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Permeation of a 2,4-D Isooctyl Ester Formulation through Neoprene, Nitrile, and Tyvek® Protection Materials

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Tyvek® (laminated saranax) and unsupported nitrile gloves gave protection from permeation against formulation concentrates and aqueous emulsions of Esteron 99® [isooctyl ester of (2,4-dichlorophenoxy)acetic acid] under conditions simulating extremes of field conditions. Neoprene gloves, whether unsupported or supported, lined or unlined, were permeated much more than unsupported nitrile gloves. An initial penetration was observed for all the materials. A cosolvent effect involving the "inert components" was observed, as implied by the appearance of inert components in the hexane collection medium of the ASTM cell before and with the 2,4-D ester. Degradation occurred in the neoprene and supported glove materials since nonformulation components also were detected on the collection side. The glove selection procedure involved the characteristics of single surrogate compounds in the brochure of a glove manufacturer, in addition to the characteristics of the carrier and inert ingredients. This procedure was sufficient to predict correctly that nitrile would protect better than neoprene; however, direct experimental confirmation was necessary to select the type of nitrile material which provided optimum protection.

Introduction

Gloves are the first line of protection when chemicals are handled, spilled, or splashed.(1) Gloves must be able to withstand the rigors of the job being performed; hence their strength, flexibility, and their facilitation of manual dexterity are important.(1) Other factors considered are stability with temperature, the type of challenge chemical, and cost.(1) Another consideration is permeation.(2-4)

The permeation information required to select the most protective glove for workers exposed to specific chemical mixtures is still not yet readily available(1-3) in spite of a large literature on the permeation of single chemicals. Such information is vital for worker safety during simultaneous or sequential exposure to the many chemicals in waste dumps and to pesticide formulations which are all complex mixtures of chemicals. Manufacturers traditionally have rated the protection offered by gloves by the physical stability of the glove material to the specific chemical.(1) This stability is gauged by qualitative ratings of such physical properties as abrasion resistance, elongation, and tear resistance. Until recently no information has been given in the brochures from glove manufacturers on the breakthrough times and permeation rates of even specific chemicals.(5-7) The establishment of a computer data bank(8,9) for permeation data and the development of the standard ASTM method for permeation(4,10,11) have catalysed this process. The information on permeation of chemical mixtures still is limited to a few papers in the peer review literature.(2,3,12-16)

It is known that a chemical which does not permeate a material or permeates poorly alone, may permeate when mixed with another chemical which does.(12,13) Exposure to mixtures of chemicals, therefore, may cause more risk than expected on the basis of the individual behavior of the components. This also suggests that the most rapidly permeating components of a mixture may carry along compounds which may not permeate alone, or do so slowly; this is the so-called "cosolvent effect." The permeation behavior of individual components, therefore, could be misleading for a mixture.

In the peer review literature, only one study(14) has been published on the permeation of a pesticide formulation through gloves. This involved the frequently used fungicide pentachlorophenol in different challenge media against nitrile, neoprene(14) and polyvinyl chloride (PVC) glove materials. Pentachlorophenol is a major wood preservative. Two challenge solvents were used: one was diesel oil and the other was a sodium hydroxide solution where the phenol was in the form of a phenolate salt (4.2%). Both breakthrough times and steady-state rates differed for the two media for a given glove material. The phenol in the diesel oil carrier, in most cases, showed a quicker breakthrough time and a higher steady-state rate than the phenolate in the alkaline solution. Because of the change of the phenol to phenolate, the effect of the carrier was impossible to assess. The possibility of the "inert components" of the formulations facilitating the diffusion of pentachlorophenol across the material also was suggested but not proven.

The aims of the present study were (1) to assess the permeation of a commercial, formulated isooctyl ester of (2,4-dichlorophenoxy)acetic acid (2,4-D) through selected commercially available glove and clothing materials; (2) to determine the kinetic characteristics of the permeation under conditions simulating those experienced in the field; (3) to establish the role of the inert material and surfactants in the formulation and of the carrier on the kinetics; and (4) to evaluate whether the use of manufacturers' data on deg-

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radation of a protective material would allow permeation behavior to be predicted.

Experimental Materials and Methods

Rationale

Glove and clothing material potentially resistant to permeation by the formulated isooctyl ester of 2,4-D had to be selected for the study. A liquid collection medium was to be used for the permeation cell because the 2,4-D isooctyl ester is not volatile enough for gas-phase collection—a situation common to most pesticides. The solvent for the collection side had to be similar to that found in the inert ingredients of the formulation, be compatible with the selected glove and clothing materials, and allow chromatographic resolution of the inert and active ingredients without interference. Thus, gas chromatography/mass spectrometry (GC/MS) examination of the formulation was performed to identify the inert components. The glove selections then were made using the manufacturer's current degradation rating scale(17) for single compounds for the major active and inert ingredients or their surrogates.

