

## Permeation of Telone EC<sup>TM</sup> through protective gloves

Hanaa Zainal, Shane S. Que Hee\*

Department of Environmental Health Sciences and UCLA Center for Occupational and Environmental Health, School of Public Health,  
University of California at Los Angeles, 650 Charles Young Jr. Drive South, Los Angeles, CA 90095-1772, USA

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### Abstract

Telone is a potent fumigant that is based on the chlorinated unsaturated hydrocarbon, 1,3-dichloropropene (1,3-DCP). It is often applied without dilution and so poses severe inhalation and air pollution threats. Urinary metabolites of 1,3-DCP have been detected after Telone skin exposure, so that preventing dermal exposure is also important. The objective of the study was to assess if nitrile and multi-layer (“laminated”) gloves provide adequate protection against Telone EC<sup>TM</sup> formulation. To accomplish this, disposable (Safeskin<sup>TM</sup>) and chemically resistant (Sol-Vex<sup>TM</sup>) nitrile and laminated (Barrier<sup>TM</sup> and Silver Shield<sup>TM</sup>) glove materials were challenged by Telone EC<sup>TM</sup> with hexane liquid collection in an ASTM-type I-PTC-600 permeation cell. Analyses of *cis*- and *trans*-1,3-DCP in the collection fluid at specified times were performed on a moderately polar capillary column by gas chromatography-electron capture detection. Telone EC<sup>TM</sup> caused microholes in both nitrile materials, though the chemically protective material was degraded slower than the disposable nitrile. The laminated gloves offered limited protection. Silver Shield<sup>TM</sup> protected best because 1.5–2.3 mg 1,3-DCP permeated by 8 h relative to 2.5–7.6 mg for Barrier<sup>TM</sup>, implying about 2.5 times more protection for 8 h. Even for Silver Shield<sup>TM</sup>, the extent of protection was inadequate as illustrated by a risk assessment of the skin exposure situation. The normalized breakthrough times for both types of laminated gloves varied between 27 and 60 min. It is recommended that Viton gloves still be worn for protection.

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### 1. Introduction

Telone is the commercial name of the nematocidal/fungicidal/insecticidal fumigant that contains the active ingredient 1,3-dichloropropene (1,3-DCP; CAS RN 542-75-6). 1,3-DCP is a colorless liquid of boiling point of about 108 °C, with a vapor pressure at 25 °C of 34 Torr, a log octanol/water partition coefficient ( $K_{ow}$ ) of 1.82 at 20 °C, and a water solubility of 2.8 g/L at 20 °C [1]. 1,3-DCP is a mixture of *cis*- and *trans*-isomers, the ratio varying with chemical supplier [2]. 1,3-DCP quantification involves adding the *cis*- and *trans*-isomer contents [2]. Telone and its mixtures with such other active ingredients as chloropicrin (trichloronitromethane; CAS RN 76-06-2) [3] are primarily used as alternatives to methyl bromide due to the latter's cut-off

under the Montreal Protocol [4]. Telone caused air pollution problems after spraying in Central California that led to its withdrawal in 1990 by the State of California, but it was reinstated in 1995 [5,6]. Telone is also an animal carcinogen [7–13], but benefits have been calculated by the U.S. EPA to outweigh the risks [14], as did Dow Chemical [15]. The California EPA public health goal for drinking water is 0.2 µg/L based on cancer and 90 µg/L based on non-cancer effects [16]. The 2004 American Conference of Governmental Industrial Hygienists recommended threshold limit value (TLV) for personal breathing zone air sampling over 8 h is 1 ppm (v/v) = 4.54 mg/m<sup>3</sup> (skin) set on irritation effects [17], the same as the recommended exposure limit of the National Institute for Occupational Safety and Health [18]. OSHA has no permissible exposure limit.

