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QUANTIFICATION OF SURFACE DEFECTS ON CHEMICALLY PROTECTIVE GLOVES FOLLOWING THEIR USE IN AGRICULTURE

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Abstract: Chemically protective gloves are one of the most widely used barriers against hand exposure to pesticide contamination available to workers in primary industry. Polyvinyl chloride and nitrile butadiene rubber gloves were collected from four typical agricultural enterprises in Tasmania. Surface images of new and used gloves, up to 1000 × magnification, were obtained from an environmental scanning electron microscope and were used to classify defects, such as cracks, crazes, cavities, convexities, smooth areas and slumps. Some defects, e.g. cracks, were related to the working life of the gloves, whereas others, e.g. slumps, were associated with the manufacturing process. After viewing, the gloves were analysed by X-ray energy-dispersive spectroscopy. Phosphorus and sulfur peaks were indicative of pesticide retention. Rinsates from the interior of used polyvinyl chloride gloves were analysed by gas chromatography and mass spectrometry. Pesticide traces were found suggesting inadequate protection against dermal exposure. It is concluded that these gloves were unable to withstand the rigours of agricultural work because of the nature of the surface defects and they were contaminated with pesticides, outside and inside. Thus, their management needs improvement.

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

INTRODUCTION

Do the widely used chemically protective gloves (CPGs) benefit the agricultural worker? These gloves are readily available, low in cost and widely promoted in the occupational health and safety brochures as an efficacious item of protective clothing when mixing and applying pesticides and other toxic chemicals. A variety of CPGs are sold to Australian farmers, of which supported polyvinyl chloride (PVC) gloves retain more than three quarters of the market share followed by unsupported nitrile-butadiene rubber (NBR) gloves [2].

It is readily observed that most farmers tend to treat their gloves poorly, and many continue to use them long after their effectiveness has been compromised by wear and tear. Although gross membrane failure and macroscopic tears are obvious manifestations of the problem, little attention has been paid in the past to smaller scale failures [12]. These may either provide a conduit for toxic materials to the skin in their own right [5, 8, 10], or else serve as early warning of more serious failure in the near future. Few studies have attempted to describe defects on a microscopic scale and these have been for illustrative purposes only [3, 7]. In material science there has been much research on flaws within the material and their impact upon failure. These paradigms originated from the Griffith Theory of Flaws, which states that the discrepancy between the expected strength of the material and the actual strength is due to inherent flaws [11]. However, these theories have generally not been applied to CPG studies. Most CPG investigations have been performed in controlled laboratory conditions with the

