid which has limited water solubility.

Research on permeation of dry organic solids through glove pieces began in 1992 with Fricker and Hardy (1992,1994) who used a modification of the ASTM permeation cell at 25°C with open-loop helium gas collection at 7 mL/min, gas sampling valve-GC-FID, and detection-BTs.

The Bunge group (Ley and Bunge 2007; McCarley and Bunge 2003; Parks et al. 1997; Romonchuk and Bunge 2006) studied the permeation of methylparaben and cyanophenols through silicone rubber (thickness 0.0338 cm) using 10 mM phosphate buffered saline liquid collection at 37°C (Romonchuk and Bunge 2006) or water and 0.01 N sodium hydroxide at $22\text{--}25^\circ\text{C}$ (Ley and Bunge 2007) without recirculation for a Neoflon gravity permeation cell and subsequent LC-UV, and directly by total attenuated reflectance-Fourier transform infrared spectrometry (McCarley and Bunge 2003). The degree of contact of the powder with the outside membrane surface determined the permeation kinetics.

Que Hee and Zainal (2010a,b) detected the active ingredients of solid pesticide formulations of dichlobenil and chlorothalonil in the 2.54 cm ASTM cell at 35°C using GC-MS, but permeated mass differed with collection solvent (water, isopropanol, hexanes) in the closed-loop without recirculation system, and glove

type (CPC and disposable nitrile). Water always had the lowest and hexanes the highest permeated mass at 480 min. The concentrations in water were well below the water solubilities of the pesticides.

Summary

Solids like benzoic acid in aqueous ethanol permeated gloves via the ethanol component at 25°C . The permeation of dry organic solids into a liquid collection system of a permeation cell was demonstrated for cyanophenols and methylparaben at $23\text{--}25^\circ\text{C}$ and 37°C , and varied with collection solvent, water always inducing less collection than hexanes for the solid pesticides dichlobenil and chlorothalonil from their solid formulations at 35°C . The degree of contact of the solid with the outside surface of the membrane affected permeation kinetics.

The observation that permeation kinetics of solids is dependent on the degree of contact with the external surface of a glove piece in permeation cell experiments is analogous to permeant masses collected by a solid medium being controlled by the degree of contact with the inner surface of the glove piece as discussed in the section on solid collection for low boiling point solvents, gases/vapors, and their mixtures. The other major concern is how important is collection solvent back permeation that may dissolve solid on the collection surface or within the membrane and allow transport of the challenge chemical back into the collection solvent compartment. More work needs to be done in this area.

Mathematical models not related to Fick's law

Simple permeation models based on consideration of solubility parameter, chromatographic theory, polarity, and liquid partition theory were tested relative to BT and SSPR data for single compounds in the 5th edition *Ansell-Edmont Chemical Resistance Guide* for nitrile, neoprene, neox-supported neoprene, polyvinyl alcohol, natural rubber, and PVC (Que Hee 1996). Snyder eluent strength (a chromatographic parameter for liquid chromatography) and the logarithm of the compound partition coefficient for heptane/water at 25°C provided the best correlation results.

Lin and Que Hee (1998b,c) developed a mathematical model to describe the permeation of 12 components of a malathion emulsifiable concentrate at 30°C in a ASTM F739 permeation cell closed loop system without recirculation. There was dependence of mixture permeation kinetics on chemical mass fraction, the chemical molar volume reflecting molecule size,

and the chemical log K_{ow} partition coefficient at 25 °C for the interaction of the chemical with the glove material. The kinetics at 30 °C of the reconstituted mixture were no different than the original mixture. This approach also explained the permeations of three aminophenol isomers (2–3%) and *p*-phenylene diamine (4%) singly in ethanol, in the presence of 12% hydrogen peroxide, and in admixture in an ASTM cell with ethanol liquid collection at 21 °C (Lee and Lin 2009).

The links between immersion method data, solubility parameter theory via the square root of the result of heat of vaporization divided by the molar volume (often also called Hansen's parameters) and permeation parameters have occupied many investigators with much conflicting data generated. For permeation to occur, the challenge solvent must show sufficient solubility in the material to be able to travel from the challenge side to the other. The studies discussed below all employed open-loop gas collection systems at 20–25 °C and GC-FID unless otherwise stated.

There were correlations (Perron et al. 2000) between cyclohexane and acetone swelling, liquid volume solubilized and BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$, and SSPR for neoprene, no agreement between solubility and SSPR for the nonvolatile solvents nitrobenzene and *m*-cresol, but good agreement between swelling and BT. The solubility and SSPR of ethyl acetate in neoprene and butyl materials correlated (Vahdat and Sullivan 2001); as did the solubilities of 32 low boiling organic solvents in viton relative to SSPR and BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ (Evans and Hardy 2004); also for 26 solvents for butyl gloves relative to SSPR, BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ and lag-BT (Evans et al. 2008); and for the solubility of benzene, toluene, ethyl benzene, and *p*-xylene in nitrile relative to diffusion coefficients and SSPR, but not for neoprene (Chao et al. 2006); and with binary and ternary mixtures also obeying the correlation for nitrile (Chao et al. 2008).