Challenge conditions using the ASTM test cell during the study were to reflect the extremes of actual high exposure conditions for persons exposed dermally to the herbicide. Both the formulation concentrate and the highest recommended(18) field spraying concentration of aqueous formulation (1/7 dilution) were used as challenge conditions. The aqueous mixture solution simulated the worst exposure of a farmer or a worker mixing the emulsion concentrate with water and of people exposed to spray drift. The formulation challenge simulated the highest exposures in formulating plants, to workers on reentry, to exposures during and after spraying using diesel oil carrier, and to people exposed to evaporating deposited spray drift.

Two collection media were desired. An organic collection medium would allow the permeation step to be rate limiting and simulate exposure to oily skins. An aqueous collection medium containing everything except the active ingredient still would allow the permeation step to be rate limiting and simulate exposure under sweaty conditions. Without the surfactant in the aqueous solution, little 2,4-D would be collected in the aqueous medium.

An 8-hr screening study was performed to rank herbicide permeation. A 2-hr kinetic experiment in triplicate then followed to determine breakthrough time and permeation rate, primarily for the isooctyl ester. The 8-hr screening period simulated the longest period the material would be exposed to 2,4-D if exposure was continuous in the workplace or field for a normal shift. The 2-hr period approximates the duration of the longest continuous work time between breaks. Gloves are often disposed of at the break.

Selection of Study Materials

The concentrated 2,4-D formulation chosen for this study was(18) Esteron 99®, EPA Regist. No. 39511-75 (Vertac Chemical Corporation, Memphis, Tenn.). Its stated composition was 65.4% isooctyl ester (an acid equivalent of 43.4%) and 34.6% inert ingredients. The isooctyl ester presently is much used in agriculture and, unlike 2,4-D salts, is detectable by gas chromatography.(19) GC/MS analysis of Esteron 99 revealed the presence of a high boiling paraffinic fraction in the inert components (high molecular weights with many peaks separated by 14 mass units). The collection media selected were hexane (pesticide grade, Fisher Scientific, Fair Lawn, N.J.) and an aqueous solution of herbicide (1/7 dilution) with the active ingredient extracted (extraction from a saturated saline solution with hexane). Hexane is a volatile compound that is a good solvent for the ester, does not interfere chromatographically, and is similar chemically to the inert components of the formulation. The aqueous phase remaining after extraction of 2,4-D ester did not foam as expected if the surfactant was present. Subsequent screening tests with this aqueous phase showed no ester was detected because the ester could not be solubilized. This was proven by spiking 2,4-D ester into the collection medium and monitoring the 2,4-D concentration in the experimental configuration for a permeation experiment. All of the 2,4-D ester adsorbed onto the glove material. Thus, the hexane collection medium was used for all screening and kinetics experiments.

Data on worker protection against the 2,4-D isooctyl ester are not available in any of degradation/permeation tables published by glove or clothing manufacturers. Thus, the glove materials chosen for this study had to be selected from the protection properties of compounds simulating the 2,4-D ester. Amyl (C_5) acetate is the closest ester surrogate in the Edmont Company (Division of Becton Dickinson and Company, Coshocton, Ohio) degradation chart since it is the longest chain ester listed.(17) While esters are nonpolar, they are more polar than hydrocarbons of the same chain length, though the acid moiety also determines polarity. Chlorobenzene is an appropriate surrogate because it is a nonpolar chlorinated aromatic compound like the isooctyl ester itself, and it simulates the chlorinated aromatic portion of the ester in terms of polarity and geometry.

According to the chemical degradation chart,(17) the only recommended material for both hexane and amyl acetate is nitrile-butadiene rubber (nitrile) but it is not recommended for chlorobenzene. Neoprene is recommended for hexane but not for amyl acetate and chlorobenzene. Polyvinyl alcohol is recommended for chlorobenzenes and is moderately recommended for amyl acetate and hexane. Polyvinyl alcohol gloves cannot be used for aqueous solutions, however.(5) Thus, to minimize the effect of the collection liquid (hexane) to account for the effects of the inert components and the differences in the types of carriers (aqueous/diesel oil) that can be encountered, the two materials recommended for hexane (nitrile and neoprene) were chosen for the study (Table 1). The gloves chosen were all manufactured by the Edmont Company (division of Becton Dickinson and Company, Coshocton, Ohio). They were Neox®, neoprene, and Neoprene Soft Lined® for neoprene and Sol-Vex® thin, Sol-Vex Soft Lined, Sol-Vex thick, and Edge® for Nitrile NBR, each of two thicknesses and supported (S) and unsupported (US). Prior work using the same permeation system had shown a difference between the protection from chlorinated benzenes and toluenes

