ORIGINAL ARTICLES AAEM

Ann Agric Environ Med 1998, 5, 155–167

LABORATORY SIMULATION OF SPLASHES AND SPILLS OF ORGANOPHOSPHATE INSECTICIDES ON CHEMICALLY PROTECTIVE GLOVES USED IN AGRICULTURE

Kathleen M. Canning, Peter B. McQuillan, Wieslaw Jablonski

School of Geography and Environmental Studies, University of Tasmania, Hobart, Tasmania, Australia

Canning KM, McQuillan PB, Jablonski W: Laboratory simulation of splashes and spills of organophosphate insecticides on chemically protective gloves used in agriculture. *Ann Agric Environ Med* 1998, **5**, 155–167.

Abstract: Agricultural workers rely on chemically protective gloves for protection from dermal exposure to insecticides. In Australia the most widely used gloves are manufactured from polyvinyl chloride or nitrile butadiene rubber. During insecticide application splashes and spills frequently occur on the external surfaces of gloves which may compromise the integrity of the membrane. Interaction of two organophosphate insecticides, chlorpyrifos (Lorsban 500 EC®) and diazinon (Jetdip®), with glove surfaces was investigated in laboratory conditions. The external surface of gloves was treated with concentrated insecticides for one minute and diluted and concentrated insecticides for 24, 36 and 48 hours and later examined by environmental scanning electron microscopy. Two classes of defects, cavities and convexities, were evident in the polyvinyl chloride gloves following all treatments, whereas cracking was significant in the nitrile butadiene rubber gloves after 24 hours. In addition, X-ray energy-dispersive microanalysis was used to evaluate chemical changes on the glove surfaces. Phosphorus and sulfur were useful indicators for organophosphate retention over specific time frames. Results corroborated the need for more robust chemically protective gloves to be developed for routine agricultural use.

Address for correspondence: Dr Peter B. McQuillan, School of Geography and Environmental Studies, University of Tasmania, GPO Box 252-78, Hobart, Tasmania 7001, Australia. E-mail: P.B.McQuillan@utas.edu.au

Key words: Chemically protective gloves (PVC, NBR), electron microscopy, image analysis, X-ray microanalysis, pesticide exposure, agricultural workers.

INTRODUCTION

Agricultural workers applying pesticides are subject to a variety of dermal exposures to these toxic chemicals, especially on their hands [8, 13]. Most pesticides comprise several components, such as active ingredients, surfactants, carrier solvents and inert substances. The formulation of the pesticide is arguably the most critical factor for human exposure, with greater risks posed by aqueous and emulsifiable concentrates. The latter exhibit the most aggressive interaction with chemically protective gloves (CPGs).

Australian farmers typically use two types of CPGs, namely supported polyvinyl chloride (PVC) or unsupported nitrile-butadiene rubber (NBR) gloves [3]. During normal usage these gloves accumulate a variety of splashes and spills that may compromise their efficacy by altering the surface integrity or allowing for the transmission of chemicals by permeation or penetration.

Permeation is the transmission of a chemical at the molecular level of the glove material. Testing typically involves a permeation cell that is divided by the clamped glove specimen. The hazardous test chemical is placed in the cell so that it contacts the external surface of the glove and the collecting medium contacts the internal surface. Analysis of the permeation products, as recommended by British Standard BSEN 374-3 1194, includes gas chromatography, colorimetry and UV and IR spectroscopy [2, 6, 9, 10, 11]. Penetration is the transmission of a

Received: 6 October 1998
Accepted: 6 November 1998

chemical through pin holes, imperfections, seams and tears in the glove [1, 7]. Simple air and water leak tests can be used to test for penetration opportunities. Degradation of the glove material can be measured by several means, which include elongation, weight gain or loss, tensile and tear strength and by direct visualisation [5, 12].

There have been a variety of tests developed to evaluate glove quality and their suitability for use with some pesticides, but little has been conducted at the microscopic level. The aim of this paper is to examine the short term effects of two widely used organophosphate insecticides, diazinon and chlorpyrifos, on the surface of PVC and NBR gloves in controlled laboratory conditions.

MATERIALS AND METHODS

Rationale for the experiments. Two series of experiments were conducted which involved immersion of the external surfaces of the CPGs in two common organophosphate pesticides. The first series involved immersion of PVC and NBR gloves in concentrated formulations of pesticides for one minute, representative of a splash or a spill of pesticide during field application, which may not be noticed and therefore not washed off.

In the second series of experiments, glove specimens were immersed in both concentrated and diluted formulations for periods of 24, 36 and 48 hours, representative of cumulative seasonal exposure where gloves remain contaminated for longer periods.

In preliminary experiments, not detailed, several different sized droplets of diluted and concentrated Top Clip Blue Shield® (a diazinon-based sheep dip) were placed on the proximal section of both glove fingers and excised samples (5 × 5 cm) and then tilted to the vertical position; the mean time for roll off was about one minute. This models the field situation where the hands are either actively moving or held down by the sides.

Experimental

1) One minute immersion. The organophosphate insecticides used were Jetdip® (Virbac Ltd., a sheep dip, jetting fluid and blowfly dressing, 200 g/l diazinon in 522 g/l liquid hydrocarbon, batch 11762v1) and Lorsban 500 EC® (Dow Elanco Australia Ltd., chlorpyrifos 500 g/l, liquid hydrocarbon 491 g/l manufactured February 1995 Batch 950204-01). Two pairs of matching PVC gloves (made in China without a brand name) and NBR (Sol-Vex™ Ansell Edmont) were immersed for one minute in the concentrated formulations. Both types of gloves used were from the same respective batches. The glove specimens were secured with coated wire and suspended in beakers of concentrated Jetdip® or Lorsban 500 EC®, so that approximately 2 cm remained above the solutions.

After exposure the specimens were air dried in a fume cabinet. Samples were cut from the PVC fingers and from the palm sections of the NBR gloves, as the NBR fingers were too textured to provide useful comparisons. These samples were mounted on environmental scanning electron microscope (ESEM) stubs for examination. Control samples were taken from the same regions on new gloves from the same batches.

2) Extended immersion. Experiments were conducted on matching fingers cut from new PVC gloves, and on whole NBR gloves. The specimens were immersed in neat or diluted Jetdip® or Lorsban 500 EC®. Jetdip® was diluted with water to give a diazinon concentration of 0.1 g/l, as recommended for dipping. Lorsban 500 EC® was diluted to 0.25 g/l, a dose recommended for treating wingless grasshoppers. The glove preparation was as for the previous experiments, but the specimens were immersed for 24, 36 and 48 hours, then removed from the beakers and gently irrigated with distilled water, then air dried in a fume cabinet.

