

Permeation of Telone C-35 EC™ and Chloropicrin Through Protective Gloves

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ABSTRACT: Telone is a potent volatile liquid chlorinated hydrocarbon pesticide based on 1,3-dichloropropene that is applied without dilution for fumigation purposes, and so poses an inhalation and air pollution threat, as proven by past monitoring. 1,3-Dichloropropene also causes allergic skin effects, is absorbed through the skin, and metabolites have been shown to be excreted after skin absorption, so making it a skin exposure threat too, one that may become most important in the situations of adequate respirator protection or cleaning up spills. It is often coformulated with agents like chloropicrin, a chemical warfare agent, to substitute for methyl bromide fumigant. The aim of the study was to assess if nitrile and laminated gloves provided adequate protection against Telone C-35 EC™, using an ASTM-type I-PTC-600 permeation cell containing disposable (Safe-skin™) and chemically-resistant (Sol-Vex™) nitrile and laminated (Barrier™ and Silver Shield™) glove materials with hexane liquid collection. Analyses of *cis*- and *trans*-1,3-di-

chloropropene and chloropicrin in the collection fluid at various times were performed on a moderately polar capillary column, using gas chromatography–electron capture detection by the internal and external standards methods. Both nitrile materials were degraded by the formulation and pure chloropicrin, and so were unsuitable for protection. Both laminated glove materials offered some protection with Silver Shield™ the better, since less mass had permeated by 8 h, but the extent of protection was still inadequate, as illustrated by a risk assessment of the skin exposure situation. It is recommended that Viton gloves be worn rather than the laminated ones when Telone C-35 EC™ is handled. Laminated gloves may protect against pure chloropicrin. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 18–25, 2006

Key words: telone; 1,3-dichloropropene; glove; chloropicrin; nitrile; laminated gloves; risk

INTRODUCTION

Telone is the commercial name of the nematocidal/fungicidal/insecticidal fumigant that contains the active ingredient 1,3-dichloropropene (DCP; CAS RN 542–75–6). The latter is a colorless liquid of boiling point of about 108°C, with a vapor pressure at 25°C of 34 torr, a log K_{ow} of 1.82, and a water solubility of 2.8 g/L at 20°C.¹ It is a mixture of *cis*- and *trans*-isomers, the ratio varying with chemical supplier.² Quantification involves adding the isomer contents.² DCP 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 2005 cut-off under the Montreal Protocol.⁴ Telone caused air pollution problems after

spraying in Central California that led to its withdrawal in 1990 in California, but it was reinstated in 1995.^{5,6} Telone is also an animal carcinogen,^{7–13} but benefits have been adjudged by 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 noncancer effects.¹⁶ The 2004 American Conference of Governmental Industrial Hygienists (ACGIH) recommended threshold limit value (TLV) for personal breathing zone air sampling over 8 h is 1 ppm (v/v) = 4.54 mg/m³ (skin) set on irritation effects,¹⁷ as is the Permissible Exposure Limit (PEL) of the Occupational Safety and Health Administration (OSHA), and Recommended Exposure Limit (REL) of the National Institute for Occupational Safety and Health (NIOSH).¹⁸

The risk of skin exposure to a volatile solvent like DCP is often discounted because of the known inhalation exposure. DCP does cause skin irritation, allergic contact dermatitis, and is absorbed through the skin.^{1,19–21} There were at least 19 reportable spills that involved Telone, in 2001.²² There are no peer-reviewed literature data on the type of glove appropriate to protect against DCP exposure. North Safety Products does recommend 10- or 12-mil Viton gloves,