TABLE I
Characteristics of Selected Neoprene and Nitrile Gloves

	Neoprene		Nitrile	
Property	Unsupported[A]	Supported[B]	Unsupported[C]	Supported[D]
Tensile strength	excellent	NT[E]	excellent	NT
Elongation	excellent	NT	good	NT
Tear resistance	good	NT	good	NT
Abrasion resistance	good	fair	excellent	excellent
Heat resistance	excellent	NT	good	NT
Ozone resistance	excellent	NT	good	NT
Cut resistance	NT	excellent	NT	good
Dry grip	NT	good	NT	excellent
Flexibility	NT	good	NT	excellent
Puncture resistance	NT	excellent	NT	excellent
Wet grip	NT	fair	NT	fair
Chemical Degradation				
Amyl acetate	NR[F]	NR	excellent	excellent
Chlorobenzene	NR	NR	NR	NR
Hexane	excellent	excellent	excellent	excellent
Permeation Rate				
Amyl acetate	NT	NT	NT	NT
Chlorobenzene	NT	NT	NT	NT
Hexane	fair	good	excellent	excellent
Permeation Breakthrough				
Amyl acetate	NT	NT	NT	NT
Chlorobenzene	NT	NT	NT	NT
Hexane	45 min	90 min	NO[G]	NO

[A] Edmont Neoprene (29-840, 0.410 ± 0.034 mm; 29-865, 0.573 ± 0.031 mm)
[B] Edmont Neox® (9-924, 1.418 ± 0.038 mm)
[C] Edmont Solvex® (37-145, 0.300 ± 0.005 mm; 37-155, 0.446 ± 0.012 mm; 37-175, 0.382 ± 0.005 mm)
[D] Edmont Edge® (40-105, 1.314 ± 0.008 mm)
[E] NT = not tested
[F] NR = none recommended
[G] NO = none observed

offered by S and US gloves and by lined (L) and unlined (UL) gloves.[(4)] Saranex-laminated Tyvek® (DuPont de Nemours) also was tested because of its resistance to trichlorobenzene[(7)] and its general usage in hazardous waste situations.

After completion of the present experimental work, the 1986 edition[(5)] of the Edmont chemical resistance guide also listed permeation characteristics, and these data also are summarized in Table I. Based on the characteristics for the above surrogate chemicals, nitrile gloves should perform better than neoprene ones.

Materials and Reagents

The gloves (Table II) and the saranex-laminated Tyvek (Kappler 77414) were obtained from Orr Safety, Cincinnati, Ohio; Esteron 99 was from the Vertac Chemical Corp., Memphis, Tennessee; Type I and Type II water were produced from Continental Systems, El Paso, Texas; 2,4-D isooctyl ester standard was supplied by Poly Science Corp., Niles, Illinois; sodium chloride, pesticide grade hexanes and sodium dichromate were obtained from Fisher Scientific, Fair Lawn, New Jersey.

Apparatus

The (I-PTC 600) ASTM Test Cell (Pesce Lab Sales, Kennett Square, Pa.) had an inner diameter of 2.6 cm; the volume of the collection and challenge sides were 20 mL and 15 mL, respectively. Materials of known thickness (measured by micrometer screw gauge, L.S. Starrett Co., Athol, Mass.) were cut from the palm of the hand[(20)] for gloves and from an area above the elbow of the same sleeve, avoiding seams and closures, for Tyvek.[(21)] The materials (1.93 ± 0.04 cm in diameter as measured by vernier calipers, manufactured by

TABLE II
Amounts Detected in the Collection Medium after 8-hr Screening Tests on Protective Materials

	Unsupported Lined			Unsupported Unlined			Supported Lined		
Material	Initial Thickness (mm)	Formulation[A] (μg)	Aqueous[B] (μg)	Initial Thickness (mm)	Formulation (μg)	Aqueous (μg)	Initial Thickness (mm)	Formulation (μg)	Aqueous (μg)
Nitrile	0.38 ± 0.01	12.8	1.5	0.30 ± 0.03	0.31	16	1.31 ± 0.01	90 000	3000
Neoprene	0.57 ± 0.03	7040	1600	0.44 ± 0.01	2500	730	1.41 ± 0.05	40.6	4100
Tyvek®							0.17 ± 0.01	35	4.4

[A] Formulation challenge permeated mass

[B] Aqueous formulation challenge permeated mass

Mitutoyo, Japan) were placed between two Teflon® gaskets, and the two glass chambers then were screwed into the stainless steel flanges. The nuts were tightened to 30 inch-pound using a torque wrench (True Value Hardware, Cincinnati, Ohio) to assure no leaks and equal tightening from experiment to experiment.(10,20) The assembled test cell was attached to a rod by clamps on top of the moving tray of a waterbath (Magni Whirl, Blue M. Electric Company, Blue Island, Ill.) at 29.3 ± 0.5°C.(4)

The gas chromatograph was a Hewlett Packard Model 5730A equipped with a ^{63}Ni-electron capture detector (ECD). It was interfaced with a Sargent-Welch Recorder (Sargent-Welch, Model XKR, Skokie, Ill.). The full-scale deflection setting was 1 mV, and the recorder speed was 1 cm/min. The conditions used to analyze samples from the screening and kinetic studies were the following: 95% argon/5% methane carrier, 27 PSI and 32 mL/min; detector and injector temp, 250°C; column, 2% OV-101 on 80/100 mesh Chromosorb W (AW/DMCS) 0.91 m × 4 mm ID Pyrex® (Supelco, Inc., Supelco Park, PA).