The interiors of the PVC samples that were immersed in Lorsban 500 EC® for 36 and 48 hours became visibly moist, due to permeation or penetration. To eliminate the possibility of condensation forming on the interior of the gloves this section of the experiment was repeated and the tops of the fingers were firmly secured with electrical tape.

Electron microscopy and X-ray microanalysis. The instruments and methods have been described in our previous paper [4]. It should be emphasised that use of the ESEM reduced the sample preparation to nil. Therefore there was no interference of any kind with the sample prior to ESEM or energy-dispersive spectroscopy (EDS) examinations.

Census of defects and statistical analyses. The suitable classification of glove defects has been previously reported [4]. Observed defects were classified as cavities, convexities, cracks, or smooth areas, and counted with the aid of a gridded template that sampled 50% of the surface area of the micrograph.

Table 1. Defects detected on PVC glove fingers immersed in diazinon (Jetdip®) for one minute. The medians and percentiles (25th and 75th) are given (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	0	0	0
	Immersed	20	2	2	4
Convexities	New	20	0	0	0
	Immersed	20	2	2	5
Cracks	New	20	0	0	0
	Immersed	20	0	0	1
Smooth	New	20	0	0	1
	Immersed	20	0	0	0

Table 2. Elements (cps) detected on PVC glove fingers immersed in diazinon (Jetdip®) for one minute. The means ± standard errors are shown (t-test). The medians and percentiles (25th and 75th) are given for aluminium (Mann-Whitney Rank Sum Test).

Elements	Glove finger	n	Mean ± SE	Difference of means
C	New	6	5862 ± 1146	643
	Immersed	3	5219 ± 489	
			(t = 0.373, p = 0.7203)	
O	New	6	6027 ± 680	–4365
	Immersed	3	10392 ± 898	
			(t = –3.78, p = 0.0069)	
Si	New	6	531 ± 64	–2005
	Immersed	3	2536 ± 202	
			(t = –12.4, p < 0.0001)	
S	New	6	390 ± 43	–4776
	Immersed	3	5166 ± 141	
			(t = –42.8, p < 0.0001)	
Cl	New	6	30437 ± 675	21804
	Immersed	3	8633 ± 487	
			(t = 21, p < 0.001)	

Elements	Glove finger	n	Median	25%	75%
Al	New	6	363	303	494
	Immersed	3	239	214	286

Table 3. Defects detected on PVC glove fingers immersed in chlorpyrifos (Lorsban 500 EC®) for one minute. The medians and percentiles (25th and 75th) are given (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	0	0	0
	Immersed	20	3	1	3
Convexities	New	20	0	0	0
	Immersed	20	3	2	4
Cracks	New	20	0	0	0
	Immersed	20	0	0	1
Smooth	New	20	0	0	1
	Immersed	20	0	0	0

The data from the defect census and the EDS were not normally distributed (Kolmogorov-Smirnov Test) nor were the variances equal (Levene Median Test). Data from the one minute immersion tests were analysed with a t-test or a Mann-Whitney Rank Sum Test as appropriate. The extended immersion data were analysed using One Way ANOVA or Kruskal-Wallis One Way ANOVA on Ranks. The all-pairwise multiple comparison tests used were either Dunn's Test or Student Newman-Keuls Test. The statistical program SigmaStat was used to conduct the analyses. The SNK multiple comparison test is not always efficient at detecting pairwise differences when the data has many 0 values, and several comparisons in Table 5 are therefore unresolved.

RESULTS

PVC Gloves

One Minute PVC Immersion in Diazinon (Jetdip®)

Defects. The mean density of cavities on the glove surface increased following immersion in Jetdip® (T = 576, p < 0.001) as did the mean density of convexities (T = 544.5, p < 0.001). However, there were no significant difference between the control and pesticide treated gloves in the mean density of cracks (T = 360, p = 0.177) or smooth areas (T = 480, p = 0.058) (Tab. 1).

EDS. All the PVC data sets passed the normality and equal variance tests (Tab. 2). Phosphorus was not detected on these samples. Carbon did not differ between the control and pesticide treatment (t = 0.373, d.f. = 7, p = 0.720). Oxygen differed between treatments (t = –3.78, d.f. = 7, p = 0.007) as did aluminium (d.f. = 7, p = 0.048), and there were strong differences for silicon (t = –12.4, d.f. = 7, p < 0.0001), sulfur (t = –42.8, d.f. = 7, p < 0.001) and chlorine (t = 21, d.f. = 7, p < 0.001).

One Minute PVC Immersion in Chlorpyrifos (Lorsban 500 EC®)

Defects. The mean density of cavities increased strongly following immersion in Lorsban 500 EC® (T = 259.5, p < 0.001) as did the density of convexities (T = 528.5, p < 0.001). There were no differences between the control and treated finger specimens for cracks (T = 8, p = 0.726) and smooth areas (T = 340, p = 0.058). A summary of the data is presented in Table 3.

EDS. Phosphorus was also not detected in these samples. There were no differences between the groups for concentrations of carbon (t = 0.069, d.f. = 7, p = 0.947) or aluminium (t = 0.324, d.f. = 7, p = 0.756). Oxygen increased considerably following immersion in pesticide (T = 24, p = 0.023) while silicon increased almost five-fold (t = –8.84, d.f. = 7, p < 0.001). Sulfur

Table 4. Elements (cps) detected on PVC glove fingers immersed in chlorpyrifos (Lorsban 500 EC®) for one minute. The means ± standard errors for the normal distribution are shown (t-test). The medians and percentiles (25th and 75th) are shown for the non-normal distribution (Mann-Whitney Rank Sum Test).

Elements	Glove finger	n	Mean ± SE		Difference of means
C	New	6	5862 ± 1146		142
	Immersed	3	5720 ± 1581		
			(t = 0.0689, p = 0.9470)		
Al	New	6	479 ± 127		63
	Immersed	3	416 ± 83		
			(t = 0.324, p = 0.7555)		
Si	New	6	531 ± 64		–1937
	Immersed	3	2468 ± 302		
			(t = –8.84, p < 0.0001)		
Cl	New	6	30437 ± 675		14253
	Immersed	3	16184 ± 727		
			(t = 13, p < 0.0001)		
			Median	25%	75%
O	New	6	6560	4308	6949
	Immersed	3	11424	9265	16706
S	New	6	373	329	475
	Immersed	3	5675	5513	8858

increased 15-fold (T = 24, p = 0.024) but chlorine concentration declined by almost half (t = 13, d.f. = 7, p < 0.001). The data are summarised in Table 4.