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which resist for at least 8 h, and secondarily 13-, 16-, 17-, and 32-mil butyl gloves that exhibit a 1.3 h breakthrough time and a $192 \mu\text{g cm}^{-2} \text{min}^{-1}$ permeation rate.²³ Although Ansell does not provide information for DCP,²⁴ it does not recommend nitrile, unsupported neoprene, polyvinyl chloride, natural rubber, or neoprene/natural rubber blend for protection against trichloroethylene, ethylene dichloride, and for perchloroethylene except for nitrile where the breakthrough time is 300 min. and the permeation rate is $0.9\text{--}9 \mu\text{g cm}^{-2} \text{min}^{-1}$. All three compounds can be resisted by BarrierTM laminate and supported polyvinyl alcohol, though not the latter for aqueous solutions. As trichloroethylene has a water solubility at 25°C of 1.1 g/L²⁵ and that for perchloroethylene is 0.15 g/L²⁵, these two analog compounds are more nonpolar than DCP of water solubility 2.8 g/L at 20°C. As ethylene dichloride (1,2-dichloroethane) has a water solubility of 8.7 g/L at 20°C²⁵, it is more polar than DCP. The implication is that nitrile has the best but still not promising chance to be protective other than the more expensive laminate and Teflon-based gloves for situations involving organic and aqueous solution exposures. A *cis,trans*-dichloroethylene mixture degraded butyl, natural rubber, and neoprene gloves, while it broke through gloves of polyvinyl chloride in <1 min, nitrile in 7 min, polyvinyl alcohol in 14 min, and VitonTM in 57 min, and through LifeguardTM responder material in >180 min.²⁶ Similarly, *cis*-2,3-dichloroethylene degraded butyl, natural rubber, neoprene, nitrile, polyvinyl alcohol, and polyvinyl chloride, with breakthrough for gloves of polyvinyl chloride in 1 min, neoprene in 5 min, butyl in 19 min, and VitonTM in 101 min.²⁶ Since dichloroethylene is more polar than DCP, the breakthrough times for DCP will be longer, and this emphasizes that only VitonTM and probably laminates may adequately protect against TeloneTM. There are some permeation data for chemically-resistant fabrics. DuPont²⁷ 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 $1.6 \mu\text{g cm}^{-2} \text{min}^{-1}$) and Tychem Responder (breakthrough time >480 min with permeation rate $<0.1 \mu\text{g cm}^{-2} \text{min}^{-1}$). The permeation of DCP vapor across plastic films used to enhance the fumigant effect and for storage purposes has been investigated.^{28,29}

Chloropicrin is not only a pesticide (rodenticide, fumigant, insecticide, nematocide, bactericide, fungicide, herbicide), but it has also been used as a chemical weapon "tear agent".³ It is a colorless liquid of boiling point of about 112°C, with a vapor pressure at 0°C of 5.7 torr, and a log K_{ow} of 2.09, with water solubility of 1.62 g/L at 25°C.³ In the past, it has often been applied as pesticide with methyl bromide and sulfuryl fluoride. It is now increasingly used with DCP as a methyl bromide substitute.⁴ Chloropicrin is not an animal

carcinogen,³⁰ though it is mutagenic in the presence of glutathione.³¹ The ACGIH recommended TLV for personal breathing zone air sampling over 8 h is 0.1 ppm (v/v) = 0.7 mg/m^3 set on irritation effects¹⁷ as is the OSHA PEL, and the NIOSH (10-h exposure) REL.¹⁸ Studies on chloropicrin vapor permeation through polyethylene and other plastic films are available.^{29,32–35} No reports of permeation of liquid chloropicrin through glove materials have been published. DuPont has indicated that TychemTM F suit material resists²⁷ permeation for 480 min with a permeation rate $<0.1 \mu\text{g cm}^{-2} \text{min}^{-1}$. Neoprene gloves are recommended in the Toxic and Hazardous Chemicals Safety manual.³

The present study sought to demonstrate the protective capabilities of nitrile and laminates against a liquid DCP/chloropicrin formulation. This is the first study to report permeation of two active ingredient pesticides in the same mixture.