The risk of skin exposure to a volatile solvent like 1,3-DCP is often discounted because of the attention of health and safety personnel is often focused only on the inhala-

\* Corresponding author. Tel.: +1 310 206 7388; fax: +1 310 794 2106.  
E-mail address: squehee@ucla.edu (S.S. Que Hee).

tion exposure hazard. 1,3-DCP does cause skin irritation, allergic contact dermatitis, and is absorbed through the skin [1,19–21]. There were at least 19 spills that were reported to the U.S. EPA in 2001 [22]. There are no peer-reviewed literature data on the type of glove appropriate to protect against Telone.

North Safety Products recommends 9-mil Viton gloves to prevent permeation against 1,3-DCP for at least 8 h [23]. Shorter protection times are shown by 17-mil butyl gloves because they exhibit a 1.3-h normalized breakthrough time  $t_b$ , and a steady-state permeation rate  $P_s$  of 192  $\mu\text{g}/(\text{cm}^2 \text{ min})$  [23].

Ansell Occupational Healthcare does not provide information for Telone or 1,3-DCP in its permeation/chemical degradation charts [24]. It does not recommend gloves of nitrile, unsupported neoprene, polyvinyl chloride (PVC), natural rubber, or neoprene/natural rubber blend for protection against trichloroethylene and ethylene dichloride, and also for perchloroethylene except for nitrile where the breakthrough time is 300 min and the permeation rate is 0.9–9  $\mu\text{g}/(\text{cm}^2 \text{ min})$ . All three compounds do not permeate Barrier<sup>TM</sup> laminate (multiple chemical layers on the glove support material) and supported polyvinyl alcohol (PVA) [24]. The latter gloves are not protective when exposed also to any aqueous solution [24]. Because trichloroethylene has a water solubility at 25 °C of 1.1 g/L [25] and that for perchloroethylene is 0.15 g/L [25], these two analog compounds are more non-polar than 1,3-DCP. Ethylene dichloride has a water solubility of 8.7 g/L at 20 °C [25], and it is more polar than 1,3-DCP. The implication is that nitrile might be somewhat protective for situations involving organic and aqueous solution exposures. A *cis,trans*-dichloroethylene mixture degraded butyl, natural rubber, and neoprene gloves while it broke through PVC in <1 min, nitrile in 7 min, PVA in 14 min, Viton<sup>TM</sup> in 57 min [26], and Lifeguard<sup>TM</sup> Responder material in >180 min [26]. Similarly, *cis*-2,3-dichloroethylene degraded butyl, natural rubber, neoprene, nitrile, PVA, and PVC with breakthrough for gloves of PVC in 1 min, neoprene in 5 min, butyl in 19 min, and Viton<sup>TM</sup> in 101 min [26]. Because dichloroethylene is more polar than 1,3-DCP, the breakthrough times for 1,3-DCP should be longer than for dichloroethylenes, and nitrile should protect longer than PVC, butyl, neoprene, or natural rubber.

Some 1,3-DCP permeation data for chemically resistant fabrics exist also. DuPont [27] lists immediate breakthrough time (<10 min) for Tychem CPF 2, Tychem SL, and Tychem CPF 3, but more protection by Tychem F (25 min breakthrough and permeation rate 1.6  $\mu\text{g}/(\text{cm}^2 \text{ min})$ ) and Tychem Responder (breakthrough time >480 min with permeation rate <0.1  $\mu\text{g}/(\text{cm}^2 \text{ min})$ ). The permeation of 1,3-DCP vapor across plastic films used to enhance the fumigant effect and for storage purposes has been investigated [28,29]. The present study sought to demonstrate the protective capabilities of nitrile and laminates against liquid Telone formulations.