PVC Extended Immersion in Diazinon (Jetdip®)

Defects. The defects observed in PVC following immersion in diazinon are presented in Table 5. The density of cavities differed strongly between treatments for all time periods (H = 8.12, d.f. = 2, p = 0.017 after 24 hours, H = 33.5, d.f. = 2, p < 0.001 after 36 hours, and H = 25.3, d.f. = 2, p < 0.001 after 48 hours). Convexities became more evident after 36 hours (H = 4.07, d.f. = 2, p = 0.131 after 24 hours, H = 18.3, d.f = 2, p < 0.001 after 36 hours, H = 12.9, d.f. = 2, p = 0.002 after 48 hours). Cracks were only found on the new gloves (H = 10.7, d.f. = 2, p = 0.004 for all time intervals). Smooth areas became significant after 36 hours (H = 0, d.f. = 2, p = 1 after 24 hours, H = 10.1, d.f. = 2, p = 0.004 after 36 hours, and H = 10, d.f. = 2, p = 0.007 after 48 hours).

EDS. Carbon concentrations differed between treatments for all time intervals, and was lowest following immersion in concentrated pesticide ($F_{2,9}$ = 12.3, p = 0.003 after 24 hours, $F_{2,9}$ = 13.1, p = 0.002 after 36 hours, and $F_{2,9}$ = 20.4, p = 0.005 after 48 hours); a similar pattern was evident for oxygen concentration ($F_{2,9}$ = 14, p = 0.002 after 24 hours, $F_{2,9}$ =10.9, p = 0.002 after 36 hours, and $F_{2,9}$ = 15.1, p = 0.001 after 48 hours). After 24 hours there was a decrease in aluminium concentration ($F_{2,9}$ = 5.52, p = 0.027), but no difference between treatments after 36 hours $F_{2,9}$ = 1.22, p = 0.341, or 48 hours $F_{2,9}$ = 0.663, p = 0.539). There were no differences in silicon concentrations (24 hours: H = 1.96, d.f. = 2, p = 0.417 and 36 hours: $F_{2,9}$ = 0.919, p = 0.433) until after 48 hours ($F_{2,9}$ = 8.835, p = 0.009). Phosphorus differed between all time intervals and was highest after 48 hours immersion (H = 10, d.f. = 2, p = 0.003 after 24 hours, H = 8.12, d.f. = 2, p = 0.028 after 36 hours, and H = 10, d.f. = 2, p = 0.0003 after 48 hours). Sulfur concentrations varied between treatments for all time intervals and were also highest after the longest exposure (H = 6.58, d.f. = 2, p = 0.0003 after 24 hours, H = 6.27, d.f. = 3, p = 0.004 after 36 hours, and after 48 hours $F_{2,9}$ = 383.7, p < 0.001). Chlorine concentrations were very high and differed between treatments for all immersion times (H = 6.58, d.f. = 2, p = 0.021 after 24 hours, H = 6.27, d.f. = 2, p = 0.029 after 36 hours, and after 48 hours $F_{2,9}$ = 83.7, p < 0.001). A summary is given in Table 6.

PVC Extended Immersion in Chlorpyrifos (Lorsban 500 EC®)

Defects. The defects on PVC following immersion in Lorsban 500 EC® are presented in Table 7. The density of cavities increased especially after 24 and 36 hours immersion. (H = 25.9, d.f. = 2, p < 0.001 after 24 hours, H = 41.6, d.f. = 3, p < 0.001 after 36 hours, and H = 9.77, d.f. = 3, p = 0.021 after 48 hours.) Convexities generally peaked after 36 hours immersion (H = 7.82, d.f. = 2, p = 0.001 after 24 hours, H = 30.8, d.f. = 3, p < 0.001 after 36 hours, and H = 4.77, d.f. = 3, p = 0.190 after 48 hours). Defects in the form of cracks were not characteristic of the treated gloves and smooth areas were present at very low densities before and following treatment.

EDS. Carbon differed unpredictably between treatments after 24 and 36 hours immersion, $F_{2,9}$ = 13.3, p = 0.002 and $F_{3,11}$ = 39.3, p < 0.001 respectively (Tab. 8). After 48 hours immersion carbon did not differ from the new samples ($F_{3,11}$ = 4.17, p = 0.034). Oxygen concentrations also differed between treatments for the 24 and 36 hour immersions ($F_{2,9}$ = 6.94, p = 0.015, $F_{3,11}$ = 23, p < 0.0001), but there were no significant differences after 48 hours (H = 7.23, d.f. = 3, p = 0.065). Aluminium concentrations did not differ between treatments after 24 hours immersion (H = 1.72, d.f. = 2, p = 0.455), but there were modest differences after 36 hours ($F_{3,11}$ = 5.37, p = 0.016) and after 48 hours ($F_{3,11}$ = 4.17, p = 0.033). Silicon did not vary between treatments after 24 hours immersion

Table 5. Defects on PVC gloves that had been immersed in concentrated or diluted diazinon (Jetdip®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks). Those with the same letters are not significant (Student-Newman-Keuls method); n = 20 for each of the treatments.

		24 hours			36 hours			48 hours		
	Treatments	Median	25%	75%	Median	25%	75%	Median	25%	75%
Cavities	New	0	0	0 a	0	0	0 a	0	0	0 a
	Diluted	1	0	1 a	4	2	5 b	1	0	3 b
	Concentrated	1	0	1 a	3	3	4 b	3	1	5 c
Convexities	New	0	0	0	0	0	0 a	0	0	0 a
	Diluted	1	0	1	3	2	4 b	3	2	4 b
	Concentrated	1	0	1	3	1	5 b	1	0	4 c
Cracks	New	0	0	1 a	0	0	1 a	0	0	1 a
	Diluted	0	0	0 a	0	0	0 a	0	0	0 a
	Concentrated	0	0	0 a	0	0	0 a	0	0	0 a
Smooth	New	0	0	1	0	0	1 a	0	0	1 a
	Diluted	0	0	1	0	0	0 a	0	0	0 a
	Concentrated	0	0	1	0	0	0 a	0	0	0 a

(H = 0.423, d.f. = 2, p = 0.861), but concentrations did vary after 36 hours (H = 10.2, d.f. = 3, p = 0.0167) and after 48 hours (H = 11.2, d.f. = 3, p = 0.010). There were no differences for phosphorus concentrations after 24 hours immersion (H = 3.15, d.f. = 2, p = 0.777), but there were after 36 hours immersion (H = 12.1, d.f. = 3, p = 0.007) and after 48 hours (H = 11.7, d.f. = 3, p = 0. 008). Sulfur concentrations did not differ between treatments after 24 hours immersion (H = 4.32, d.f. = 2, p = 0.120), but there were differences after 36 and 48 hours immersion (H = 11.7, d.f. = 3, p = 0.0085) for both tests. Chlorine concentrations did not differ between treatments for the 24 and 36 hours immersion times (H = 1.30, d.f. = 2, p = 0.230 and H = 6.60, d.f. = 3, p = 0.085 respectively), but there were variations after 48 hours immersion (H = 12.4, d.f. = 3, p = 0.006).