EXPERIMENTAL

Chemicals

Telone C-35 ECTM [EF-1499] (nominally 60.5% 1,3-DCP, 33.3% chloropicrin, and 6.2% "inert ingredients") was provided by Dow AgroSciences (Indianapolis, IN). *cis*-DCP (97%) neat standard was obtained both from Aldrich (Milwaukee, WI) and Chem Service (West Chester, PA). *trans*-1,3-DCP (97%) and chloropicrin (98%) neat standards were obtained from Chem Service. 1,2-Dichlorobenzene (99%) for use as an internal standard (IS) and trichloronitromethane (98%) for permeation challenge studies were from Aldrich. Optima methanol, Optima 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 wore laboratory coats, charcoal-lined disposable respirators, double SafeSkinTM gloves, and worked in fume hoods whenever possible.

Gloves

The gloves utilized were 11-mil thick and 33 cm in length embossed unsupported/unlined powderless Sol-VexTM nitrile (catalog no. 37–145) and BarrierTM laminate from Ansell (Coshocton, OH) and disposable powderless unsupported/unlined SafeskinTM nitrile exam gloves (Kimberley Clark, San Diego, CA) of unspecified thickness and 24.1 cm in length. Silver ShieldTM laminated gloves were purchased from North Safety Products (Cranston, RI). The Material Safety Data Sheet (MSDS) for Telone C-35 ECTM states³⁶ "Use protective clothing impervious to this material."

Equipment

The gas chromatograph (GC)–electron capture detector (ECD) was a Hewlett–Packard 5890 with a splitless 30 m 32×0.25 mm DB-1701 (1- μ m film) chemically bonded, fused-silica capillary column (Alltech, Folsom, CA) and a constant-current pulse modulated ^{63}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 ± 0.05 mL/min, 2.5 ± 0.2 mL/min for septum purge, 40 ± 3 mL/min for detector makeup, and 4.0 ± 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*-DCP isomers were 5.184 and 5.902 min, respectively, with complete resolution. Chloropicrin eluted at 6.77 min. 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) was equipped with a HP 5-MS 30 m $\times$ 0.25 mm (0.25- μ m film) fused-silica capillary column. The system was basically used to confirm purity and identify formulation components. 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*-DCP isomers were 3.86 and 4.08 min, respectively, and were not completely resolved. Chloropicrin was resolved from the DCP isomers.

Infrared (IR) spectra were obtained with a Avatar 360 Fourier transform (FT) spectrometer system (Thermo Nicolet, Madison, WI), a single-beam FTIR 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^{-1} . 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 $\times$ 15 cm OD $\times$ 133 mm ID) 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 sus-

pension 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.

Chromatographic analyses

The formulation sample was diluted into the GC–ECD working linear range of the *cis*- and *trans*-DCP and chloropicrin, and the 1,2-dichlorobenzene IS in hexane added to each vial to a concentration of 7.0 ng/ μ L. The amounts of *cis*- and *trans*-DCP and chloropicrin in the sample were determined in triplicate by the method of internal standards. The DCP content was obtained by summing the isomer amounts, and correcting for the fraction injected, and the dilution factor. Total chloropicrin was obtained after interpolation by correcting for fraction injected and dilution. GC–MS analyses in the scan mode allowed identification of other compounds in the formulation. Neat chloropicrin was analyzed by GC–ECD and GC–MS as for the formulation analysis.

Permeation procedure

The detailed procedure is provided elsewhere,^{37,38} and is based on the standard ASTM F739–99 permeation method.³⁹