Many investigators found no correlation between solubility and diffusion coefficient for: benzene, toluene, and styrene through nitrile and neoprene (Chao et al. 2004); swelling and BT of 5 ppm with MIRAN detection for vapor mixtures of toluene and 2-butanone challenging nitrile gloves though the opposite was true for natural rubber (Georgoulis et al. 2005); and solubility and diffusion coefficient for benzene, toluene, ethyl benzene, and *p*-xylene relative to neoprene but not nitrile (Chao et al. 2006). The BT and SSPR appear better correlated when the solvent swells the glove material, that is, when the material is slightly degraded. This has been responsible for the

demise of the solubility theory to explain glove permeation since permeation is defined as diffusion through the material without chemical degradation.

Degradation test parameters were not necessarily related to ASTM/ISO permeation kinetic parameters (SSPR, BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ at 20 °C) for acetone, carbon disulfide, trichloroethylene, and N,N-dimethyl formamide relative to 9 different glove types, with many materials classified as “good” via degradation criteria permeating within 5 min (43%) and with permeation ability underestimated in 67% (Miyauchi et al. 2004).

The National Institute for Occupational Safety and Health (NIOSH) in 2017 revised its Permeation Calculator for open- and closed-loop testing data and now provides the various BTs, SSPR, cumulative permeation, and average permeation rate for single chemicals in an Excel and graphical framework (National Institute for Occupational Safety and Health 2017). The results do not account for penetration, degradation or swelling, variables that should be measured before permeation testing (Banaee and Que Hee 2019).

The Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST) (2016) in its *Protective Gloves Selection Guide* similarly provides an interactive tool that allows selection of protective gloves according to need including for protection against chemicals (also degradation data), risk assessment, and regulatory information.

The glove permeation of mixtures has been modeled by other methods. The heat of mixing, related to solubility theory of regular solutions (Que Hee 1996), was able to reconcile swelling and ASTM F739 permeation parameters with BT at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$ at room temperature empirically for 73% of the cases of butyl, nitrile, and neoprene rubber glove membranes challenged by acetone, chloroform, *p*-dioxane, dimethyl sulfoxide, heptane, hexane, diisopropyl ether, 2-propanol, tetrachloromethane, tetrahydrofuran, and toluene singly and in binary and ternary mixtures (Perron et al. 2002). For mixtures that did not degrade the gloves, those with large and exothermic heats of mixing permeated less than expected based on single solvent permeation, initial swelling rate, and on its mole fraction, while those with large and endothermic heats of mixing permeated more. A solvent with high affinity for the membrane carried singly non-permeating components through with it when the high affinity solvent was the dominant component. Challenge solvent molecule size and polarity, fluorocarbon glove thickness, and swelling behavior were investigated as

the basis of a predictive breakthrough time model that showed BTs for homologous series were exponentially related to molar volume (Geerissen et al. 2008a), and also for binary mixtures of *t*-butyl acetate/toluene, acetone/*n*-hexane, and *t*-butyl acetate/*n*-propyl acetate for bromobutyl rubber where an inverse mixing rule was predictive (Geerissen et al. 2008b).

Summary

Direct permeation testing of gloves is still necessary especially when chemical mixtures are involved. The dominant solvent in solutions often determines the permeation rate of the other components. The most promising predictive approach to BTs and SSPRs appears to be solubility theory when glove swelling is present. For permeation with no swelling or shrinking, an approach that combines the molar volume of the challenge molecule, its log octanol/water partition coefficient, and its mass or mole fraction has been the most successful.

More results are still needed to prove the validity of the latter model.

Exposure/risk assessment

The previous sections have focused on the methods and technology used to produce or predict glove permeation data at various conditions and collection configurations. The current section is focused on how glove permeation data can be linked to human health effects, the ultimate concern for an industrial hygienist with a workplace glove program.

This research area has been previously investigated relative to glove toxins that expose the skin whether with or without a challenge solvent, permeant toxins, and epidemiology studies.

Glove toxins

Latex allergens have been well studied and there are excellent discussions elsewhere (Balbiani and Sossai 2008; Berthelot et al. 2016; Chowdhury and Maibach 2004; Norman et al. 2002; Palosuo 2014; Sartorelli and Montomoli 2008).

Chemical species other than tree latex allergens can be extracted from gloves: heptanes extracted from disposable nitrile gloves the vulcanization accelerators zinc di-*n*-butyldithiocarbamate and zinc diethyl dithiocarbamate, the plasticizer dioctylphthalate, five antioxidant alkyl butylphenols, and 1,4-dione-2,5-bis(1,1-dimethylpropyl)cyclohexadiene in mg/g concentrations at 37 °C (Mutsuga et al. 2002). Hexane at

20–80 °C extracted five types of (1,1,3,3-tetramethylbutyl)phenols and 1,4-dione-2,5-bis(1,1-dimethylpropyl)cyclohexadiene. Dioctyl and dibutyl phthalates plasticizers were extracted in mg/g concentrations from neoprene, nitrile, and PVC gloves by methanol, hexane, diethyl ether, acetone, and aromatic solvents with the more non-polar solvents and increasing the temperature extracting more (Chao et al. 2013). Similar results occurred for dioctylphthalate (DOP) when leached by benzene, toluene, ethyl benzene, and xylenes in ASTM cell permeations with nitrile and PVC glove pieces at 25 °C (Chao et al. 2015). DOP is an expected/probable human carcinogen and estrogen (National Toxicology Program 2016). These extractions by liquids occur on direct challenge of the glove, and when liquids are used as collection solvents. The non-allergen studies used GC-MS for identification and quantitation.