NBR Results

One Minute NBR Immersion in Diazinon (Jetdip®)

Defects. Cavities did not differ in their density on the surface of NBR gloves between treatments (T = 455, p = 0.228), nor did convexities (T = 445, p = 0.350). There were no differences between treatments for cracks, which were very scarce (T = 390, p = 0.594). There were no smooth areas observed in any samples. The data are summarised in Table 9.

EDS. Phosphorus was not detected on these samples. There were no differences between the treatments in surface concentrations of carbon (t = 0.843, d.f. = 7, p = 0.427), aluminium (t = 0.771, d.f. = 7, p = 0.466) or chlorine (t = 0.741, d.f. = 2, p = 0.483). Oxygen, silicon and sulfur increased significantly on the surface of the glove following immersion in Jetdip: (oxygen, t = –3.28, d.f. = 7, p = 0.013, silicon (t = –806, d.f. = 7, p < 0.001, sulfur, t = –4.42, d.f. = 7, p = 0.0031) (Tab. 10).

One Minute NBR Immersion in Chlorpyrifos (Lorsban 500 EC®)

Defects. Cavities increased in NBR gloves following their immersion in Lorsban 500 EC® (T = 537.5, p < 0.001), as did convexities (T = 269, p < 0.001). Cracks were rare and did not differ in density between the new and the immersed gloves (T = 470, p = 0.105). The data are presented in Table 11.

EDS. Phosphorus was not detected on these samples. There were no differences between treatments for carbon (t = 0.313, d.f. = 7, p = 0.764), aluminium (t = 0.345, d.f. = 7, p = 0.741) or chlorine concentrations (t = 0.260, d.f. = 7, p = 0.802). The concentration of oxygen was higher following immersion (T = 23, p = 0.047) as was silicon and sulfur (T = 24, p = 0.024) (Tab. 12).

NBR Extended Immersion in Diazion (Jetdip®)

Defects. Cavities did not differ between treatments for 24 and 36 hours (H = 0.0986, d.f. = 2, p = 0.952 and H = 5.80, d.f. = 2, p = 0.055 respectively). After 48 hours

Table 6. Elements as analysed by EDS (cps) on PVC gloves that had been immersed in concentrated or diluted diazinon (Jetdip®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks) or the mean ± SE are shown for the normal distributions (One Way ANOVA). Those with the same letters are not significant (Dunn's method or Student-Newman-Keuls method); n = 6 for the new untreated gloves and n = 3 for both of the treatments.

Elements	Treatments	24 hours Median	24 hours 25%	24 hours 75%	24 hours Mean ± SE	36 hours Median	36 hours 25%	36 hours 75%	36 hours Mean ± SE	48 hours Median	48 hours 25%	48 hours 75%	48 hours Mean ± SE
C	New				3491 ± 293 a				3491 ± 293 a				3491 ± 293 a
	Diluted				3252 ± 233 a				4725 ± 440 b				4879 ± 414 b
	Concentrated				1448 ± 231 b				2034 ± 27 c				1600 ± 39 c
O	New				5903 ± 292 a				5903 ± 292 a				5903 ± 292 a
	Diluted				4911 ± 131 a				6386 ± 532 a				5703 ± 558 a
	Concentrated				3407 ± 476 b				3975 ± 19 b				3262 ± 97 b
Al	New				398 ± 55 a				398 ± 55				398 ± 55
	Diluted				366 ± 84 a				453 ± 91				359 ± 93
	Concentrated				118 ± 8 b				284 ± 66				289 ± 51
Si	New	505	428	578					507 ± 33				507 ± 33 a
	Diluted	350	274	463					435 ± 51				422 ± 44 a
	Concentrated	491	488	498					486 ± 23				676 ± 43 b
P	New	0	0	0 a		0	0	0 a		0	0	0 a	
	Diluted	1109	904	1312 ab		0	0	1 ab		123	75	159 ab	
	Concentrated	3171	3132	3209 b		2168	2164	2368 b		1354	1323	1626 b	
S	New	305	249	314 a		305	249	314 a					324 ± 46 a
	Diluted	1630	1342	1842 ab		487	460	530 ab					500 ± 7 b
	Concentrated	3992	3982	4002 b		2932	2872	3158 b					2327 ± 79 c
Cl	New	28379	25936	30506 a		28379	25936	30506 a					28517 ± 1147 a
	Diluted	26682	25649	27266 a		27434	26485	27920 a					24463 ± 1236 b
	Concentrated	41460	41332	41594 a		34282	33635	34590 a					48031 ± 979 c

there were strong differences for cavities between treatments (H = 20.2, d.f. = 2, p < 0.0001). Convexities varied markedly between treatments (H = 35.2, d.f. = 2, p < 0.0001, at 24 hours and H = 19.6, d.f. = 2, p < 0.0001, at 36 hours). The differences were not quite as marked after 48 hours (H = 10.3, d.f. = 2, p = 0.005). There were very strong differences for cracks between treatments (H = 43 after 24 hours, H = 45.8 after 36 hours and H = 40.9 after 48 hours, d.f. = 2, p < 0.0001) for all periods. Table 13 provides a summary of the data.

EDS. Carbon differed strongly between treatments after 24 hours immersion ($F_{2,9}$ = 46.9, p < 0.0001), but there were no differences after 36 hours immersion ($F_{2,9}$ = 3.11, p = 0.093) or 48 hours immersion (H = 1.45, d.f. = 2, p = 0.536). Oxygen varied between treatments following 24 hours immersion ($F_{2,9}$ = 169.5, p < 0.0001) and after 36 hours ($F_{2,9}$ = 7.11, p = 0.014), but there were no differences after 48 hours immersion ($F_{2,9}$ = 2.57, p = 0.131). Aluminium did not differ between treatments (H = 4.54, d.f. = 2, p = 0.103 after 24 hours, H = 0.846, d.f. = 2, p = 0.697 after 36 hours, and H = 2.02, d.f. = 2, p = 0.390 after 48 hours). There were differences for silicon concentrations between the treatments only after 24 hours (H = 9.35, d.f. = 2, p < 0.001) but not after 36 and 48 hours immersion ($F_{2,9}$ = 1.66, p = 0.243 and $F_{2,9}$ = 2.58, p = 0.130 respectively). There were no variations for phosphorus after 24 hours immersion (H = 3, d.f. = 2, p = 0.761) nor after 36 hours (H = 3, d.f. = 2, p = 0.761). However, there were differences following 48 hours immersion (H = 10.7, d.f. = 2, p = 0.0331). Sulfur concentrations differed between treatments for all immersion times ($F_{2,9}$ = 253.5, p < 0.0001 after 24 hours, $F_{2,9}$ = 8.67, p = 0.008 after 36 hours and, H = 6.58, d.f. = 2, p = 0.021 after 48 hours). Chlorine concentrations varied between treatments after 24 hours (H = 9.35, d.f. =

Table 7. Defects on PVC gloves that had been immersed in concentrated or diluted chlorpyrifos (Lorsban 500 EC®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks). Those with the same letters are not significant (Student-Newman-Keuls method); n = 20 for each treatment.