## 2. Experimental/materials and methods

### 2.1. Chemicals

Telone EC<sup>TM</sup> (nominally 93.6% 1,3-DCP and 6.4% “inert ingredients”) and Telone II<sup>TM</sup> (nominally 97.5% 1,3-DCP and 2.5% inert ingredients) were provided by Dow Agro-Sciences, Indianapolis, IN. *cis*-1,3-DCP (97%) neat standard was obtained from Aldrich, Milwaukee, WI, and from Chem Service, West Chester, PA. *trans*-1,3-DCP (97%) was obtained from Chem Service. 1,2-Dichlorobenzene (99%) from Aldrich was the internal standard for gas chromatography. Optima grades methanol and hexane, and concentrated nitric acid (for cleaning glassware) were purchased from Fisher Scientific, Tustin, CA. Helium (99.999%), 5% methane in argon, and nitrogen (99.999%) were obtained from Air Liquide, Long Beach, CA. Personnel handling chemicals wore laboratory coats, charcoal-lined disposable respirators, double SafeSkin<sup>TM</sup> gloves, and worked in fume hoods whenever possible.

### 2.2. Gloves

The gloves utilized were 11-mil thick and 33 cm in length embossed unsupported/unlined powderless Sol-Vex<sup>TM</sup> nitrile (Catalog No. 37–145) and Barrier<sup>TM</sup> laminate from Ansell, Coshocton, OH, and disposable powderless unsupported/unlined Safeskin<sup>TM</sup> nitrile exam gloves (Kimberly Clark, San Diego, CA) of unspecified thickness and 24.1 cm in length. Silver Shield<sup>TM</sup> laminated gloves were purchased from North Safety Products, Cranston, RI.

The container labels for Telone EC<sup>TM</sup> [30] and Telone II<sup>TM</sup> [31] recommend “PPE constructed of Saranex, neoprene, and chlorinated polyethylene provide short-term contact or splash protection against liquid in this product. Longer term protection is provided by PPE constructed of Viton<sup>TM</sup>, Teflon<sup>TM</sup>, and EVAL<sup>TM</sup> barrier laminates (for example, Responder<sup>TM</sup> suits manufactured by Lifeguard<sup>TM</sup> or SilverShield<sup>TM</sup> gloves manufactured by North)”. The older Material Safety Data Sheets (MSDS) for Telone EC<sup>TM</sup> [32] and Telone II<sup>TM</sup> [33] merely state “use protective clothing impervious to this material”.

### 2.3. Equipment

The gas chromatograph (GC)-electron capture detector (ECD) was a Hewlett-Packard 5890 with a splitless 30 m  $\times$  0.25 mm DB-1701 (1  $\mu\text{m}$  film) chemically bonded, fused-silica capillary column (Alltech, Folsom, CA), and a constant-current pulse modulated <sup>63</sup>Ni-ECD, whose signal was displayed on a Hewlett-Packard 3396 integrator (Agilent Technologies, Palo Alto, CA). The temperature of the injector was 180 °C and that of the detector was 260 °C. The flow of 5:95 methane/argon carrier column gas was 0.80  $\pm$  0.05 mL/min, 2.5  $\pm$  0.2 mL/min for septum purge, 4.0  $\pm$  3 mL/min for detector makeup, and 4.0  $\pm$  0.3 mL/min

for anode purge. The column was held at 80 °C for 3 min, and then heated at 10 °C/min to 200 °C. The retention times of the *cis*- and *trans*-isomers were 5.184 and 5.902 min, respectively, with complete resolution. 1,2-Dichlorobenzene eluted at 6.33 min.

Agilent Technologies Model Number 6890N Network Gas Chromatograph/Agilent Model Number 5973 Network Mass Selective Detector (MSD) equipped with a HP 5-MS 30 m × 0.25 mm (0.25 μm film) fused silica capillary column. The system was basically used to confirm purity and identify components of the formulation. The MSD was a quadrupole with an electron multiplier detector operated over the *m/z* range 50–550 for scan mode analyses. The temperature of the injector was 200 °C and that of the transfer line was 210 °C. The 70 eV ion source was held at 250 °C. The flow of helium carrier was 0.50 ± 0.05 mL/min. The purge delay was 3 min. The column temperature program was initial temperature 80 °C for 3 min (the same as the solvent delay time) and then heating at 5 °C/min to 200 °C for 10 min. The retention times of the *cis*- and *trans*-isomers were 3.86 and 4.08 min, respectively, and were not completely resolved.