Summary

Allergen transfer from natural rubber latex to the skin of hypersensitive workers has occurred, but solvents used as challenge and collection solvents do extract glove plasticizer carcinogens like the dialkyl phthalates, vulcanizing accelerators like the zinc dithiocarbamates and antioxidant alkyl butylphenols. Increasing temperature enhances extraction. All the non-allergen studies relied on GC-MS identification and quantitation.

More research needs to be done to identify other glove chemicals extracted by solvents at 35 °C.

Permeant toxins

Risk assessment of the challenge solvent that actually permeated through a glove piece has been previously referred to in 30 studies of this review. Of the 19 in-vitro permeation studies performed at 35–37 °C, only 11 were performed with ASTM F739, EN 374, and ISO 6529 permeation cells or robot hands that are more suitable for risk assessment purposes (Table 2).

The key glove chemical permeation parameters directly related to dermatitis or irritation in the absence of sensitization are the differential signal or chemical permeation rate at 35 °C as well as the chemical cumulated permeation mass at 35 °C, both at and over a specific time span. The integrated signal or the cumulated permeation mass at 35 °C is also potentially related to systemic health effects. The temperature of 35 °C is based on the surface and inner temperatures measured for tight-fitting gloves, and those measured

Table 2. Studies of this review performed at 35–37 °C with ASTM F739 and EN 374/ISO 6529 permeation cells and robot hands. The number after each glove is average or nominal thickness in cm; after BT is average time in minutes with standard deviation if specified; after SSPR, the average steady state permeation rate in $\mu\text{g}/\text{cm}^2/\text{min}$ with standard deviation if specified.

Permeant	Notes	Reference
Acetone, Ethyl acetate	Open-loop EN 374 with CPC nitrile Acetone (5 gloves): BT 6.3 ± 0.6 ; SSPR 660 ± 50 Ethyl acetate (6 gloves): BT 14 ± 3 ; SSPR 125 ± 3 Note: glove thicknesses and determinant method were unspecified.	Evans et al. (2001)
Straight oil metalworking fluid Deolene-D4	10 mL in 1-inch ASTM F739 glass permeation cell with Safeskin nitrile (0.011) with 10-mL hexane closed-loop non-circulating collection in a moving tray water bath (MTWB) at 8.4 cm/sec and GC-MS and gravimetry. Detection BT, 0.7 ± 0.3 hr; lag BT, 1.3 ± 0.2 hr; SSPR, 3.5 ± 2.2 ; 8-hr cumulated mass, 6.7 ± 4.4 mg.	Xu and Que Hee (2006b)
Straight oil metalworking fluid Deolene-D4	As for Xu and Que Hee (2006b) except Safeskin nitrile (0.012), latex (0.013), chloroprene (0.016), vinyl (0.018), and perfluorohexane solvent and gravimetry; 8-hr cumulated mass (mg): latex, 167.3 ± 3.5 ; chloroprene, 50.7 ± 6.1 ; vinyl, 3.6 ± 1.0 ; nitrile, ≤ 0.3 .	Xu and Que Hee (2007b)
Captan	Dextrous robot hand with Captan aqueous emulsion of 217 mg/mL for three different disposable nitrile gloves, all unsupported, unlined, and powderless with cotton glove solid collection with GC-MS after extraction/wiping; clenching force, 1.9 ± 0.1 kg; 8-hr cumulated mass (ng): N-Dex Free no movement, 3.8 ± 1.9 ; movement, 3.5 ± 2.4 (not statistically significant $p \leq 0.05$); Lifeguard no movement, 10.9 ± 3.1 ; movement, 8.6 ± 1.2 (not statistically significant $p \leq 0.05$); Safeskin for 2-hr cumulated mass no movement, 3.9 ± 5.2 ; movement, all 3 gloves tore.	Phalen and Que Hee (2008)
n-Dioctyl sulfide	As for Xu and Que Hee (2007b) except Safeskin nitrile (0.012) was evaluated with perfluorohexane collection solvent and GC-MS. Detection BT, 30–75; BT at $0.25 \mu\text{g}/\text{cm}^2$, 30–75; cumulated mass at 8 hr, $194 \pm 58 \mu\text{g}$; SSPR, $6.9 \pm 2.3 \mu\text{g}/\text{cm}^2/\text{min}$.	Xu and Que Hee (2008)
Dichlobenil	As for Xu and Que Hee (2006b) except MTWB speed of 12 cm/sec, an aqueous concentration of 2.0 mg active ingredient/mL, water collection, Safeskin nitrile (0.011) and Solvex nitrile (0.037). 8-hr cumulated mass (ng): Safeskin, 2.48 ± 0.40 ; Solvex, 4.87 ± 0.82 ; For granular solid formulation 8-hr cumulated mass (ng): Safeskin, 26.9 ± 6.1 ; Solvex, ≤ 3.0 .	Que Hee and Zainal (2010a)
Chlorothalonil	Same as Que Hee and Zainal (2010a) except for aqueous concentration of 2.2 mg active ingredient/mL. 8-hr cumulated mass (ng): Safeskin, 70 ± 100 ; Solvex, 20 ± 20 ; For dispersible granule formulation solid challenges 8-h cumulated mass (ng): Safeskin, 300 ± 300 ; Solvex, 37.2 ± 5.5 .	Que Hee and Zainal (2010b)
Tetramethyl ammonium hydroxide 25% in water	ASTM F739-99 closed-loop system without water recirculation for CPC nitrile and CPC natural rubber. BT ($n=6$) at $0.25 \mu\text{g}/\text{cm}^2/\text{min}$: natural rubber, 69; nitrile, 457; SSPR: natural rubber, 7.1; nitrile, 69. (Note: glove thickness, however, measured and sensor were not specified. The ASTM-99 BT criterion for a closed-loop system is $0.25 \mu\text{g}/\text{cm}^2$).	Su et al. (2013)
Cyclohexanol	Dextrous robot hand with closed-loop circulating water at 100 mL/min and ASTM F739-99 (1-inch cell) closed-loop system without water recirculation in MTWB (8.36 cm/sec; GC-MS analysis; four types of disposable unsupported, unlined, powderless nitrile: Safeskin Blue (0.013), Kimtech Science Blue (0.013), Purple (0.012), Sterling (0.0081); respective BT at $0.1 \mu\text{g}/\text{cm}^2/\text{min}$ for ASTM F739-12/motionless hand: $40 \pm 15/20 \pm 4$, $17 \pm 5/20 \pm 4$, $15 \pm 0/20 \pm 4$, $15 \pm 0/12 \pm 0$; respective SSPR $2.2 \pm 0.6/10.0 \pm 0.7$, $12 \pm 1/9 \pm 1$, $12 \pm 2/14 \pm 3$, $21 \pm 1/18 \pm 2$.	Mathews and Que Hee (2017a)
Cyclohexanol	Same dextrous robot hand system and gloves but hand was motionless/clenching at 1.9 ± 0.1 kg; respective BT at $0.1 \mu\text{g}/\text{cm}^2/\text{min}$: $20 \pm 4/16 \pm 4$, $20 \pm 4/20 \pm 4$, $20 \pm 4/18 \pm 0$, $12 \pm 0/6 \pm 0$. SSPR: $10.0 \pm 0.7/11.8 \pm 0.7$, $9.0 \pm 1.0/7.0 \pm 1.0$, $14 \pm 1/11.4 \pm 0.6$, $18 \pm 2/29 \pm 3$. Only the last set of BT and SSPE data differed statistically at $p \leq 0.05$.	Mathews and Que Hee (2017b)
Limonene	Same comparison as for Mathews and Que Hee (2017b) with the same gloves except Safeskin Blue deleted and Kimtech Science Lavender (0.0058) added; motionless/clenching at 2-kg respective BT at $0.1 \mu\text{g}/\text{cm}^2/\text{min}$ in order of decreasing glove thickness: 30/30, 15/15, 15/15, 5/5; SSPR: 0.010/0.012, 0.067/0.078, 0.10/0.10, 0.42/0.49. Only the SSPR data for the last set differed statistically at $p \leq 0.05$.	Banaee and Que Hee (2017)