	Treatments	24 hours			36 hours			48 hours		
		Median	25%	75%	Median	25%	75%	Median	25%	75%
Cavities	New	0	0	0 a	0	0	0 a	0	0	0 a
	Diluted	4	2	5 b	3	2	4 b	2	0	2 bc
	Concentrated	4	2	5 b	2	1	3 c	1	0	3 bd
	Taped				2	1	2 c	2	0	3 cd
Convexities	New	0	0	0 a	0	0	0 a	0	0	0
	Diluted	2	2	6 b	3	3	4 b	1	0	1
	Concentrated	2	2	4 b	2	1	2 c	1	0	1
	Taped				2	1	2 c	2	0	2
Cracks	New	0	0	1 a	0	0	1 a	0	0	1 a
	Diluted	0	0	0 a	0	0	0 a	0	0	0 a
	Concentrated	0	0	0 a	0	0	0 a	0	0	0 a
	Taped				0	0	0 a	0	0	0 a
Smooth	New	0	0	1 a	0	0	1 a	0	0	1
	Diluted	0	0	1 a	0	0	0 a	0	0	0
	Concentrated	0	0	0 a	0	0	0 a	0	0	1
	Taped				0	0	0 a	0	0	1

2, $p < 0.001$), but not after 36 hours (H = 1.04, d.f. = 2, p = 0.653) or 48 hours (H = 1.65, d.f. = 2, p = 0.476). Table 14 summarises the data.

NBR Extended Immersion in Chlorpyrifos (Lorsban 500 EC®)

Defects. The defects on NBR gloves following immersion in Lorsban 500 EC® are presented in Table 15. There were no slumps or smooth areas observed on these samples. There were no differences for cavities between treatments for all time spans. (H = 3.01, d.f. = 2, p = 0.222 after 24 hours, H = 3.53, d.f. = 2, p = 0.175 after 36 hours, $F_{2,59} = 2.24$, p = 0.115 after 48 hours.) Convexities differed between treatments until 48 hours (H = 19.1, d.f. = 2, $p < 0.0001$, following 24 hours immersion and H = 11.6, d.f. = 2, p = 0.003 after 36 hours immersion, and $F_{2,57} = 1.37$, p = 0.262 after 48 hours). There were very strong differences for cracks between treatments for all time periods. (H = 41.1, d.f. = 2, $p < 0.0001$ after 24 hours, H = 42.6, d.f. = 2, $p < 0.0001$ after 36 hours, and H = 41.3, d.f. = 2, $p < 0.0001$ after 48 hours.)

EDS. Carbon concentrations did not vary between treatments following 24 hours ($F_{2,9} = 4.17$, p = 0.052) or 48 hours immersion ($F_{2,9} = 1.67$, p = 0.243), however, there was an increase in carbon on gloves immersed in concentrated pesticide for 36 hours ($F_{2,9} = 7.86$, p = 0.011). Oxygen concentrations varied between treatments after 24 and 36 hours immersion (H = 8.94, d.f. = 2, p = 0.001 and $F_{2,9} = 32.9$, $p < 0.0001$ respectively), but there were no differences after 48 hours ($F_{2,9} = 1.24$, p = 0.334). There were no variations for aluminium after 24 hours ($F_{2,9} = 1.08$, p = 0.379). Differences were found after 36 hours immersion ($F_{2,9} = 5.99$, p = 0.022), however, there were none after 48 hours (H = 2.54, d.f. = 2, p = 0.318). Silicon differed between treatments (H = 9.35, d.f. = 2, $p < 0.001$ after 24 hours, H = 8.32, d.f. = 2, p = 0.003 after 36 hours), but there were no differences after 48 hours ($F_{2,9} = 3.56$, p = 0.073). Phosphorus was not detected on the samples immersed for 36 hours, but there were differences after 24 hours (H = 10.7, d.f. = 2, p = 0.034) but none after 48 hours (H = 6.55, d.f. = 2, p = 0.264). Sulfur concentrations increased strongly following 24 hours ($F_{2,9} = 101.7$, $p < 0.0001$) and 36 hours immersion in both dilute and concentrated insecticide ($F_{2,9} = 58.2$, $p < 0.0001$), however, after 48 hours there were no significant differences between the treatments (H = 5.15, d.f. = 2, p = 0.068). Chlorine concentrations increased after immersion for 24 hours (H = 9.35, d.f. = 2, $p < 0.001$), and 36 hours ($F_{2,9} = 5.17$, p = 0.032), but there was no significant difference after 48

Table 8. Elements as analysed by EDS (cps) on PVC gloves that had been immersed in concentrated or diluted chlorpyrifos (Lorsban 500 EC®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks) or the mean ± SE are shown for the normal distributions (One Way ANOVA). Those with the same letters are not significant (Dunn's method or Student-Newman-Keuls method); n = 6 for the new untreated gloves and n = 3 for both of the treatments.