In summary, glove materials cut from out-of-the box gloves were conditioned at least for 24 h in a desiccator with $(55 \pm 1)\%$ relative humidity (saturated aqueous sodium dichromate). The material was held between two Teflon™ gaskets and the Pyrex™ chambers by a uniform torque. A volume of 10-mL hexane was added as the collection medium, and then 10 mL of neat formulation was pipetted into the challenge chamber. Three permeation cells were immersed into the water bath at $(30.0 \pm 0.5)^\circ\text{C}$ and horizontal shaking speed of 8.4 ± 0.5 cm/s begun to ensure no concentration gradients in the challenge and collection sides as confirmed by prior challenge solution opacity observations at different shaker speeds. Initially, 0.1-mL samples were withdrawn every hour, and deposited into 1-mL vials with Teflon-lined screw caps. After adding 1,2-dichlorobenzene internal standard in hexane to a vial concentration of 7.0 ng/ μ L, aliquots of 1 μ L were injected into the GC–ECD, and quantitation of *cis*- and *trans*-DCP and/or chloropicrin done by the method of internal standards except in the case of the formulation where the internal standard interfered and the external standards method was used. The sum of the isomer DCP in each sample corrected for fraction injected and dilution factor yielded the sample

total DCP content. Correction for the fraction taken from the collection side gave the collection side mass.

Quality assurance procedures included tests for leaking of the assembled permeation cell, and challenge and collection side solvent back diffusion.^{37,38} 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.

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 negative control exposure situation 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⁻¹. Difference spectra for exposure situations of interest were also measured, e.g., exposed and blanks. When areas appeared visually 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 reflectances before and after challenges as well as possible detection of pesticide and its formulation.

Statistics

Student *t* 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 (SD), and coefficients of variation (CV). Linear regression analyses allowed calculation of slopes and intercepts, their corresponding SDs, the correlation coefficient *r*, and *P*-values.

RESULTS

Purity and formulation analyses

Chloropicrin showed a GC-ECD linear range from 0.2 to 3.6 ng, and that for the *cis*- and *trans*-DCP was 0.5–7

ng. The purity of the neat chloropicrin was (97.5 ± 1.2)% not significantly different from the 98% nominal purity. There was a very small molecular ion (*m/z* 163) in the mass spectrum, the base peak being *m/z* 110 (2 Cl), and with *m/z* 117 (3 Cl) next most abundant. The major chloropicrin impurity was dichloronitromethane. The purities of both neat *cis*- and *trans*-DCP standards were confirmed, their major common impurities (<2%) being 1,3,3-trichloropropene (*cis*- and *trans*-isomers).

The DCP content of the formulation was shown to be (59.50 ± 0.98)% (w/w), the chloropicrin content was (29.27 ± 0.65)%, with the “inert content” (unaccounted balance) being (11.23 ± 0.67)%. Thus, although the DCP content did not differ from the nominal 60.5% at $P \leq 0.05$ (assuming the same relative standard deviation for the latter as for the formulation analysis), the chloropicrin content was significantly lower than the nominal content of 33.3%. Similarly, the unaccounted balance content was higher than the nominal of 6.2%. The *cis/trans*-DCP isomer mass ratios were (1.76 ± 0.15)% (w/w).

GC-MS analysis of the formulation showed the presence of 1,3- and 1,2-dichloropropane, 1,3,3-trichloropropene (*cis*- and *trans*-isomers), and allyl chloride, all being reaction products of the chlorination of propylene, the usual method of synthesis of DCP.⁴⁰ Isomers of *m/z* 120 (trimethyl benzenes, methyl ethyl benzenes, cumene, and propyl benzene) were also present.

Glove permeation

The permeations of chloropicrin and formulation DCP/chloropicrin through different gloves are summarized in Tables I and II, respectively, in terms of steady-state permeation rate P_s , the normalized breakthrough time t_b (time to reach 250 ng/cm² for a closed system), and the total mass collected at 8 h. The results are the first in the peer-reviewed literature for Telone C-35 ECTM and pure chloropicrin for disposable/chemically-resistant nitrile, and laminated gloves.

Chloropicrin

SafeskinTM was degraded within 60 min. The amounts collected were a result mostly of penetration rather permeation, and were extremely variable. The other materials were permeated early on, but Sol-VexTM was also penetrated after 60 min.