within and outside thick CPC gloves that are worn for some time or when physical activity is moderate and high (Evans et al. 2001).

The first approximation is to assume that inner glove transfer of the permeant to the skin is 100% as the worst-case scenario. For the current ASTM F739 primary cell 1 inch (2.54 cm) in glove contact exposure diameter or a glove contact area of 0.786 in^2

(5.07 cm^2), the total potential dose to the exposed skin over 8 hr is cumulated dose \times (workplace exposed glove area divided by permeation cell glove contact area, here 5.07 cm^2). The industrial hygienist needs to measure or estimate the actual glove area exposed. If an occupational exposure limit (OEL) based on a systemic health effect is available, the method of biological equivalents at a specific physical activity can be

used to calculate a worst-case inhalation exposure dose threshold to assess the relative health risk. For example, for an OEL of 1 mg/m^3 at a lung inspiration rate of $10 \text{ m}^3/\text{min}$ for 480 min has an exposure dose of $1 \times 10 \times 480 = 4,800 \text{ mg}$. If the glove permeated mass for the chemical is below the guidance dose threshold, its contribution to the observed systemic effect will probably be negligible unless the chemical causes sensitization, carcinogenicity or developmental/reproductive effects that are not the basis of the OEL. The same comparison process can be done for chemicals with short term exposure limits or surrogates based on systemic effects for the wearing of disposable gloves as well as for short-term wearing of CPC gloves.

If the cumulated permeant mass is higher than the guidance dose threshold, an estimated maximum skin permeation rate should be calculated with such tools as the NIOSH skin permeation calculator (National Institute for Occupational Safety and Health 2020) based on the revised Robinson skin permeation model (Wilschut et al. 1995), and the American Industrial Hygiene Association IH SkinPerm (American Industrial Hygiene Association Dermal Project Team, 2017). The results from both permeation calculators rely on water solubility and log octanol/water coefficient data at 25°C so that skin permeation rates will be underestimated. The maximum skin exposure rate will allow estimation of whether skin occlusion (saturation) or complete absorption is likely when the glove area of exposure (for example for one hand after immersion) and the time of skin exposure/glove are also known from worker self report or by field industrial hygienist observation. If this potential absorbed dose is below the guidance threshold (assuming 100% absorption through the lung as a worst-case scenario as above), the permeated chemical is probably not responsible for the observed systemic effect, with the same qualifications as above.

The next layers of complexity may involve skin chemical exposure measurements, estimating the inner glove surface-to-skin transfer factor for the permeant, accounting for other routes of exposure, and calculating actual absorbed inhalation doses at OEL concentrations adjusting for lung uptake efficiency, and using PBPK models. These items may require the aid of a toxicologist.