Elements		24 hours				36 hours				48 hours			
	Treatments	Median	25%	75%	Mean ± SE	Median	25%	75%	Mean ± SE	Median	25%	75%	Mean ± SE
C	New				3491 ± 293 a				3491 ± 293 a	3255	2970	4194	
	Diluted				7190 ± 333 b				6501 ± 274 b	5257	4354	5310	
	Concentrated				5759 ± 1070 b				1265 ± 116 c	1600	1550	1651	
	Taped								4135 ± 371 a	5307	2549	6882	
O	New				5903 ± 292 a				5903 ± 292 a	5675	5351	6608	
	Diluted				9425 ± 751 b				7895 ± 480 b	5928	4965	6391	
	Concentrated				7771 ± 1345 ab				1952 ± 271 c	3326	3136	3373	
	Taped								8199 ± 821 b	10827	5763	13466	
Al	New	396	272	494					398 ± 55 ab				398 ± 55 ab
	Diluted	482	387	523					384 ± 97 bc				306 ± 119 ac
	Concentrated	691	378	1130					339 ± 33 ac				289 ± 51 bc
	Taped								695 ± 46 d				761 ± 180 d
Si	New	505	428	578		505	428	578 ab		505	428	578 abc	
	Diluted	482	481	496		477	376	594 acd		422	385	488 ad	
	Concentrated	523	473	651		647	625	667 bed		712	621	721 bde	
	Taped					1794	1670	1911 ce		1754	1459	2320 ce	
P	New	0	0	0		0	0	0 ab		0	0	0 ab	
	Diluted	0	0	0		0	0	56 acd		123	75	159 acd	
	Concentrated	0	0	62		2646	2602	2788 bde		1354	1323	1626 bce	
	Taped					10463	7201	11578 ce		9734	6544	10848 de	
S	New	305	249	314		305	249	314 ab		305	249	314 ab	
	Diluted	424	417	449		376	341	423 acd		495	492	509 acd	
	Concentrated	499	459	500		3565	3470	3729 bce		2355	2223	2425 bce	
	Taped					10661	10301	11982 de		11854	9573	12957 de	
Cl	New	28379	25936	30506		28379	25936	30506		28379	25936	30506 abc	
	Diluted	26935	26631	27120		25836	25071	26057		25491	22874	25794 ad	
	Concentrated	26121	25053	26371		49609	48644	50052		48908	46784	49060 bde	
	Taped					45227	19621	101819		124118	109044	132339 ce	

hours ($F_{2,9} = 434$, $p = 0.661$). The data are summarised in Table 16.

DISCUSSION

PVC Defects

A loss of surface integrity of PVC was apparent even following short exposure to these insecticides. Cavities were formed on the exterior glove surface after only one minute's immersion in Jetdip®, although these disappeared following 24 hours' immersion. This might be explained by the viscosity of Jetdip®, which was probably absorbed by the gloves over the longer time period and caused swelling and smoothing of the surface. After 24 hours, the glove surface began to degrade further, as evidenced by an increase in smooth areas following prolonged exposure. Pre-existing cavities in the membrane were not typical of the new unused gloves, in contrast to a previous report [4], suggesting differences between batches.

It should be noted that the glove fingers were air dried in a vertical position and that the sampling was done from the finger tip region. Therefore the concentrated formulations would have gravitated to this region so that the effective exposure time was more than one minute. This more closely mimics field usage as it is unlikely that a worker would wash any splashes or spills off during operational procedures.

There were fewer convexities in the new unused glove samples. Convexities became a significant feature of all the samples treated with Lorsban 500 EC® in both the taped and untaped samples. Therefore it is likely that permeation occurred from the exterior to the interior and that condensation was not the cause of moisture on the interior lining. Exposure to Jetdip® also caused convexities after 36 and 48 hours suggesting permeation was somewhat slower than with Lorsban 500 EC®. Convexities were a characteristic of the treated samples following the one minute immersion, which indicates that permeation was significant.

The density of cracks did not increase following treatment and PVC gloves may therefore be resistant to cracking following exposure to organophosphates. Smooth areas were not a significant feature of the treated gloves and those few observed were most likely related to the manufacturing process or the absorption phase of permeation.

PVC EDS

Carbon, oxygen, aluminium, silicon, aluminium and chlorine were constituents of the new unused PVC gloves, as previously reported [3, 4]. Carbon and oxygen were present in lesser quantities on the gloves immersed in the concentrated Jetdip®, thus confirming that surface occlusion by the insecticide occurred as identified by the defect analysis. The masking phenomenon was not apparent in the Lorsban 500 EC® immersion experiments. It was expected that the taped and concentrated sample would have similar readings, but this was not the case. In both the 36 and 48 hour immersions in Lorsban 500 EC® the formulation had permeated through to the interior.

Exposure to both formulations for one minute was not long enough for phosphorus to adhere to the glove surface. Phosphorus was detected in greater quantities on the samples treated with the concentrated formulations at the extended immersion times, as expected. Generally the concentrations of phosphorus and sulfur tended to decrease over time because the formulation had either permeated further into the matrix or had volatilised. In the Lorsban 500 EC® immersions, the taped samples had much higher levels of phosphorus and sulfur than the untaped samples. This gain demonstrated that sealing the glove fingers altered the permeation rate.

Sulfur was a component of the glove material but was found in higher concentrations on the pesticide-treated gloves.

Table 9. Defects detected on NBR glove sections immersed in diazinon (Jetdip®) for one minute. The medians and percentiles (25th and 75th) are given (Mann-Whitney Rank Sum Test).

Defects	Glove finger	n	Median	25%	75%
Cavities	New	20	4	4	5
	Immersed	20	4	3	4
Convexities	New	20	4	3	4
	Immersed	20	4	3	5
Cracks*	New	20	0	0	0
	Immersed	20	0	0	0

* The mean for cracks = 0.05

NBR Defects

In the Jetdip® immersion experiments cavities were only a significant feature after 48 hours exposure, with the diluted insecticide being more aggressive. Cavities were significant following one minute immersion in Lorsban 500 EC® but were not significant after the longer immersion times. This may be related to the different absorption rates of the insecticides on the NBR gloves. Thus, it would appear that both PVC and NBR interactions with these insecticides are similar, although the rates differ.

There was no definite pattern between the occurrence of surface convexities and chemical treatments, and it seems likely that most of those observed on the glove samples were related to the manufacturing process.

Table 10. Elements (cps) detected on NBR gloves immersed in diazinon (Jetdip®) for one minute. The means ± standard errors and the differences of the means are shown (t-test).

Elements	Glove finger	n	Mean ± SE	Difference of means
C	New	6	6196 ± 761	977
	Immersed	3	5219 ± 489	(t = 0.834, p = 0.4273)
O	New	6	5481 ± 939	–4911
	Immersed	3	10392 ± 894	(t = –3.28, p = 0.0134)
Al	New	6	553 ± 269	304
	Immersed	3	249 ± 28	(t = 0.771, p = 0.4657).
Si	New	6	562 ± 141	–1974
	Immersed	3	2536 ± 202	(t = –8.06, p <0.0001)
S	New	6	2292 ± 411	–2744
	Immersed	3	5036 ± 232	(t = –4.42, p = 0.0031)
Cl	New	6	14221 ± 5150	5588
	Immersed	3	8633 ± 487	(t = 0.741, p = 0.4830)

Table 11. Defects detected on NBR glove sections immersed in chlorpyrifos (Lorsban 500 EC®) for one minute. The medians and percentiles (25th and 75th) are given (Mann-Whitney Rank Sum Test).