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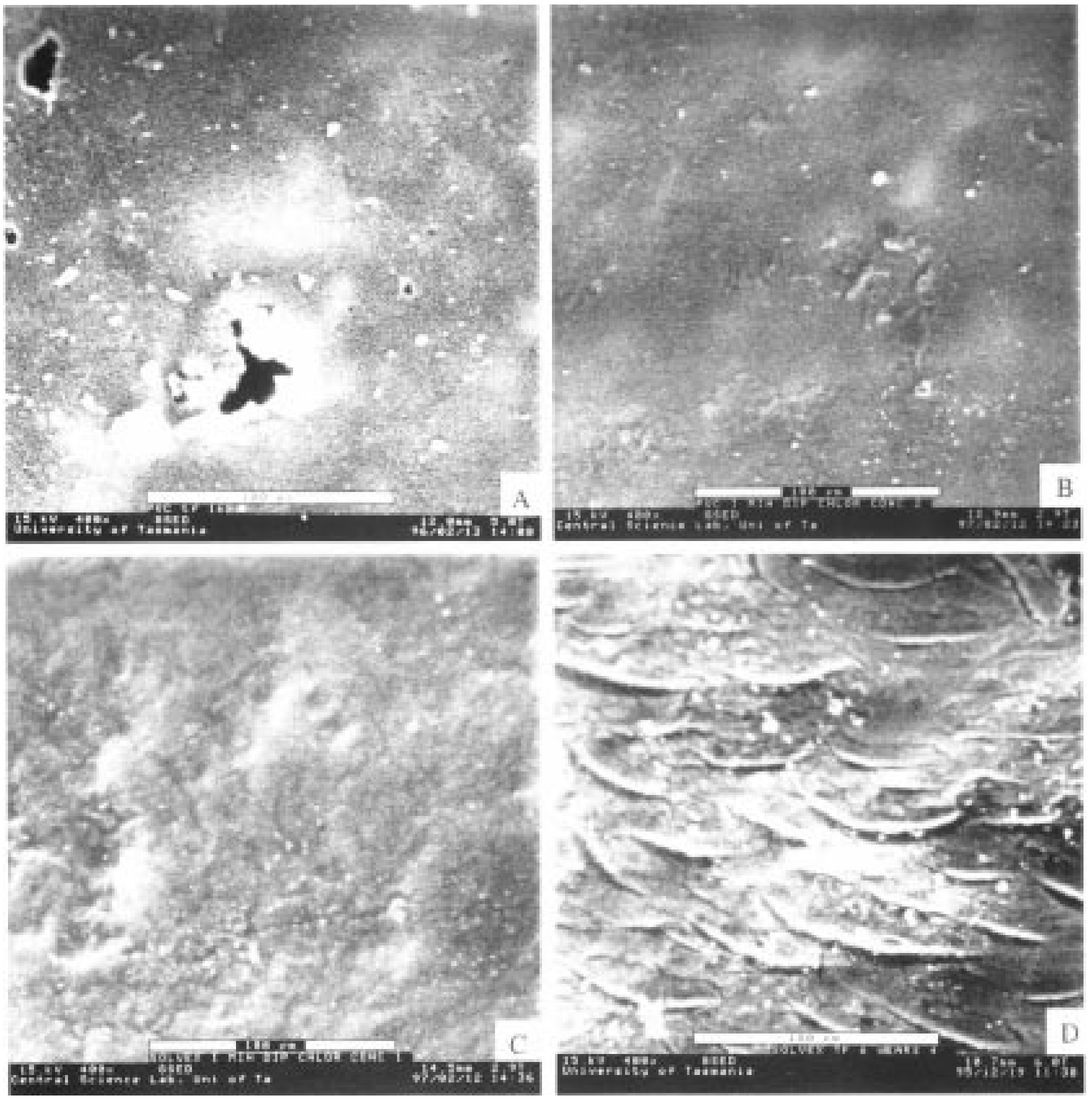

Figure 1a. Environmental scanning electron micrographs (400 ×) showing the surface defects on PVC and NBR gloves. A: Cavities and contaminants on PVC; B: Convexities on PVC; C: Convexities and contaminants on NBR (Sol-Vex™); D: Slumps and contaminants on NBR (Sol-Vex™).

primary focus on permeation following Fickian diffusion models, or penetration testing [6, 9].

This work describes the impact of normal field use on the state of the surface of PVC and NBR gloves. The aims have been achieved by determining the types of defects that occur in new and used CPGs for agricultural use, which involved developing a taxonomy of defects for CPGs; comparing PVC and NBR CPGs within this classification system; and ascertaining if there are any pesticides residing within the matrix of used CPGs.

MATERIALS AND METHODS

Origin of Gloves

An exchange CPG program was instigated in Tasmania where farmers were issued with new gloves of their choice after they handed in their used gloves. Participants were invited to complete a short questionnaire about the histories of their gloves, details of glove age and pesticides used. Four typical agricultural enterprises were represented in the exchange program (Tab. 1). New gloves, to serve as controls, were purchased locally to match the types that were handed in.

Experimental

Specimens measuring 3 × 3 cm were cut from the palm section of all the surrendered gloves, 2 cm in from the thumb junction. The specimens were then sampled haphazardly with a punch to produce 6 mm diameter samples, which were mounted on ESEM (environmental scanning electron microscope) aluminium stubs. No further preparation for the ESEM observation was required.