Sometimes the only permeation data available are a BT and a SSPR and there is no cumulated permeation dose provided. To use these data properly requires the permeation curves from which the data are derived. Computing cumulated mass from permeation curves has already been addressed in Banaee and Que Hee

(2019). If the permeation curves are not available, it can be assumed as a worst-case scenario that the steady-state period begins at the BT and ends at the desired time. A detection BT permeation rate can be back-calculated if the determinant method detection limit is specified.

No risk assessments are available in the scientific literature for chemicals without OELs and for mixtures. There are also no general models linking chemical exposure dose to dermatitis.

The American Industrial Hygiene Association had a Biological Environmental Exposure Level Project Team devoted to quantitative chemical skin risk assessment between 2008 and 2011 (American Industrial Hygiene Association 2010).

Summary

The literature studies of quantitative risk assessment for specific chemicals from permeation experiments often used the cumulated mass permeated up to a specific time requiring the availability of the cumulated permeated mass versus time curve for the glove at 35°C , and, after correcting for actual glove area exposed, assumed all of this mass was available for skin absorption as a worst-case scenario. This mass was then compared with the guidance threshold mass dose at the compound's OEL at its reference physical activity for the same time interval assuming complete lung absorption as a worst-case scenario. The next refinement if the guidance threshold was exceeded was to calculate the skin permeation rate from skin permeation calculators and models, and then calculate the skin permeation dose that also requires measurement of the skin area exposed and the time of exposure before comparison with the OEL threshold dose, assuming complete lung absorption of the chemical. Further refinements make the quantitative risk assessment overly complicated for the average field industrial hygienist who should seek the aid of a toxicologist. No risk assessments are available in the permeation scientific literature for chemicals without OELs and for mixtures. There are also no general models linking chemical exposure dose to dermatitis.

The alternatives are better qualitative and semi-quantitative methods of surrogate risk assessment through exposure assessment. Thus, the further development of portable sensors, microarrays and colorimetric techniques (for example, Swypes) to detect permeated chemicals cited in previous sections is also necessary. Similarly, a glove embedded/implanted with microsensors on its inside surface or the skin

embedded with microsensors are other avenues of research. Wireless technology could facilitate transmission of sensor signals to achieve real-time exposure assessment to improve on the current near real-time technology of data logging. If the signal receptor is equipped with a memory bank of risk assessment data, near real-time risk assessment could be realized. Since there are no methods for quantitative risk assessment for compounds without OELs, mixtures, and for appearance of dermatitis these knowledge gaps need filling. Exposure/hazard banding for a chemical without an OEL also needs investigation to derive guidance threshold bands. Utilization of non-OEL guidelines such as allowable daily intakes is another tack. Most of the predictive permeation models have been based on room temperature permeation data. Such models may not describe permeation at 35 °C, the temperature of the surface of the skin and of most donned gloves. This applies not only for permeation and solubility data but also for such physical constants as the octanol/water coefficient, vapor pressure, and liquid density. A correlational approach with 25 °C data allows the probable form of the relationship between dependent and independent variables (for example, linear or exponential) to be observed at 35 °C but with different slopes, intercepts, and coefficients. Even this concept needs validation since all the skin permeation calculators still use 25 °C-based physical parameters.

Epidemiology studies

Some other exposure assessment/risk assessment studies in the literature included a case control epidemiology study that found enhanced risk for gloved workers in the field in the simultaneous presence of the insect repellent N,N-diethyl-*m*-toluamide (DEET) for phenoxy herbicide use to account for the observed non-Hodgkin's lymphoma incidence (McDuffie et al. 2005).

In another study (Furlong et al. 2015), protective glove use for farm workers nullified the non-user associations between paraquat and permethrin use with Parkinson's disease; both glove users and non-users had positive associations between rotenone use and Parkinson's disease; and trifluralin exposed workers needed to use more than two hygiene practices before the associations between workers with fewer than two hygiene practices were nullified.

Perceived risk and risk awareness relative to wearing gloves for a group of automotive spray painters via interviews, focus groups and questionnaires have

been evaluated (Ceballos et al. 2014b). Unawareness of why different glove types were necessary to resist different chemicals, and of why there had to be a compromise between safety and comfort when wearing gloves were the major findings.

Summary

The epidemiology studies on glove resistance and other hygienic practices to pesticides involved how many hygienic practices were necessary to cause significant lowering of toxicity for non-Hodgkin's lymphoma (exposure to phenoxy herbicides and DEET) and Parkinson's disease (paraquat, permethrin, rotenone, and trifluralin). Workers appeared unaware of why wearing different glove types to resist different chemicals was necessary, and why safety should take precedence over comfort when wearing gloves to resist chemicals.

Much more research remains to be done on the exposure/risk assessment and risk awareness of wearing gloves as well as on perceived versus actual risk, and how these factors contribute to the psychosocial atmosphere and safety of the work environment. Direct reading exposure assessment technology, and sensors implanted in gloves and in the skin will facilitate prospective epidemiology studies. Development of hazard banding and utilization of non-OEL guidelines should also be explored.

Glove manufacturer permeation classifications

Introduction

The major glove thickness classification system defines disposable, household, industrial, and special gloves as having respective thicknesses of 0.0007–0.025 cm, 0.020–0.040 cm, 0.036–0.085 cm, and variable depending on purpose (Mellstrom and Boman 1994). Glove material type is the basis of the other major classification system: rubber, plastic, leather, textile, and any combination of these. The US Department of Energy uses a six-way classification system for gloves: disposable, fabric, metal, leather, aluminized, and chemical-resistant (U.S. Department of Energy Office of Science User Facility 2019).