Table I shows that Sol-VexTM was less protective than the Silver ShieldTM laminate. The permeation through the nitrile glove contained two distinct steady-state periods, the first phase (30–178 min) being 2.27 ± 0.48 times faster than the second (232–480 min) on average. The average P_s of the first period was also more variable (40%) than that of the second phase

TABLE I
Permeation of Neat Chloropicrin at 30°C Through
Different Gloves in a ASTM-type I-PTC Permeation
Cell with Hexane Collection Fluid

Glove	Run	P_s ($\mu\text{g cm}^{-2}$ min^{-1})	t_b (min)	Mass in collection side at 8-h (μg)
Sol-Vex™	1	A. 4.56 (20–178)	<10	8,800 ^a
		B. 2.49 (178–480)		
	2	A. 3.56 (30–176)	<10	8,770 ^a
		B. 1.62 (232–480)		
	3	A. 7.58 (14–176)	<10	10,000 ^a
		B. 2.72 (176–480)		
Silver Shield™	1	0.0394 (120–360)	15	97
	2	0.0292 (120–480)	20	71
	3	0.0334 (120–480)	20	85

The times in parentheses in the permeation steady-state rate (P_s) column relate to the time period from which the steady-state permeation rate was derived. The variable t_b is the normalized breakthrough time, the time to reach 250 ng/cm².

(A) signifies the first steady-state phase and (B) the second steady-state phase.

^a Degradation by the end of the experiment.

(25%). All the t_b were less than 10 min. The average mass in the collection side after 8 h permeation was 9.19 ± 0.70 mg (8.7–10 mg), about $(0.056 \pm 4)\%$ of the original challenge mass.

In contrast, only one steady-state phase (120–360 min) occurred for the laminated gloves, the average P_s of $0.0340 \pm 0.0051 \mu\text{g cm}^{-2} \text{min}^{-1}$ having a CV of 15%. The average mass permeated after 8 h was $84.3 \pm 13 \mu\text{g}$ with a CV of 15%, this being about $(0.051 \pm 0.008)\%$ of the original challenge mass. The t_b values were between 15 and 20 min. There were no significant ($P \leq 0.05$) thickness and weight differences between pre- and postexposure glove specimens.

According to the 8-h permeated/penetrated mass criterion, the laminated glove was 9190/84.3 ~109 times more protective than the nitrile glove, but according to the t_b parameter there was not that much difference in protectiveness. Since chloropicrin is not a carcinogen,³⁰ the t_b criterion is not as important as the exposure mass in risk assessment for the situation. The laminated glove is on average more than $2.28/0.034 = 67$ times more protective relative to the second steady-state phase P_s of the Sol-Vex™ glove, and about $5.24/0.034 = 154$ times more than the first steady-state P_s . The 8-h criterion is favored because

TABLE II
Permeation of Total 1,3-Dichloropropene and Chloropicrin (CLP) at 30°C from Telone C-35 EC™ Through Different
Gloves in a ASTM-Type I-PTC Permeation Cell with Hexane Collection Fluid

Glove	Run	P_s ($\mu\text{g/cm}^2/\text{min}$)	t_b (min)	Mass in Collection Side at 8-hours (μg)
Sol-Vex™	1	DCP: 3,360 (20–60)	16	741,000 ^a
		CLP: 1,153 (30–60)	26	20,700 ^a
	2	DCP: 3,458 (30–50)	15	1,029,000 ^a
		CLP: 1,153 (30–60)	28	17,500 ^a
	3	DCP: 3,096 (20–60)	15	676,000 ^a
		CLP: 949 (30–60)	20	19,300 ^a
Barrier™	1	DCP: A. 0.0603 (19–270)	10	95 ^c
		B. 0.831 (270–480)		980
		CLP: A. 0.0112 (30–90)	25	10.7
	2	B. 0.00357 (90–480)		83 ^c
		DCP: A. 0.043 (30–270)	<10	1,160
		B. 1.54 (360–480)		8.34
	3	CLP: 0.00409 (200–480)	110	136 ^c
		DCP: A. 0.0849 (30–360)	<10	853
		B. 1.15 (360–480)		
		CLP: A. 0.0103 (70–120)	60	8.90
Silver Shield™	1	B. 0.00112 (180–480)		22.3
		DCP: 0.00422 (120–480)	<120	2.48
	2	CLP: 0.000330 (120–480)	<120	13.2
		DCP: 0.00349 (180–480)	<120	2.53
	3	CLP: 0.000665 (180–480)	<120	21.8
		DCP: 0.00362 (180–480)	<120	2.64