Infrared (IR) spectra were obtained with a Avatar 360 Fourier-transform (FT) spectrometer system (Thermo Nicolet, Madison, WI), a single-beam FT-IR spectrophotometer using reflectance mode and operated with OMNIC 6.0a Software controlled by Windows 98. The crystal was diamond in a single-reflection horizontal attenuated total reflectance mode. The spectral range was 4000–600 cm<sup>-1</sup>. The number of scans was 128.

ASTM-type I-PTC-600 permeation cells were from Pesce Lab Sales (Kennett Square, PA). The moving tray shaker water bath used for immersion of three permeation cells simultaneously was a Fisher Scientific Model 125 No. 429. Three copper metal tubes (23 cm × 15 cm o.d. × 133 mm i.d.) were mounted on the two rails of the shaker after hacksawing 1-mm wide grooves in the bars and using emery paper to smooth the jagged edges. Three-prong clamps allowed suspension of three permeation cells above and into the bath water as desired. A micrometer screw gauge (L.S. Starrett Co., Athol, MA) was used to measure glove thickness before and after experiments to indicate glove swelling or shrinkage. Vernier calipers (Mitutoyo, Japan) allowed measurement of the glove diameters cut for permeation studies.

#### 2.4. Formulation analyses

The formulation sample was diluted into the GC-ECD working linear range of the *cis*- and *trans*-isomers (0.5–7.0 ng), and the 1,2-dichlorobenzene internal standard in hexane added to the vial to a concentration of 22 ng/μL. The amounts of *cis*- and *trans*-isomers in the sample in triplicate were determined by the method of internal standards and the 1,3-DCP content obtained by summing the isomer amounts, and correcting for the fraction of the solution injected, and any dilution factor. GC-MS analyses allowed identification of other compounds in the formulation.

#### 2.5. Permeation procedure

The detailed procedure is provided elsewhere [34,35] and is based on the standard ASTM F739-99 permeation method [36].

In summary, glove materials cut from out-of-the-box gloves were conditioned at least for 24 h in a desiccator with 55 ± 1% relative humidity (saturated aqueous sodium dichromate). The material was held between two Teflon<sup>TM</sup> gaskets and the Pyrex<sup>TM</sup> chambers by a uniform torque. A volume of 10-mL hexane was added as the collection medium, and then 10 mL of formulation was pipetted into the challenge chamber. Three permeation cells were immersed into the water bath at 30.0 ± 0.5 °C and horizontal shaking speed of 8.4 ± 0.5 cm/s begun so as to ensure no concentration gradients in the challenge and collection media. Initially, 0.1-mL samples were withdrawn every hour and deposited into 1-mL vials with Teflon<sup>TM</sup>-lined screwcaps. After adding 1,2-dichlorobenzene internal standard in hexane to a vial concentration of 22 ng/μL, 1 μL aliquots were injected into the GC-ECD, and quantitation of *cis*- and *trans*-isomers done by the internal standards method. The sum of the isomer masses in each injection, applying any dilution factor, and knowing the fraction of collection fluid injected, yielded the sample 1,3-DCP content.

Quality assurance procedures included tests for leaking of the assembled permeation cell, and hexane backdiffusion as outlined elsewhere [34,35]. Aliquots of 1-mL challenge solution were obtained fresh, before the permeation began, and from it after each permeation run. Blank runs in triplicate involved no challenge solvent with hexane in the collection side.