All samples taken during the kinetic studies were stored in small glass vials (Wheaton, "400" brand, 1 mL borosilicate glass, 5 × 11 mm ID, Wheaton Scientific, Millville, N.J.) and sealed with aluminum-rubber tops (aluminum seals, 11 mm) using a manual crimper (Model 06-406-13, Fisher Scientific). These samples were placed in a freezer at 0°C for storage until analysis.

Analytical Methods

The GC/MS spectrometer used was a high performance mass spectrometer with DS55 data system on a NOVA 4X computer interfaced with a Carlo/Erba gas chromatograph (Kratos, Ramsey, N.J.) using a SPB1 column, 25-m and 0.32-mm ID. The MS inlet temperature was 150°C and the ion voltage, 50 eV. The temperature program was as follows: injector temperature 60°C; the column was maintained at 70°C for two minutes, and the temperature increased 4°C/min to a final temperature of 220°C until all peaks eluted.

The 2,4-D in the formulation concentrate (Esteron 99) was comprised of greater than 99% isooctyl ester along with a trace (< 1%) of the normal ester. The mass spectra of other components in the formulation were obtained also. These appeared to be high molecular weight paraffins like dodecanes and tetradecanes.

Reagent Purity

The standard proved to be only 27% pure, with 73% being normal ester, as shown by ECD/GC, GC/MS, and use of peak areas. Hexane used for collection and extraction procedures was > 99% pure and contained no peaks in the area of the isooctyl ester or of other peaks in the formulation.

Permeation Measurements

All glassware was acid washed overnight in an aqueous solution of 10% nitric acid (volume/volume) and rinsed three times with Type I water before drying in a dustless oven.

The permeation studies were performed over periods of 2 or 8 hr using a published technique(4) based on the ASTM method(10) that utilized a moving tray thermostated water bath. In summary, each material specimen was preconditioned in a desiccator containing a saturated solution of sodium dichromate for 24 hr at a temperature of 28 ± 8°C to generate a relative humidity of 57 ± 6%.(10) A volume of 10 mL of hexane was placed in both chambers with a glove sample in place. The 2,4-D isooctyl ester level was determined, to assure cleanliness. If any 2,4-D was found, the chambers were filled and emptied repetitively until the 2,4-D ester level was near the least quantifiable level. A new material test specimen was used if the cell was contaminated. The collection chamber of the clean ASTM cell was filled with 10 mL of thermally-equilibrated hexane collection medium. The challenge chamber then was filled with either 15 or 10 mL of thermally-equilibrated challenge solution of the formulation concentrate and aqueous formulation mixture, respectively. Adequate mixing at 20 cm/sec in a horizontal direction was demonstrated directly with a dye solution.(4) Temperature equilibration and integrity of the moving tray were monitored continuously. The collection medium was removed after 8 hr in the screening study, and after stopping the water bath, 0.1-mL samples were taken from the collection side in the kinetic study at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 min. Each sample was analyzed by ECD/GC, using 10 μL aliquots, and diluted if necessary to allow use of the calibration curve (isooctyl ester in hexane). The lowest quantifiable limit for the isooctyl ester (established using dilutions of the standard) was 115 pg at a column temperature of 190°C. After preconditioning in the desiccator as before, the material was measured for swelling (micrometer screw gauge) and any physical changes observed microscopically. The materials in the subsequent kinetics studies were examined in decreasing order of permeation rate observed from the screening experiment. All kinetic experiments were run in triplicate. Permeation curves then were generated by plotting total mass permeated versus contact time to determine breakthrough times and steady-state permeation rates. Steady-state rates were calculated only for permeations with a coefficient of variation greater than 0.80 ($p < 0.001$).

Results and Discussion

Screening Study

The 8-hr screening results are given in Table II. The S/L nitrile glove allowed the greatest mass of the 2,4-D isooctyl ester to cross; US/UL and US/L nitrile gloves were at least 200 times better. All of the neoprene gloves performed worse than the US/UL and US/L nitrile gloves. Tyvek was more of a barrier to the 2,4-D isooctyl ester than nitrile gloves were. For unknown reasons, the thinner, US/UL nitrile gloves performed better as a barrier to the ester than the thicker ones.

The change in thickness of the materials measured at the end of the 8-hr contact period revealed that US/UL neoprene swelled significantly in response to both types of challenges. The formulation caused the thick US/UL and US/L nitrile materials to swell, but the reverse occurred for the aqueous solution. The formulation caused S/L nitrile to swell also. The swelling effects were caused by the hexane collection medium. In the case of the US/L and US/UL nitrile gloves, this did not result in permeation of 2,4-D ester.

Kinetics Study

The results of the 2-hr kinetic experiments are shown in Tables III and IV and Figures 1 to 3. All samples showed an initial 2,4-D isooctyl ester penetration (Figures 1 to 3). For both challenges, little subsequent permeation of Tyvek or US/UL nitrile occurred compared with all neoprenes. The L nitrile and neoprene gloves offered less protection than their UL counterparts, as observed previously for chlorobenzenes and chlorinated toluenes.(4) The data in Tables III and IV indicate that the quality of the gloves does vary.