The times in parentheses in the permeation steady state permeation rate (P_s) column relate to the time period from which the steady state rate was derived. The variable t_b is the normalized breakthrough time, the time to reach 250 ng/cm².

(A) signifies the first steady state phase and (B) the second steady state phase.

^a At 60 min.

^b Degradation by the end of the experiment.

^c At 270 min.

this mimicks what would permeate in an 8-h work day and is used in risk assessment.

The reflectance infrared investigation of the conditioned Silver ShieldTM gloves showed that the two surfaces of the conditioned unexposed gloves differed in their reflectance minima. Common minima (in cm^{-1}) were at 2916–2917 (strong aliphatic C—H stretch), 2848–2849 (strong aliphatic C—H stretch), 1462–1464 (moderate C—C stretch), 1367–1368 (very weak C—N stretch), 719–721 (moderate C—F stretch), and 729–730 (moderate C—F stretch). The outer surface showed additional minima (in cm^{-1}) at 3345–3346 (broad hydrogen-bonded O—H stretch from 4600–3200), 2306–2307 (very weak C=N stretch), 1703–1704 (moderate —C=O stretch), 1107–1108 (moderate broad —OH bend with other weak minima near 1349–1350, 1237–1238, and 947–951). Chloropicrin exposure did not change these minima significantly, except the minima at 719–721 and 729–730 cm^{-1} merged more closely for the inner surface, and the —OH related bands disappeared so leaving only a very weak broad minimum at 1232–1235 cm^{-1} (weak —CF₂/—CF₃ wags) for the outer surface.

For Sol-VexTM exposed to chloropicrin, new stronger minima than the 969–970 cm^{-1} most intense one before exposure⁴¹ appeared for the outer side (in cm^{-1}) at 669–671, 857–859, 900–902, 707–709, and 1603–1605. These data are consistent with surface degradation because the minima from 669 to 859 cm^{-1} are consistent with carbon–chlorine bonds.

Formulation

The formulation caused SafeskinTM gloves to be degraded within the initial 60 min by permeation and penetration. The extremely variable amounts collected after 60 min of exposure were about on average: 880 mg for the *cis*-1,3-dichloropropene, 560 mg for the *trans*-1,3-dichloropropene, and 280 mg of chloropicrin, with an almost immediate t_b after contact. These amounts represent about 17% and 7.1% of the DCP and chloropicrin challenge masses, respectively. It was not possible to conduct valid permeation experiments with SafeskinTM gloves because of the micropuncture effect of the DCP so leaving the material swollen, deformed, and with microholes. Research papers on the infrared reflectance characteristics of these SafeskinTM gloves have been published by our research group.^{41,42}

Table II presents the permeation data for chemically-resistant nitrile (Sol-VexTM), and two laminated gloves, BarrierTM and Silver ShieldTM. There were no significant ($P \leq 0.05$) thickness and weight differences between pre- and postexposure laminated glove materials, and in infrared reflectance minima of the surfaces of the latter gloves.

For Sol-VexTM, the material did not remain flat but bulged towards the collection side at the end of the exposure period and therefore swelled significantly. The average chloropicrin amount permeated after 1 h of exposure to the formulation is greater ($19,167/9190 = 2.1$) than for pure chloropicrin alone through Sol-VexTM for 8 h. This implies influence of the more polar and concentrated DCP. For Sol-VexTM and BarrierTM, the t_b for chloropicrin is always longer than for DCP. There are two steady-state periods for the BarrierTM material (slow followed by a fast phase for DCP, and usually the reverse for chloropicrin). There is only one for Silver ShieldTM.