Defects	Glove section	n	Median	25%	75%
Cavities	New	20	4	4	5
	Immersed	20	6	5	8
Convexities	New	20	4	3	4
	Immersed	20	6	5	7
Cracks	New	20	0	0	0
	Immersed	20	0	0	1

Table 12. Elements (cps) detected on NBR gloves immersed in chlorpyrifos (Lorsban 500 EC®) for one minute. The medians and percentiles (25th and 75th) are shown for the non-normally distributed data (Mann-Whitney Rank Sum Test). The means ± standard errors and the differences of the means are shown for the normally distributed data (t-test).

Elements	Glove finger	n	Median	25%	75%
O	New	6	5086	3705	7023
	Immersed	3	11424	9265	16706
Si	New	6	374	312	942
	Immersed	3	2250	2129	2861
S	New	6	1742	1617	3018
	Immersed	3	5675	5513	8858
			Mean ±	SE	Difference of means
C	New	6	6196 ±	761	476
	Immersed	3	5720 ±	1581	
			(t = 0.313, p = 0.7635)		
Al	New	6	553 ±	269	137
	Immersed	3	416 ±	83	
			(t = 0.345, p = 0.7405)		
Cl	New	6	14221 ±	5150	–1963
	Immersed	3	16184 ±	727	
			(t = 0.260, p = 0.802)		

Cracks were not a significant feature of the one minute immersion experiments, but were characteristic of the longer immersion times. Overall, there were slightly more cracks on the samples treated with the diluted formulations. A possible explanation for this is that the NBR absorbed water during immersion, which resulted in swollen areas that contracted during the drying out process which may lead to crack propagation.

NBR EDS

Carbon, oxygen, aluminium and silicon are components of both the formulations and the glove material. After a certain time, when the permeation process is more advanced, carbon, oxygen and silicon are retained on the surface and then lost by diffusion or volatilisation. Generally, chlorine was detected in greater quantities on the new gloves thus highlighting the masking effect of the formulations.

Phosphorus was not retained on the surface of the gloves in the one minute treatments, but was detected on the samples treated with the concentrated insecticides in the extended immersion times. An unusual result was recorded with the Lorsban 500 EC® treatments as there was no phosphorus detected after 36 hours but there were significant concentrations after 24 hours and some after 48 hours. Phosphorus may have been masked by a by-product from the permeation process.

Table 13. Defects on NBR gloves that had been immersed in concentrated or diluted diazinon (Jetdip®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks). Those with the same letters are not significant (Student-Newman-Keuls method); n = 20 for each of the treatments.

		24 hours			36 hours			48 hours		
	Treatments	Median	25%	75%	Median	25%	75%	Median	25%	75%
Cavities	New	4	4	5	4	4	5	4	4	5 a
	Diluted	5	3	6	4	3	4	6	6	9 b
	Concentrated	5	3	5	3	2	5	5	4	7 c
Convexities	New	3	3	4 a	3	3	4 a	3	3	4 a
	Diluted	0	0	4 b	1	0	3 b	6	4	8 b
	Concentrated	0	0	0 c	5	3	7 c	5	4	7 b
Cracks	New	0	0	0 a	0	0	0 a	0	0	0 a
	Diluted	6	5	8 b	4	3	4 b	5	4	7 b
	Concentrated	4	3	5 c	6	4	7 c	4	3	5 b

Table 14. Elements as analysed by EDS (cps) on NBR gloves that had been immersed in concentrated or diluted diazinon (Jetdip®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks) or the mean ± SE are shown for the normal distributions (One Way ANOVA). Those with the same letters are not significant (Dunn's method or Student-Newman-Keuls method); n = 6 for the new untreated gloves and n = 3 for both of the treatments.

Elements		24 hours				36 hours				48 hours			
	Treatments	Median	25%	75%	Mean ± SE	Median	25%	75%	Mean ± SE	Median	25%	75%	Mean ± SE
C	New				5228 ± 696 a				5228 ± 696	5213	3721	6400	
	Diluted				10008 ± 326 b				2611 ± 848	4071	3559	4262	
	Concentrated				17109 ± 1418 c				4349 ± 405	4349	4237	4416	
O	New				6171 ± 791 a				6171 ± 791 a				6171 ± 791
	Diluted				14995 ± 957 b				8206 ± 621 ab				7621 ± 483
	Concentrated				38561 ± 2298 c				10254 ± 335 b				8832 ± 990
Al	New	311	136	965		311	136	965		311	136	965	
	Diluted	1128	984	2243		241	234	258		376	265	441	
	Concentrated	1372	1322	1862		287	268	377		652	587	723	
Si	New	674	314	1063 a					700 ± 163				700 ± 163
	Diluted	2636	2433	2853 ab					991 ± 214				1160 ± 126
	Concentrated	4867	3903	5571 b					1115 ± 24				1170 ± 200
P	New	0	0	0		0	0	0		0	0	0 a	
	Diluted	0	0	0		0	0	0		0	0	0 a	
	Concentrated	0	0	1049		0	0	152		109	69	234 b	
S	New				2680 ± 476 a				2680 ± 476 a	2409	1617	4017 a	
	Diluted				8446 ± 263 b				3154 ± 182 a	3589	3437	3691 ab	
	Concentrated				18513 ± 534 c				5252 ± 100 b	4581	4454	4777 b	
Cl	New	18325	6261	29682 a		18325	6261	29682		18325	6261	29682	
	Diluted	57361	57339	57920 ab		27205	26800	28312		26794	25957	29621	
	Concentrated	71198	70097	72237 b		16693	15245	16970		20469	19814	21180	

Table 15. Defects on NBR gloves that had been immersed in concentrated or diluted chlorpyrifos (Lorsban 500 EC®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks). Those with the same letters are not significant (Student-Newman-Keuls method). The mean ± SE are shown for the normal distributions (One Way ANOVA); n = 20 for each of the treatments.