#### 2.6. Infrared reflectance experiments

Reflectance spectra of both the challenge and collection sides of the conditioned and unconditioned gloves of the same lot were examined before a permeation experiment. The method blank to account for any solvent effects was to expose a specimen of the same conditioned glove to air on the challenge side and hexane on the collection side for the appropriate time. The glove specimen examined for permeation after experiments was dried to constant weight in the constant humidity desiccator before being examined on both sides.

The major reflectance peaks were tabulated from the spectra obtained from 4000 to 600 cm<sup>-1</sup>. Difference spectra for exposure situations of interest were also measured, for example, exposed versus method blank. When areas appeared homogeneous for a given glove side, the reflectances at a minimum of three distinct positions were measured and the data averaged if statistically homogeneous. The number of scans for each measurement was 128 as a compromise between sensitivity and analysis time. The tabulated data facilitated the characterization of changes in reflectance minima and intensities and the appearance and disappearance of reflectance

minima before and after challenges as well as possible detection of pesticide and its formulation.

### 2.7. Statistics

Student's *t*-test and analysis of variance (ANOVA) analyses assigned statistical significance ( $p \leq 0.05$ ) necessitated at least triplicate samples in each experiment to define arithmetic means, standard deviations (S.D.), and coefficients of variation (CV). Linear regression analyses allowed calculation of slopes and intercepts, their corresponding S.D.s, the correlation coefficient *r*, and *p*-values.

## 3. Results and discussion

### 3.1. Telone formulation analyses

The 1,3-DCP content of Telone II<sup>TM</sup> was  $97.5 \pm 0.6\%$  (w/w) and that of Telone EC<sup>TM</sup> was  $84.8 \pm 1.7\%$  (w/w). The *cis/trans*-isomer mass ratios were  $1.42 \pm 0.18$  and  $1.48 \pm 0.04$ , respectively, and were statistically different at  $p \leq 0.05$ .

While the 1,3-DCP content of Telone II<sup>TM</sup> did not differ statistically at  $p \leq 0.05$  from nominal (assuming the same relative standard deviation for the nominal as observed experimentally), the content for Telone EC<sup>TM</sup> was less than its nominal concentration. GC-MS analysis of Telone EC<sup>TM</sup> showed the presence of 1,3- and 1,2-dichloropropene, 1,3,3-DCP (*cis*- and *trans*-isomers), and allyl chloride, all being reaction products from the chlorination of propylene, the usual method of synthesis of 1,3-DCP [37]. There was also a trace amount of trimethylbenzenes.

### 3.2. Permeation of gloves

The permeation of total 1,3-DCP through different gloves is summarized in Table 1 in terms of  $P_s$ ,  $t_b$  (the time to reach 250 ng/cm<sup>2</sup> for a closed system), and the total mass collected at 8 h. These results are the first in the peer-reviewed literature for Telone EC<sup>TM</sup> for disposable and chemically resistant nitrile, and laminated gloves.

#### 3.2.1. Nitrile gloves

**3.2.1.1. Permeation.** The Safeskin<sup>TM</sup> disposable gloves were degraded as evidenced by the large and variable  $P_s$  for 1,3-DCP, very short  $t_b$  of 1–12 min, and large 1,3-DCP mass collected after 8 h. An extremely variable fast permeation/penetration phase was followed by an extended slow phase. The degraded Safeskin<sup>TM</sup> gloves were sticky and fragile.

The Sol-Vex<sup>TM</sup> gloves yielded  $t_b$  of 6.0–7.0 min which allowed a rapid permeation phase up to 60 min of contact with no visible degradation (average  $P_s$  of  $21.7 \pm 20.3 \mu\text{g}/(\text{cm}^2 \text{min})$ ), followed by a slower phase (average  $P_s$  of  $3.10 \pm 0.21 \mu\text{g}/(\text{cm}^2 \text{min})$ ) where visible swelling and

bleaching of the material occurred that culminated in hole formation after about 250 min of contact, with 1,3-DCP amounts collected at 8 h being about the same as for the disposable nitrile gloves. The swollen Sol-Vex<sup>TM</sup> material protruded into the collection chamber by the end of the permeation experiments. As expected, the chemically resistant nitrile glove was a better barrier than the disposable nitrile glove. Both are unsuitable for hand protection against Telone EC<sup>TM</sup> because of the short  $t_b$  (<10 min) and large initial  $P_s$ .