There is not enough space to describe all glove material types and their manufacture in detail. The reader is directed for details of manufacture and production of all types of gloves to the *Kirk-Othmer Encyclopedia of Chemical Technology* (2018), Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST) (2016), and some standard references (Dolez et al. 2012; Forsberg 2005; High Level Medical 2016; International Institute of Synthetic Rubber

Producers 2002; Mansdorf and Henry 2011; Mellstrom and Boman 1994; NPCS Board of Consultants and Engineers 2013; Perkins 2003).

Disposable (single-use) gloves have several advantages like low cost, availability, accessibility, and allowing work pieces to be manipulated and cleaned. CPC gloves are generally too thick and stiff to allow facile manipulation of small work pieces. The worldwide consumption of disposable gloves is soaring; global investment increases 20% every year. In 2007, 100 billion disposable gloves were used (Scott 2008). There are four major classes: nitrile, natural rubber latex, neoprene (chloroprene in Europe), and vinyl gloves. They have some similarities, but different thicknesses and color coding help distinguish them, although these are by no means standardized in the industry.

Natural rubber latex gloves have been used for years with many applications, but they have drawbacks such as allergic reactions with potential for skin rash, itch; red eyes, runny nose, asthma, and shortness of breath (National Research Council (U.S.) 2011). The amount of exposure needed to sensitize an individual is unknown, but when exposures are reduced, sensitization intensity decreases. Individuals with known latex allergies should never wear natural rubber latex gloves, may not be able to work in areas where such gloves are used, and should eliminate exposure. Nitrile disposable gloves use has decreased allergic reactions. Higher puncture resistance and better protection against oils and acids are also provided. Neoprene and vinyl are other alternatives, especially in Europe (Balbiani and Sossai 2008).

Permeation classifications

While glove permeation classification is uniform in Europe within the European Community based now on EN/ISO 374 2016 (Banaei and Que Hee 2019), there are no such regulations by the U.S. federal government. ASTM F739 has been the basis of most of the U.S. corporate data. Therefore, at least BT and SSPR data have been provided, but no commercial data based on ASTM F739-12 (American Society of Testing and Materials 2012) have appeared.

DuPont-Europe (2015) and Respirix (2011, 2016) have provided datasheets on glove selection containing SSPR and two normalized breakthrough times (NBTs), $0.10 \mu\text{g}/\text{cm}^2/\text{min}$ and $1.0 \mu\text{g}/\text{cm}^2/\text{min}$, for ASTM F739 and EN 374 standards, respectively. However, both DuPont-Europe and Respirix use EN performance classifications with 6 classes, from 1–6, based on NBT. Classes 1 and 6 represent the poorest

and highest performance with a NBT of greater than 10 min and 480 min, respectively.

Kimberly Clark Professional (2009) defines dual criteria for the chemical resistance rating of disposable nitrile gloves. Excellent, NBT 60–480 min; Good, 10–59 min; Poor, 1–9 min; Not Recommended; <1 min. KCP defines a CPC glove as safe with a green coding, if a high volatile compound (boiling point <25 °C) has an “Excellent” (60–480 min) or “Good” (10–59 min) BT, or if a low volatile compound has an “Excellent” BT (60–480 min). Such volatility criteria are incompatible with the definition for low-/high-volatile compounds in other references. Semi/nonvolatile chemicals are usually characterized with a boiling point of 150 °C or higher (U.S. Environmental Protection Agency 2007). ASTM defines a volatile liquid as one with a vapor pressure >1 mm Hg at 25 °C (American Society of Testing and Materials 2012). Harmonization of definitions and terms amongst glove manufacturers and countries would lessen confusion.

Ansell (2003) indicated that a chemically protective glove can be safe if either combination of the following criteria are met.

- a. The degradation rating for disposable gloves is “Excellent” with BT 30 min or greater, and permeation ranges for CPC are in 6 categories from “excellent” (with less than $0.9 \mu\text{g}/\text{cm}^2/\text{min}$) to not recommended (with more than $9,000 \mu\text{g}/\text{cm}^2/\text{min}$): Excellent, < $0.9 \mu\text{g}/\text{cm}^2/\text{min}$, 0–0.5 drops; Very Good, 0.9–9, 1–5 drops; Good, 9–90, 6–50 drops; Fair, 90–900, 51–500 drops; Poor, 900–9,000, 501–5000 drops; and Not Recommended, >9,000, >5000 drops in its 7th Edition of its *Chemical Resistance Guide*. The 8th Edition (2008) and its *Guardian Chemical Glove Resistance Guide* (2016) just retained the qualitative ranking.
- b. Permeation rate is not available and permeation breakthrough time is 240 min or more, and degradation is “Excellent,” “Good,” or “Very Good.” The latter triple criteria are even harder to meet than the first one, because it requires a 240 min or greater breakthrough time. A color-coded rating system is used to simplify the selection.