The 8-h permeated masses are lowest for Silver ShieldTM. Relative to BarrierTM and Silver ShieldTM materials, the latter two materials relative to the 8-h permeated average mass of DCP through Sol-VexTM were $1,995,000/998 = 2000$ and $1,995,000/19.1 = 104,450$ times more protective, respectively, with Silver ShieldTM being $998/19.1 = 52$ times more protective than BarrierTM. On the basis of early average P_s , the respective data become $3305/0.0627 = 52,700$, $3305/0.00378 = 874,000$, and $0.0627/0.00378 = 17$. On the basis of average t_b , it was found that BarrierTM permitted a shorter t_b relative to Sol-VexTM for DCP, even though it permeated far less at 8 h than Sol-VexTM at 1 h. The average 8-h permeated mass for Silver ShieldTM for chloropicrin was $9.31/2.55 = 3.7$ times more than the average 8-h mass permeated through BarrierTM. It is to be noted that the average 8-h permeated masses for pure chloropicrin through Silver ShieldTM of 84 ± 13 (71–97) μg is much greater than that permeated for the formulation challenge of 2.55 ± 0.08 (2.48–2.64) μg .

Relative to the average Sol-VexTM P_s , BarrierTM and Silver ShieldTM are $1085/0.00853 = 127,000$ and $1085/0.000533 = 2.04$ million times more protective to chloropicrin, and Silver ShieldTM is $0.00853/0.000533 = 16$ times more protective than BarrierTM. The latter is about the same as for DCP. Thus both the 8-h permeated mass and P_s methods agree that Silver ShieldTM is more protective than BarrierTM for both DCP and chloropicrin. The question of whether the extent of protection is adequate for human health will be discussed in the following paragraphs.

Infrared reflectance data for the BarrierTM material showed the common reflectance minima for both surfaces (in cm^{-1}): 2915–2917 (strong), 2848–2849 (strong), 2162–2172 (very weak), 1462–1464 (moderate), 1471–1472 (moderate), 1104–1106 (very weak), 717–719 (moderate), and 730–731 (moderate). Extra minima shown by the outside surface were (in cm^{-1}) 3428 (broad and weak), 1737–1741 (moderate), 1350–1352 (weak), 1016–1018 (strong), and 668–670 (strong). The spectra are very close to those for Silver ShieldTM except for the strong 1016–1018 cm^{-1} mini-

mum for Barrier™, and other diagnostic outer surface peaks being at higher wave numbers.

The outer surface of the dried conditioned Sol-Vex™ gloves after 1 h of permeation not only showed a diagnostic intense nitrile glove minimum at 967–970 cm^{-1} , but also had increased minima at 2924–2929 cm^{-1} and 2852–2857 cm^{-1} , 1604–1609 cm^{-1} , and 1130–1105 cm^{-1} . There was a highly variable 1104–1106 cm^{-1} minimum. For the inner surface, the major new peak was 1602–1604 cm^{-1} (moderate), with increased 2923–2929 and 2854–2856 cm^{-1} .

DISCUSSION

There is no doubt from the above data that Silver Shield gloves are more protective than Barrier gloves, both being much more protective than Sol-Vex or Safeskin nitrile gloves. The question is whether they are protective enough.

Glove permeation skin risk assessment

The chemically-resistant nitrile gloves are unsuitable for hand protection against Telone C-35 EC™, even though they should be more protective than neoprene, polyvinyl chloride, natural rubber, and neoprene/natural rubber blend, according to the chemical DCP analogs examination of the Ansell Chemical permeation chart as discussed previously.²⁴ The major determinant in a risk assessment is the carcinogen. The DCP component is a known animal carcinogen whereas chloropicrin is not. In addition, DCP is present at higher concentration in the formulation than chloropicrin.