**3.2.1.2. Infrared reflectance.** The outer surface of the dried conditioned Sol-Vex<sup>TM</sup> gloves after permeation showed an intense IR reflectance minimum at  $761 \text{ cm}^{-1}$  after 60 min of exposure, indicative of a C–Cl stretch. The reflectance spectra of the inner and outer surfaces of Sol-Vex<sup>TM</sup> nitrile gloves have been discussed elsewhere [38]. The reflectance IR spectra of Safeskin<sup>TM</sup> glove surfaces have also been measured previously by our research group [38,39].

#### 3.2.2. Laminated gloves

**3.2.2.1. Permeation.** The two laminated gloves definitely offered some protection against Telone EC<sup>TM</sup> (Table 1). They did not swell or shrink during the permeations as shown by micrometer measurements. The 1,3-DCP permeation of the Silver Shield<sup>TM</sup> gloves was in steady state shortly after breakthrough up until the end (average  $P_s$  of  $0.83 \pm 0.19 \mu\text{g}/(\text{cm}^2 \text{min})$ ), but the Barrier gloves (average  $P_s$  of  $1.22 \pm 0.93 \mu\text{g}/(\text{cm}^2 \text{min})$ ) showed accelerated permeation after 300–360 min. The Barrier<sup>TM</sup> gloves (CV, 76%) also allowed more variation than did the Silver Shield<sup>TM</sup> gloves (CV, 23%).

Table 1 clearly indicates that Silver Shield<sup>TM</sup> had about the same  $t_b$ , generally smaller  $P_s$ , but always smaller 1,3-DCP masses collected after 8 h than did Barrier<sup>TM</sup>. Based on the latter criterion, the average 8-h mass in milligrams for Barrier<sup>TM</sup> was  $4.61 \pm 2.62$  (range 2.51–7.55), and that for Silver Shield<sup>TM</sup> was  $1.85 \pm 0.40$  (range 1.50–2.28). Thus, on average, the latter glove protected about 2.5 times (1.1–5.0 range) better than the former over 8 h. If the average  $t_b$  were the risk criteria, Silver Shield<sup>TM</sup> with  $41 \pm 17$  min (28–60 min range) protected equally well as Barrier<sup>TM</sup> with  $40 \pm 15$  min (27–56 min range) at  $p \leq 0.05$ . As Viton<sup>TM</sup> protects against pure 1,3-DCP without breakthrough for 480 min [23], maximum protection is offered by wearing Viton<sup>TM</sup> gloves instead of the laminated ones. However, Viton<sup>TM</sup> gloves are expensive and workers complain that they are hot and easy to tear.

**3.2.2.2. Infrared reflectance.** FT-IR reflectance examination of the inner and outer glove surfaces revealed no marked glove degradation unlike for the Sol-Vex<sup>TM</sup> nitrile gloves. The reflectance minima of the unexposed inner and outer surfaces of the Silver Shield<sup>TM</sup> glove were identical at 2916.2–2916.4, 2848.4–2848.7, 1462.8–1463.4, 719.2–719.4, and 729.4–729.6 cm<sup>-1</sup>. The outer surface showed an extra minimum at 1703.7–1704.0 cm<sup>-1</sup>. After

Table 1

Permeation of total 1,3-dichloropropene at 30 °C from Telone EC<sup>TM</sup> through different gloves in a ASTM-type I-PTC permeation cell with hexane collection fluid