		24 hours			36 hours			48 hours			Mean ± SE
	Treatments	Median	25%	75%	Median	25%	75%	Median	25%	75%	
Cavities	New	4	4	5	4	4	5				4 ± 0
	Diluted	6	4	9	4	2	7				3 ± 0
	Concentrated	5	4	6	4	2	4				5 ± 0
Convexities	New	3	3	4 a	3	3	4 a				4 ± 0
	Diluted	6	4	7 b	6	4	7 b				4 ± 0
	Concentrated	1	0	4 c	2	0	5 a				5 ± 1
Cracks	New	0	0	0 a	0	0	0 a	0	0	0 a	
	Diluted	6	4	9 b	7	5	8 b	6	4	6 b	
	Concentrated	5	4	7 b	6	5	7 b	5	4	7 b	

Table 16. Elements as analysed by EDS (cps) on NBR gloves that had been immersed in concentrated or diluted chlorpyrifos (Lorsban 500 EC ®) for 24, 36 and 48 hours compared to new untreated gloves. The medians and percentiles are shown for the non-normal distributions (Kruskal-Wallis One Way ANOVA on Ranks) or the mean ± SE are shown for the normal distributions (One Way ANOVA). Those with the same letters are not significant (Dunn's method or Student-Newman-Keuls method); n = 6 for the new untreated gloves and n = 3 for both of the treatments.

Elements		24 hours					36 hours					48 hours				
	Treatments	Median	25%	75%	Mean ±	SE	Median	25%	75%	Mean ±	SE	Median	25%	75%	Mean ±	SE
C	New				5228 ±	696				5228 ±	696 a				5228 ±	696
	Diluted				7386 ±	375				5818 ±	1256 a				3921 ±	474
	Concentrated				8969 ±	1677				10753 ±	1471 b				3442 ±	863
O	New	6637	4148	7023 a						6171 ±	791 a				6171 ±	791
	Diluted	13744	13221	14970 ab						11618 ±	2533 b				7062 ±	653
	Concentrated	18539	15649	22909 b						24885 ±	2537 c				8625 ±	1930
Al	New				592 ±	261				592 ±	261 a	311	136	965		
	Diluted				508 ±	40				403 ±	87 a	208	134	286		
	Concentrated				1081 ±	291				1696 ±	212 b	587	421	622		
Si	New	674	314	1063 a			674	314	1063 a						700 ±	163
	Diluted	2090	2050	2207 ab			3409	2410	4347 ab						1164 ±	233
	Concentrated	3119	2545	3770 b			3608	2921	3684 b						1438 ±	254
P	New	0	0	0 a			0	0	0			0	0	0		
	Diluted	0	0	0 a			0	0	0			0	0	0		
	Concentrated	2041	1403	2289 b			0	0	0			770	193	874		
S	New				2680 ±	476 a				2680 ±	476 a	2409	1617	4017		
	Diluted				8057 ±	108 b				8632 ±	692 b	3897	2852	22653		
	Concentrated				11573 ±	347 c				12452 ±	1032 c	7248	4912	7361		
Cl	New	18325	6261	29682 a						18358 ±	5312 ab				18358 ±	5312
	Diluted	60708	59465	62924 ab						55817 ±	4087 ac				25390 ±	4951
	Concentrated	76846	71468	79512 b						55860 ±	21304 bc				21584 ±	2879

recorded with the Lorsban 500 EC® treatments as there was no phosphorus detected after 36 hours but there were significant concentrations after 24 hours and some after 48 hours. Phosphorus may have been masked by a by-product from the permeation process.

Sulfur was detected in higher quantities on all the samples treated with the concentrated formulations. Following exposure to Lorsban 500 EC® sulfur became depleted after 48 hours. It is possible that sulfur had permeated into the matrix of the gloves or was masked by by-products. It appears that sulfur could be used as an indicator for Lorsban 500 EC® exposure for specific time frames.

CONCLUSION

The propensity of NBR gloves to crack following challenges with these insecticides was unexpected given that NBR gloves generally have greater chemical resistance than PVC gloves. These experiments should be repeated using different types of washing and rinsing techniques to determine if crack propagation still occurs.

It is postulated that workers' risk of dermal exposure is consequential and further research is required to develop more robust gloves suitable for agricultural use. It should combine closer cooperation between manufacturers of CPGs and insecticides with consultation from field workers.

REFERENCES

1. Ansell Edmont Industrial: Ansell Edmont Chemical Resistance Guide. no. CRG-GC-REV.990. 1300 Walnut Street, Coshocton, Ohio, 43812-60000, 1990.
2. Berardinelli SP, Moyer ES: Chemical protective clothing breakthrough time: Comparison of several test systems. *Am Ind Hyg Assoc J* 1988, **49**, 89-94.
3. Canning KM: *Physico-chemical Characterisation of Surface Defects on Chemically Protective Gloves used in Agriculture.* PhD thesis. Department of Geography and Environmental Studies, University of Tasmania, Hobart 1997.
4. Canning KM, Jablonski W, McQuillan PB: Quantification of surface defects on chemically protective gloves following their use in agriculture. *Ann Agric Environ Med* 1998, **5**, 45-56.

5. Coletta GC, Mansdorf SZ, Berardinelli SP: Chemical protective clothing standard test method development: Part 11. Degradation test method. *Am Ind Hyg Assoc J* 1988, **49**, 26-33.

6. Ehntholt DJ, Bodek I, Valentine JR, Schwope AD, Royer MD, Frank U, Nielsen AP: The effects of solvent type and concentration on the permeation of pesticide formulations through chemical protective glove materials. **In:** Perkins JL, Stull JO (Eds): *Chemical Protective Clothing Performance in Chemical Emergency Response. ASTM STP 1037*, 146-156. American Society for Testing Materials, Philadelphia 1989.

7. Forsberg K, Mansdorf SZ: *Quick Selection Guide to Chemical Protective Clothing.* Van Nostrand Reinhold, New York 1993.

8. Karr C, Demers P, Costa LG, Daniell WE, Barnhart S, Miller M, Gallagher G, Horstman SW, Eaton D, Rosenstock L: Organophosphate pesticide exposure in a group of Washington State orchard applicators. *Environ Res* 1992, **59**, 229-237.

9. Mellstrom GH: Comparison of chemical permeation data obtained with ASTM and ISO permeation test cells-1. The ISO/DIS standard test procedure. *Ann Occup Hyg* 1991, **35**, 153-166.

10. Mellstrom GA: Comparison of chemical permeation data obtained with ASTM and ISO permeation test cells-11. The ISO/DIS standard test procedure. *Ann Occup Hyg* 1991, **35**, 167-180.

11. Moody RP, Ritter L: Pesticide glove permeation analysis: comparison of the ASTM F739 test method with an automated flow-through reverse-phase liquid chromatography procedure. *Am Ind Hyg Assoc J* 1990, **51**, 79-83.

12. Raheel M, Dai GX: Chemical resistance and structural integrity of protective glove materials. *J. Environ Sci Health* 1997, **A 32**, 567-579.

13. Van Sittert NJ, Dumas EP: Field study on exposure and health effects of an organophosphate pesticide for maintaining registration in the Philippines. *Med Lav* 1990, **81**, 463-473.