Ansell warns in its (2016) *Guardian Chemical Glove Resistance Guide*: “When reviewing the following recommendations, remember that tests are conducted under laboratory conditions, and that actual workplace conditions usually dictate a *combination* of performance capabilities. A product’s resistance to cuts,

punctures, and abrasion must also be taken into account as a critical usage factor. A glove with excellent permeation resistance may not be adequate if it tears or punctures easily. Always factor in the physical performance requirements of the job or application when selecting a chemical-resistant glove. Ansell's ASTM standard permeation and degradation are presented on the following pages as an aid in determining the general suitability of various products for use with specific chemicals. Because the conditions of ultimate use are beyond our control, and because we cannot run permeation tests in all possible work environments and across all combinations of chemicals and solutions, these recommendations are advisory only. The suitability of the product for a specific job must be determined by testing by the purchaser." Their legal disclaimer states: "Recommendations are based on extrapolations from laboratory test results and information regarding the composition of chemicals and may not adequately represent specific conditions of end use. Synergistic effects of mixing chemicals have not been accounted for. For these reasons, and because Ansell has no detailed knowledge of or control over the conditions of end use, any recommendations must be advisory only and Ansell fully disclaims any liability including warranties related to any statement contained herein." These two statements are self-explanatory, and similar statements are common for other glove providers.

Showa Glove Company (2008) (formerly Best with their search engine that provided pre-2012 ASTM NBT) had their CPC gloves classified relative to NBT as: 0 min, <10 min; 1, 10–<30 min; 2, 30–<60 min; 3, 60–<120 min; 4, 120–<240 min; 5, 240–<480 min; and 6, ≥480 min.

Honeywell (2010) (formerly North) provided pre-2012 NBT and SSPR with the following definitions: ND, permeation was not detected during the test; Excellent exposure has little or no effect. The glove retains its properties after extended exposure; Good exposure has minor effect with long-term exposure. Short-term exposure has little or no effect; Fair exposure causes moderate degradation of the glove. Glove is still useful after short-term exposure, but caution should be exercised with extended exposure; Poor, short-term exposure will result in moderate degradation to complete destruction; and ID, insufficient data, to make a recommendation.

Most of the other manufacturers (for example MAPA Professional 2013) provide only qualitative ratings and though MAPA's chemical resistance guide lists the standards used it is unclear if the listed breakthrough times are comparable. Use of purely qualitative rankings to choose gloves should be avoided.

Summary

The current situation is confusing because of differing guidelines in the United States and Europe, different permeation standards, and different definitions of the same terms including BTs and volatility. There is a need to harmonize descriptive criteria for disposable gloves and CPC gloves among glove manufacturers across the world to allow comparisons of their products. Qualitative ratings just deepen the confusion. Adopting ASTM F739-12 standardized breakthrough time (SBT) instead of detection BT except for carcinogens, reproductive toxins, and sensitizers would help the situation because detector sensitivity varies and therefore detection BT may not be comparable among manufacturers. A detection BT without a "less than or equal to X" permeation rate designation is also not of much help to an industrial hygienist or a scientist interested in worker risk assessment. SSPR criteria should also be included for CPC gloves in particular—not just BT criteria—and be quantitative.

Many manufacturers test their materials at room temperature (20–27 °C) rather than at skin temperature of 35 °C (Nadel et al. 1971). There is an exponential permeation rate increase with increasing temperature (Zellers and Sulewski 1993). The exceptions are Kimberly-Clark (2014) and Covidien (2008) and other providers for disposable gloves exposed to chemotherapy agents evaluated according to ASTM D6978 (Banaee and Que Hee 2019; American Society of Testing and Materials 2013). If glove relative ratings are to protect workers under the conditions of use, the permeation temperature should reflect some realistic worst-case scenario for when the glove is worn such as 35 °C as often assumed in healthcare situations in the scientific literature quoted above and as recognized by ASTM D-6978. In addition, the palm or back of palm material examined are regarded as representative of the whole glove in the current standards but thickness varies, the wrist being thinner and the fingertips being thicker. This implies that a whole glove standard should be used to validate the screening ranking of the current standards, especially for the thinner glove materials. The nearest non-human model employs a whole glove dextrous robot hand. More research is needed in this area.

Overview

The state of the art of current research is healthy because more researchers are recognizing the need for permeation cell studies to be done at 35–37 °C rather than at 20–25 °C to be closer to the temperature of a

donned glove. In this regard, healthcare research has especially benefited from the advent of ASTM-D6978 in 2005 for measuring the permeation of chemotherapy agents through gloves at 35 °C. Table 1 shows that healthcare studies comprise about 23% of the publications on the permeation of high boiling compounds. The literature does indicate that increasing temperature increases SSPRs and decreases BTs in permeation cell experiments on the same glove piece type. Therefore, there is now ample scientific literature evidence that the ASTM F739, EN 374-3, and ISO 6529 permeation standards should mandate their permeation temperature to be 35 °C following the lead of ASTM D6978. Commercial glove providers should use that permeation temperature to generate data for their chemical resistance charts.

Table 1 also indicates recent interest in the effects of forces on glove permeation with 77% of the 13 studies being in the period 2010–2018. Applying force can also increase SSPR and decrease BT on the same glove piece or whole glove relative to no applied force. The results of the dextrous robot hand studies featuring a weak fist clenching force of 2 kg show that the thinnest disposable nitrile gloves may produce increased SSPR and decreased BT relative to no clenching at the same temperature. There is also a dependence on challenge chemical type. More data need to be obtained to understand when a whole glove permeation approach is necessary.

While there were 99 publications (on high boiling point compounds in Table 1 there were 43 on low boiling point compounds. The latter figure needs to be augmented by 14 publications on mathematical models based on low boiling point compounds to make a total of 57 publications.

Pesticide permeation studies were popular comprising 21% of the literature on the permeation of high boiling point compounds as was petroleum product permeation at 15%, both percentages including the appropriate publications of the Que Heh group.