Glove	Run	Steady-state rate ( $\mu\text{g}/(\text{cm}^2 \text{min})$ )	$t_b$ (min)	Mass in collection side at 8 h (mg)
Safeskin <sup>TM</sup>	1	3860 (60–120 min)	1.0	9300 <sup>a</sup>
	2	5570 (60–120 min)	12	6160 <sup>a</sup>
	3	27900 (30–60 min)	4.0	6300 <sup>a,b</sup>
Sol-Vex <sup>TM</sup>	1	7.25 (30–60 min)	6.0	2.03 <sup>b</sup>
	2	12.8 (30–60 min)	6.5	3.51 <sup>b</sup>
	3	44.9 (30–60 min)	7.0	8.98 <sup>b</sup>
	4	3.33 (60–250)	–	4750 <sup>a</sup>
	5	2.92 (60–250 min)	–	7650 <sup>a</sup>
	6	3.06 (250–480 min)	–	7120 <sup>a</sup>
Barrier <sup>TM</sup>	1	0.177 (30–360 min)	27	2.51
	2	1.54 (30–360 min)	56	3.76
	3	1.95 (30–300 min)	38	7.55
Silver Shield <sup>TM</sup>	1	0.716 (60–480 min)	60	1.77
	2	1.051 (60–480 min)	28	2.28
	3	0.710 (60–480 min)	36	1.50

The times in parentheses in the steady-state rate column refer to the time period for which the steady state applies. The variable  $t_b$  is the normalized breakthrough time, the time to reach 250 ng/cm<sup>2</sup>.

<sup>a</sup> Degradation by the end of the experiment.

<sup>b</sup> At 60 min.

exposure, the challenge side had an additional weak maximum at 1108.2–1111.5 cm<sup>-1</sup>. The spectrum of the inner surface showed no change.

Both the inner and outer surfaces of the unexposed Barrier<sup>TM</sup> glove had identical IR reflectance minima of 2916.0–2916.2, 2848.3–2848.4, 1471.7–1472.0, 1462.6–1462.9, 729.2–730.1, and 717.6–718.9 cm<sup>-1</sup>. The outer surface showed a 1016.4–1016.6 cm<sup>-1</sup> minimum. After exposure, the inner surface had another weak minimum at 1103.0 cm<sup>-1</sup>, but the outer surface showed no changes.

### 3.3. Glove permeation skin risk assessment

Conservative risk assessment of wearing gloves involves the assumption that 100% of the bioaccessible mass to the skin over 8 h is absorbed through the skin. The 8-h permeated mass parameter of Table 1 is thus directly related to the potential risk of adverse dermal exposure over a 8-h workday. If the glove permeates equally over all its surface (area 5.07 cm<sup>2</sup>) and the average total surface area for two hands and lower forearms is 2000 cm<sup>2</sup> [40], an average of  $(1.85 \pm 0.40 \text{ mg} \times 2000)/5.07 = 730 \pm 158 \text{ mg}$  would permeate through Silver Shield<sup>TM</sup> gloves into the body. For a reference man of 70 kg, this represents a dose of  $730/70 = 10.4 \pm 2.2 \text{ mg/kg}$  body weight over a 8-h workday, assuming no other Telone exposure away from work and that inhalation exposure also does not occur.

According to Cal. EPA [16], the 0.2  $\mu\text{g}/\text{L}$  water quality guideline reflects a one in a million risk of urinary bladder carcinoma [8], after drinking water exposure at 2 L/day, and 2 L/day equivalent by simultaneous inhalation