Constituents Other than the Isooctyl Ester

The constituents responsive to ECD/GC in the formulation showed relative retention times (RRT) of 15%, 32%, 37%, and 86% relative to the isooctyl ester as 100%. Relative to the peak height of the compound with RRT = 37%, the relative peak heights were 6.3%, 38%, 100%, and 59%, respectively. Although the relative peak heights are small compared with the isooctyl ester, the response factors are certainly orders of magnitude lower, so the peak heights do not reflect the true concentrations relative to the ester. The gloves that allowed the greatest amount of the 2,4-D isooctyl ester to cross the material also allowed other constituents to be detected before the ester itself, especially neoprene. This indicates that a cosolvent effect had occurred. S/L neoprene, S and US nitrile gloves, and Tyvek also released components other than those in the formulation. The nature of these nonformulation constituents was not investigated but indicates that some degradation of the glove and Tyvek materials occurred. This was a variable effect since some materials showed no presence of nonformulation components.

Swelling

Although nitrile and neoprene(5,17) were rated E (excellent) in the Edmont degradation chart (Table I), they either were

TABLE III
Summary of Results: Formulation Challenge

Material^A	Initial Penetr.	Level of Penetration/Permeation (μg) at			Protection Period^B (min)	Mechanism
		0 hr	2 hr	8 hr		
S/L nitrile	+	10^5	10^5	9×10^4	none	penetration
US/L neoprene	+	1.1 to 3.0	3.5 to 2×10^4	7.0×10^3	20	mixed
US/UL neoprene	+	0.4 to 3	4 to 2×10^4	2.5×10^3	30	variable
S/L neoprene	+	1 to 6	50 to 400	41	10	mixed
Tyvek®	+	1.1 to 3.5	2.5 to 9	35	100	little permeation
US/L nitrile	+	2.7	0.8	13	> 120	little permeation
US/UL nitrile (thin)	+	3 to 6	6 to 99		> 120	little permeation
US/UL nitrile (thick)	+	2 to 7	6 to 100	0.31	100	little permeation

^A S = supported; US = unsupported; L = lined; UL = unlined.

^B The minimum contact time in minutes for permeation of 10 μg for all materials tested.

TABLE IV
Summary of Results: Aqueous Emulsion Challenge

Material^A	Initial Penetr.	Level of Penetration/Permeation (μg) at 0 hr	2 hr	8 hr	Protection Period^B (min)	Mechanism
S/L neoprene	+	0.35 to 0.74	26 to 47	4.1×10^3	100	mixed
S/L nitrile	+	2.9 to 6.0	1.55×10^3 to 2.22×10^3	3×10^3	None	penetration
US/L neoprene	+	0.36 to 0.83	1.96×10^3 to 3.33×10^3	1.6×10^3	30	mixed
US/UL neoprene	+	1.46	4.2	730	> 120	little penetration
US/UL nitrile (thick)	+	0.32 to 1	2 to 17	22	70	mixed
US/UL nitrile (thin)	+	0.28 to 0.93	2 to 50.5	16	40	mixed
Tyvek®	+	1.30	4.07	4.4	> 120	little penetration
US/L nitrile	+	0.45 to 2	1 to 47	1.5	20	mixed

^{A}S = supported; US = unsupported; L = lined; UL = unlined.
^{B}The minimum contact time in minutes when 10 μg permeated for all materials tested.

partially degraded or swollen after the 2-hr kinetic studies. Significant changes also occurred in those glove materials (S and US nitrile and the US/L and US/UL nitrile) that were penetrated/permeated by the ester. Tyvek thickness did not change, though one sample did swell as a result of one of the formulation challenges. Neoprene is by far the worst glove material under these conditions; swelling occurred during the kinetics study for both the formulation and aqueous challenges. The glove materials, excepting S/L nitrile, showed no swelling in hexane alone over the 2 hr. Thus, the swelling up to 2 hr but not at 8 hr is not caused by the hexane collection medium.