The exposure/risk assessment section contained most of the cross-citations in the review. This exciting area that interfaces laboratory permeation cell data and whole glove data with actual workplace activities has endless possibilities for fresh discoveries because of its multi- and inter- disciplinary complexities. The use of technical grade chemicals and formulations in the workplace and in the ambient environment also spurs more attention on the permeation of mixtures and the mathematical models to predict BTs and SSPRs of components.

However, the state of the art of current practice to *select* gloves is in a state of confusion. Glove provider

permeation information based on the current permeation standards does not apply directly to permeation of a chemical through a donned glove under workplace conditions. Since glove provider permeation testing conditions, quality assurance/quality control, and analytical chemistry conditions often differ among providers, the corresponding permeation data often disagree for the same chemical and glove material of the same thickness in the chemical resistance charts of different glove providers. Even assuming the testing conditions, analytical chemistry, and quality assurance/quality control conditions used by a given provider are the same, the permeation data of chemicals can only be used on a comparative basis.

The unrepresentative nature of the permeation data from the current standards and chemical resistance charts completely stymies any accurate quantitative risk assessments for individual workers whose gloves have been permeated, although better estimations can be done as discussed in the Exposure/Risk Assessment section with 35 °C permeation cell data.

EN 374-1 regulates only on the basis of BT for both disposable and CPC gloves. ASTM F739-12 has not yet been used as the basis of the chemical resistance charts of glove providers in the U.S.

Implications for the selection of protective gloves against chemicals

This section applies the above information for industrial hygienists and environmental professionals who recommend gloves for their workers in terms of worker health and risk assessment, and leads to the following qualitative generalizations about the permeation data in a current chemical resistance chart of a glove provider:

The BT for a donned glove (within expiry date for a disposable glove) that is not degraded or penetrated by a chemical is generally shorter than that tabulated based on the current standards because of factors like temperature (except ASTM D6978-05 based data), and the forces experienced by the gloved hand during work (all standards are deficient but especially for the thinner disposable gloves). Therefore, the glove with the longest BT from the same glove provider's chemical resistance table based on a standard is the best choice for a specific chemical in situations that involve gloved hand immersion, total surface exposures from liquid aerosols, and cleaning up a large spill since these approximate the constant contact condition of the standards and maximize glove contact area. For risk assessment purposes, the entire hand surface is potentially exposed.

For small volume exposures as for small splashes and cleaning up small spills, the situation is not as

critical but the sooner the glove can be doffed (without cross-contamination) the better. If the area of glove exposure is known and there is an OEL for the chemical, a worst-case risk scenario calculation may be possible.

Double gloving of disposable gloves and donning laminated CPC gloves are recommended for unknown liquids and mixtures of unknown composition.

If the chemical of interest or analyte is in a mixture, the composition must be known to assess if shorter or longer analyte BTs are to be expected from the BTs of the other mixture chemicals in the same chemical resistance chart. The lower the concentration the less likely will there be an effect. The presence of a chemical of shorter BT than the analyte favors shorter analyte BT and this may be significant the larger the concentration. If the other chemical degrades the glove and is of high concentration, another glove must be chosen. A longer BT for a non-analyte of high concentration will lengthen analyte BT, but may not affect if low concentration.

The SSPR for a donned glove (within expiry date for a disposable glove) that is not degraded or penetrated by a chemical is generally higher than those tabulated based on the standards because of factors like temperature (except ASTM D6978 based data), and the forces experienced by the gloved hand during work (all standards). The same remarks for BT also apply here for the just mentioned mixture situations: a chemical with higher SSPR will tend to increase analyte SSPR if of high concentration and may not affect if of low. A chemical of lower SSPR will tend to lower analyte SSPR if of high concentration and may not affect if low.

Finally, the following best work practices are recommended for those who need to use CPC and disposable gloves in the work environment:

- training on why skin protection is needed from handling and from potential exposure to chemical hazards;
- training on the status of local workplace control methods for skin protection relative to the hierarchy of control methods;
- training on how to distinguish CPC and disposable gloves from other gloves;
- training on the significance of embossing on cardboard containers for disposable gloves and where to look for expiry dates;
- training on the use of resistance to chemicals in commercial chemical resistance charts to optimize glove protectiveness for the task at hand;
- training on the proper donning and doffing of gloves;

- training to avoid cross-contamination of the surfaces of specific workplaces and how to avoid and demarcate already contaminated surfaces;
- training on the care, maintenance, storage, and reuse of CPC gloves;
- training on how and where to dispose of contaminated gloves;
- measuring worker perceptions of the effectiveness of their glove program;
- assessing workplace glove protection programs at least annually; and
- revising the glove protection program on changes in unit processes.

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*Note: There are the 8th (2008) and Ansell Guardian, 2016 editions of this guide that are non-quantitative relative to SSPR. The 8th edition is available at https://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf. [Accessed 2020 January 6]. The 2016 Ansell Guardian Chemical Glove Resistance Guide is available at <https://www.ansellpro.com/download/Ansell-Chemical-Glove-Resistance-Guide.pdf>. [Accessed 2020 January 6]. The Ansell 2013 Chemical Handling Glove Guide for Europe and the overseas Pacific rim is available at: <https://www.labtek.com.au/SuppliersData/Ansell/Chemical%20Handling%20Glove%20Guide.pdf>. [Accessed 2020 January 6]. No update relative to European Union Regulation 2016/425 has appeared though the effective date was March 2018.

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