since 1,3-DCP is volatile. Therefore, the daily dose guideline is  $(0.2 \times 4) = 0.8 \mu\text{g}$ , equivalent to a daily dose rate of  $0.8/70 = 0.011 \mu\text{g}/(\text{kg day})$  for a 70-kg man. This reference dose is about six orders of magnitude lower than the workday dose calculated for the Silver Shield<sup>TM</sup> permeation case above. Alternatively, a non-cancer effect (body weight depression and hyperplasia of the non-glandular mucosa of the stomach) provides a guideline 450 times that of the cancer reference value [16] leading to a non-cancer reference dose of 5.0  $\mu\text{g}/\text{kg}$ , still about 1/2000 of the computed dose from the permeated Silver Shield<sup>TM</sup> gloves. If the acceptable risk is instead set at 1 case in a 1000 as often assumed by OSHA [41], the respective critical doses are 0.011 and 5 mg/kg, both still less than calculated for exposure through Silver Shield<sup>TM</sup> gloves. What is acceptable risk is clearly important. Assuming a linear relationship, the average Silver Shield<sup>TM</sup> exposure of about 10 mg/kg is equivalent to a cancer risk of  $(10,400/0.011) \times 10^{-6} \sim 0.945$  or about 95%, which would be unacceptable.

If not all of the Telone on the skin is absorbed, this would decrease the risk of adverse effects from dermal absorption. Because rat oral LD<sub>50</sub> values for 1,3-DCP usually range from 25 to 713 mg/kg (average  $364 \pm 262$ ,  $n = 7$ ) relative to a dermal LD<sub>50</sub> value of 775 mg/kg [1], the degree of skin absorption relative to oral exposure absorption is about 3.2–92% or on average 47%. The corresponding data for mice are 2.3–53% and an average of <30% for five oral LD<sub>50</sub> values relative to a mouse dermal LD<sub>50</sub> of >1211 mg/kg. If the lowest relative absorption is assumed to be representative (that is 2.3%), this would mean the above calculated guidelines for 100% absorption would be multiplied by a factor of 43. Only in the non-cancer case at a risk of 1 case in a 1000 would

a guideline exceed the 10 mg/kg dose calculated for Silver Shield™ after 8-h exposure.

Another way to limit exposure is to remove (“doff”) the gloves and don new ones. However, both Silver Shield™ and Barrier™ exhibit  $t_b$  between 27 and 60 min after exposure (Table 1) so that 8–16 changes of these gloves would be necessary to prevent exposure, an expensive proposition. In addition, the  $t_b$  threshold is at a  $0.25 \times 5.07 = 1.27 \mu\text{g}$  dose in the ASTM experiment, equivalent to a  $1.27 \times 2000/5.07 = 500 \mu\text{g}$  dose to the hands and lower forearms or a  $7.1 \mu\text{g}/\text{kg}$  body weight daily threshold. This threshold is still higher than the non-cancer threshold calculated above from the Cal. EPA guidance (even if skin exposure is only 2.3% as efficient as oral exposure) but lower than the OSHA guidances or when non-cancer guidances also are adjusted for 2.3% efficiency of skin absorption relative to oral absorption, illustrating the very arbitrary nature of the  $t_b$  definition and the how uncertain the assumptions of risk assessment are. Because 1,3-DCP was detected well before the  $t_b$ , the situation is even worse.

Therefore, only Viton™ gloves should be worn for hand protection from non-cancer and cancer effects. Telone II™ is applied undiluted in the field accounting for past air pollution episodes [5,6], but this will increase the likelihood of dermal exposure also. Telone EC™ is applied generally through buried drip irrigation systems, so that the major skin exposure opportunity is during the original formulating process, whilst adding it to the irrigation system, and contact with surfaces wetted by water containing the formulation.

The above calculations show that adverse exposures may still occur dermally if Telone EC™ contacts laminated gloves, even if adequate respiratory protection is worn.

#### 4. Conclusions

While disposable and chemically resistant nitrile did not protect against 1,3-DCP in Telone EC™ in these ASTM-type permeation cell experiments, the enhanced protection of laminated gloves was also not adequate to protect against adverse effects as illustrated by a risk assessment. Thus, only Viton™ gloves are recommended to be worn to prevent dermal exposure. These results have relevance to workplace and environmental situations where spills, spraying, and splashes occur, and formulations are handled, even if the inhalation exposure is zero through the wearing of adequately protective respirators.

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