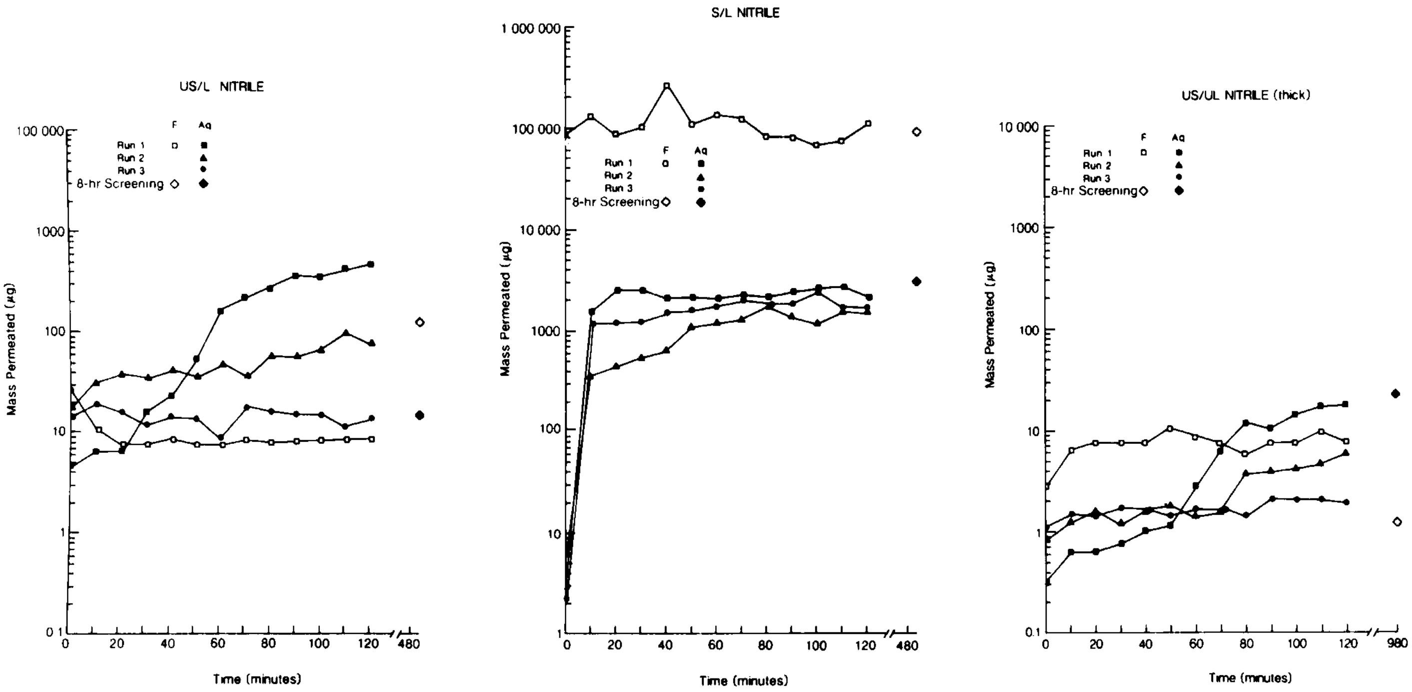

Figure 1—Permeation/penetration behavior of the isooctyl ester of (2,4-dichlorophenoxy)acetic acid in Esteron 99® through unsupported/lined (US/L), supported/lined (S/L), and unsupported/unlined (US/UL) nitrile glove materials challenged by the formulation (F) and an aqueous mixture (Aq) in an ASTM permeation cell.