Conservative risk assessment of wearing gloves involves the assumption that 100% of the bioaccessible mass to the skin over 8 h would permeate through the skin. The 8-h mass collection parameter through the 1-in. diameter (5.07 cm^2) circular piece of glove is directly related to the potential risk of adverse exposure over a workday. If the glove permeates equally over all its surface and the average total surface area for two hands and lower forearms is 2000- cm^2 surface area,⁴³ an average of $(19.1 \pm 5.1 \mu\text{g} \times 2000)/5.07 = 7500 \pm 2000 \mu\text{g}$ would permeate through Silver Shield™ gloves into the body.

According to CalEPA,^{16,44} its 0.2 $\mu\text{g}/\text{L}$ water level reflects 10^{-6} risk and a 2 L/day ingestion and 2 L/day equivalent by inhalation relative to an endpoint of urinary bladder carcinoma in female mice.⁸ Therefore the whole body daily dose assuming 100% absorption is $(0.2 \times 4) = 0.8 \mu\text{g}$. This reference dose is much lower than the Silver Shield™ daily skin permeation, from just the hands and lower forearms calculated earlier. Alternatively, a noncancer effect (body weight depression and hyperplasia of the nonglandular mucosa of the stomach of rats) provides a reference value 450

times that of the cancer reference value for California drinking water,¹⁶ leading to a noncancer reference dose of 360 μg , still about 20 times lower than the computed dose from the permeated Silver Shield™ gloves. If the acceptable risk is set at 10^{-3} , the respective critical DCP doses are 800 and 360,000 μg , the cancer dose still being lower than the average dose permeated through Silver Shield™ gloves. However, the noncancer threshold is now higher than the latter. What is acceptable risk is clearly an important factor in risk assessment, OSHA commonly tabulating cancer risks in parts per thousand.⁴⁵ Therefore, Viton™ gloves should be worn for protection from noncancer and cancer effects of DCP. Excessive exposure may still occur if this formulation is spilled on gloves except for Viton™ or Teflon™, even if adequate respiratory protection is worn.

The case of exposure to chloropicrin alone is also instructive. The California drinking water guideline for chloropicrin is 50 $\mu\text{g}/\text{L}$, but is 7.3 $\mu\text{g}/\text{L}$ in Florida.³ Assuming the same assumptions as for DCP, since chloropicrin is volatile, the threshold whole body dose is either $50 \times 4 = 200 \mu\text{g}$ or $7.3 \times 4 = 29.2 \mu\text{g}$. From Table I, the average chloropicrin mass that permeates through Silver Shield™ in 8 h is $84 \pm 13 \mu\text{g}$. If this mass is 100% absorbed, the latter is below the California guideline but above the Florida one. Wearing Sol-Vex™ gloves for just 1 h would cause an exposure that would exceed both state guidelines even if there were no concurrent inhalation exposure. Another scenario is to base the calculation on a recommended air concentration. The ACGIH¹⁷ and OSHA¹⁸ recommend 0.1 ppm = 0.7 mg/m^3 , based on lung irritation. Assuming an 8-h work day tidal volume⁴⁵ of 10 m^3 for moderate workload, the threshold body dose is 7000 μg . This exceeds the permeated mass over 8 h of wearing Silver Shield™ gloves, but is still lower than the dose from 1 h of wearing Sol-Vex™ gloves of $9190 \pm 702 \mu\text{g}$ (Table I). Silver Shield™ gloves are adequately protective against pure chloropicrin according to this scenario.

CONCLUSIONS

While disposable and chemically resistant nitrile did not protect at all against DCP in Telone-35 EC™ in these ASTM-type permeation cell experiments, the apparent better protection of laminated gloves was not good enough even to protect against noncancer effects as illustrated by a risk assessment except at higher noncancer risks of 10^{-3} and 10^{-4} . Thus, only Viton™ gloves should be worn for maximum safety when handling this formulation. The results have relevance to workplace and environmental situations where spills occur, when handling the formulations, and even when inhalation exposure has been controlled

through the wearing of adequately protective respirators.

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