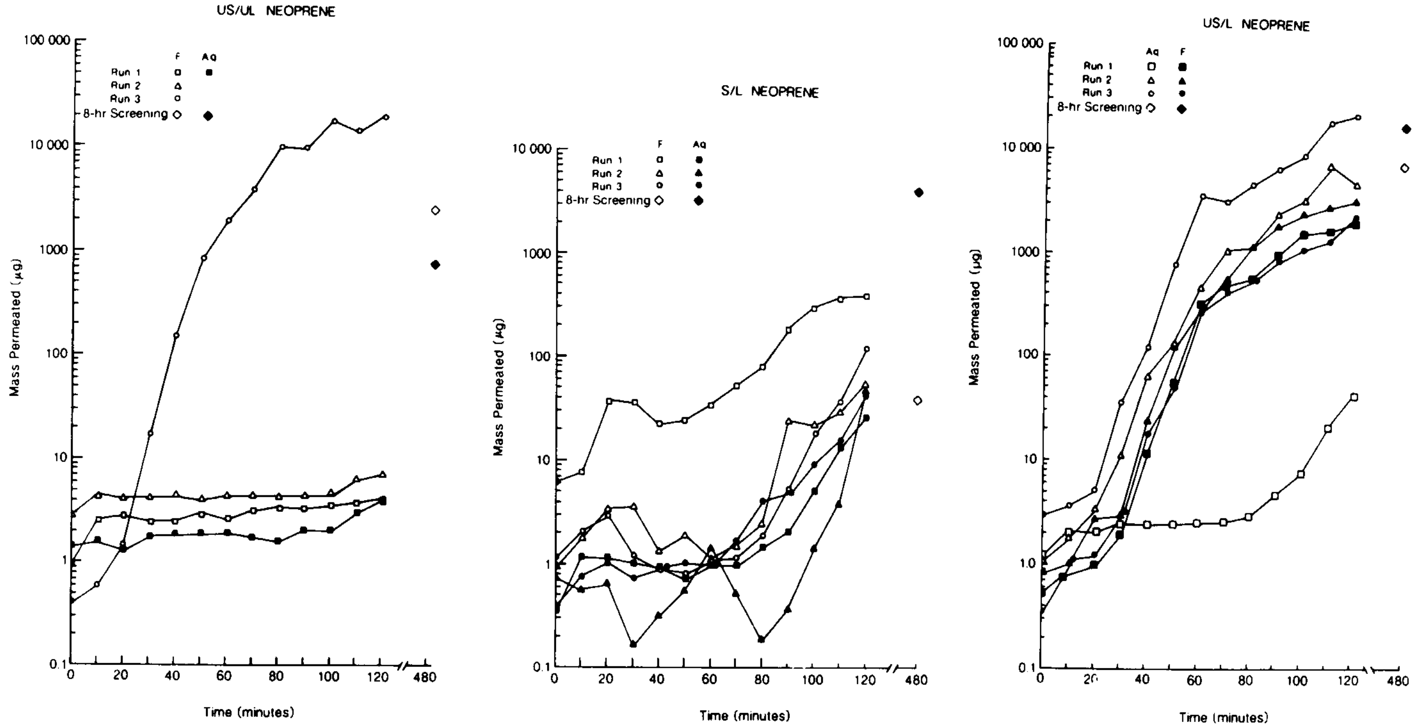

Figure 2—Permeation/penetration behavior of the isooctyl ester of (2,4-dichlorophenoxy)acetic acid in Esteron 99® through unsupported/unlined (US/UL), supported/lined (S/L), and unsupported/lined (US/L) neoprene glove material challenged by the formulation (F) and an aqueous mixture (Aq) in an ASTM permeation cell.

Discussion

Table V summarizes the slopes and correlation coefficients calculated from the observed steady-state periods; also included are the calculated permeation rates (the steady-state rate/exposed glove area) and the diffusion coefficients. Correlation coefficients were high during the steady state for all neoprene materials and also for US/UL and US/L nitrile.

The gloves showed permeation by a mixed mechanism (penetration/permeation). All materials, including Tyvek, allowed initial permeation of formulation components before the 2,4-D isooctyl ester. Tyvek material had the best quality control with all 3 triplicates showing little permeation. US and UL nitrile gloves generally showed agreement in 2 out of 3 permeation experiments. Neoprene had the worst quality control with poor and extremely variable permeation behavior. All materials except Tyvek were manufactured by the same company. They also were of the same lot. Clearly, these results should be confirmed for the products of other companies.

The permeation behavior exhibited by those materials showing permeation were similar to Type B and Type E permeations.[2] Neoprene permeation behavior is similar to Type B, with an increase in the permeation rate occurring at a point later in the kinetic study. Measurements of the thicknesses of these materials following the 2-hr kinetic test did indicate a statistically significant increase. This type of behavior usually is caused by the material being modified either chemically or physically by the challenge (or collection liquid). US/UL and US/L nitrile showed Type E behavior, with swelling occurring over the 2-hr kinetic studies. These same two nitrile gloves did not exhibit a statistically significant swelling when exposed to hexane. Thus, components in the formulation were responsible for the swelling.

Components in the formulation often appeared in the collection medium before the 2,4-D isooctyl ester and, therefore, could act as cosolvents for the ester. The possibility of such behavior has been suggested but not proven to occur for a pesticide formulation (pentachlorophenol).[14] US/L neoprene, when tested against the aqueous challenge, had more of the constituents detected than both S/L and US/UL types. Experiments on US/L neoprene with the formulation concentrate challenge resulted in fewer than half of these constituents detected. Thus, the type of carrier does affect glove degradation and permeation.

Tables III and IV summarize the data used to arrive at a protection period. The permeated quality of 10 μg was chosen arbitrarily to define the "protection period." Calculated diffusion coefficients and permeation rates differed depending on the carrier (Table V). The permeation rates for the formulation challenge of neoprene were greater than those for the aqueous challenge. When challenged with the formulation, after an initial penetration, US nitrile gloves exhibited no permeation. Only when challenged with the aqueous mixture did permeation occur after the initial penetration, though this behavior was variable. Steady-state rates were calculated for US/UL and US/L nitrile types when challenged with the aqueous mixture, with coefficients of variation of 0.98 and 0.85, respectively. Tyvek showed little permeation regardless of the challenge, though it exhibited the initial penetration.

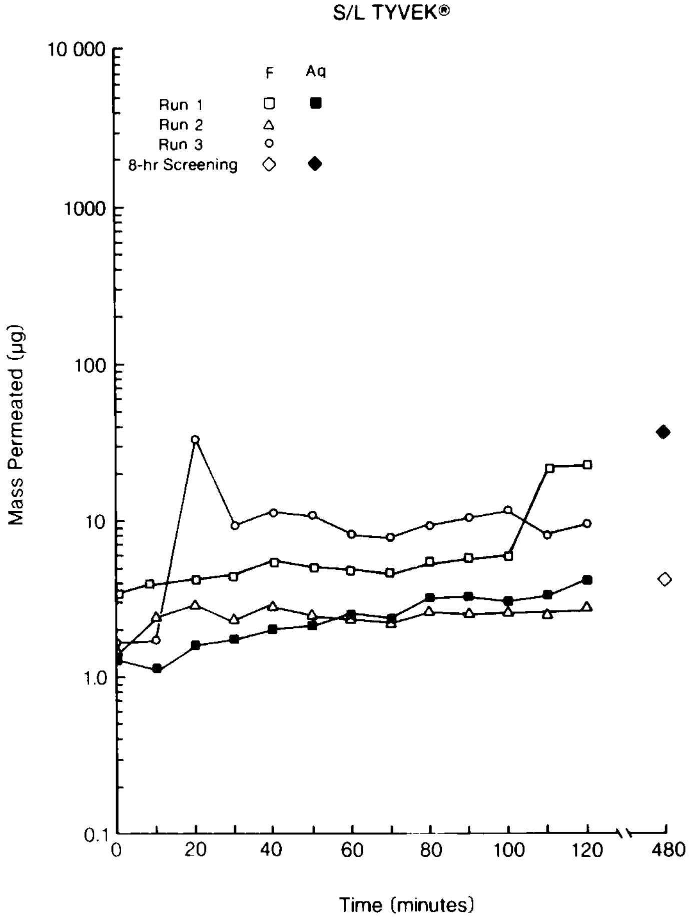

Figure 3—Permeation/penetration behavior of isooctyl ester of (2,4-dichlorophenoxy) acetic acid in Esteron 99® through supported/lined (S/L) Tyvek® (Saranax-laminated) material challenged by the formulation (F) and an aqueous mixture (Aq) in an ASTM cell.

The only previously published, peer reviewed data on permeation of a pesticide formulation is for the fungicide pentachlorophenol.(14) The nitrile rubber gloves used in that study did not show permeation after 8-hr on challenge by pentachlorophenol in diesel oil or mixed with an aqueous base. Glove material behavior differed, as demonstrated by the calculated diffusion coefficients for the tested materials (nitrile rubber, natural rubber, PVC). Similar results also were obtained in the present study. Sodium pentachlorophenolate in alkaline solution permeated through natural rubber.(14) It was concluded that nitrile rubber and PVC gloves provided adequate protection against either formulation of pentachlorophenol. Similar behavior was shown by the nitrile materials used in the present study.

The criteria used to determine the best glove were the following: the time that elapsed between initial contact and no more than 10 µg transferred; rate of any permeation over this period; amount detected initially; amount detected over the 2-hr period, and amount detected over 8 hr. From these guiding criteria, the following recommendations for the materials investigated can be made: Tyvek and US/UL nitrile provide the best protection against the concentrated formulation or aqueous mixture, followed by L nitrile and L or UL neoprene. The 10-µg criterion for acceptable protection might not be adequate if the 2,4-D isooctyl ester were a human carcinogen, based on the U.S. Environmental Protection Agency (EPA) criterion that exposure to carcinogens should be zero.(22) U.S. EPA risk assessment analysis should apply in such cases.(23) Whether 2,4-D is a carcinogen is still controversial. Such considerations also are relevant in exposures to the isooctyl ester of (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) containing 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), where TCDD, an adventitious contaminant, is a known animal carcinogen.(24)

Conclusion

The present study has demonstrated that the type of protective gloves can be chosen successfully using the characteristics of surrogate single compounds for an unlisted pesticide in addition to the characteristics of the carrier and inert components. The results also show that the permeation characteristics of the particular glove type chosen to protect against mixtures must be confirmed further by direct experiment.

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TABLE V
Summary of Permeation Rates

Challenge	Material^A	Permeation Rate (μg/min·cm^2)	Calculated Breakthrough Time (min)	Slope (μg/mL·min)	$r^{2\,B}$	Diffusion Coefficient (m^2/min)	Initial Thickness (mm)
Formulation	neoprene US/L	4.1	70	1.2	0.81	3.5×10^{-5}	0.452
		10.6	0	3.1	0.98	9.1×10^{-5}	0.532
		579	0	169	0.82	4.9×10^{-3}	0.545
Aqueous	neoprene US/L	51.4	0	15	0.86	4.4×10^{-6}	0.509
		20.2	10	5.9	0.92	1.7×10^{-4}	0.0510
		43.8	10	12.8	0.85	3.7×10^{-4}	0.524
Formulation	neoprene S/L	0.37	0	10.8	0.96	8.7×10^{-4}	1.406
		0.41	10	0.12	0.85	9.7×10^{-6}	1.451
		2.80	0	0.82	0.94	4.6×10^{-5}	1.399
Aqueous	neoprene S/L	1.80	30	0.53	0.86	4.3×10^{-5}	1.321
		0.55	10	0.16	0.83	1.3×10^{-5}	1.506
		0.52	20	0.15	0.83	1.2×10^{-5}	1.400
Formulation	neoprene US/UL	130	0	38	0.88	9.4×10^{-4}	0.438
Aqueous	nitrile US/UL	0.86	10	0.25	0.98	6.3×10^{-6}	0.432
Aqueous	nitrile US/L	2.3	10	0.66	0.85	1.6×10^{-5}	0.409
Formulation	Tyvek®	0.0064	0	0.0019	0.88	5.5×10^{-7}	0.174
Aqueous	Tyvek	0.0044	0	0.0013	0.81	1.3×10^{-7}	0.174

^{A}S = supported; US = unsupported; L = lined; UL = unlined.
^{B}r^2 = coefficient of variation.

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