Electron microscopy and X-ray microanalysis. An ESEM 2020, equipped with a Link Pentafet Super Atmospheric Window (SATW) and energy dispersive

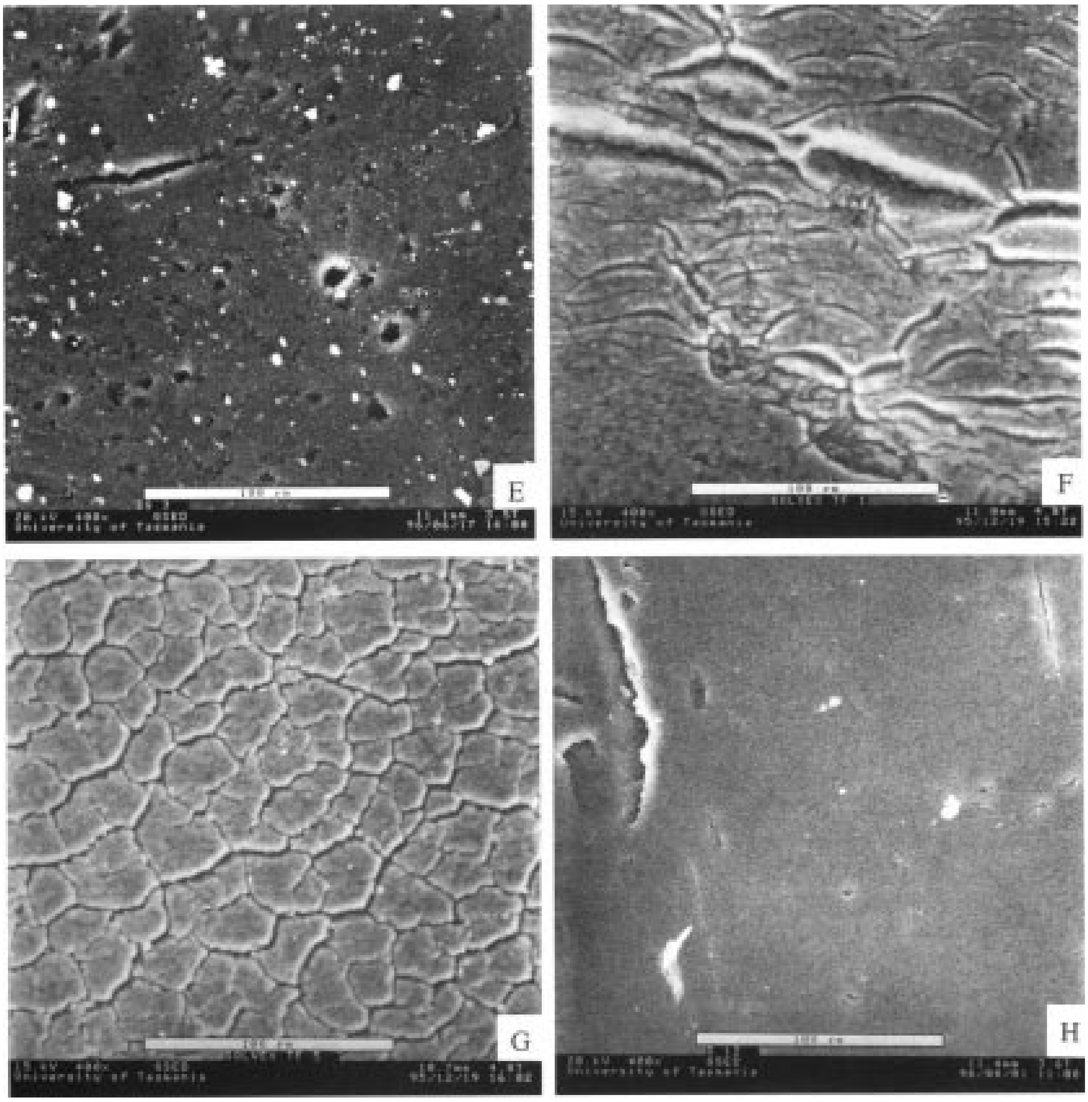

Figure 1b. Environmental scanning electron micrographs (400 ×) showing the surface defects on PVC and NBR gloves. E: Cracks, cavities and contaminants on PVC; F: Cracks and cavities on NBR (Sol-Vex™); G: Crazing on NBR (Sol-Vex™); H: Smooth areas on PVC.

detector (EDS) was used in a "wet mode" to observe physical defects of the glove surfaces.

In a viewing mode the observations were conducted with an accelerating voltage of 15–20 kV and a working pressure of water vapour in the specimen chamber of 3.5–4.5 T (torr). Samples were viewed extensively and an image of a representative region was recorded at a 400 × magnification on Ilford FP4 125 film.

In the analytical mode an accelerating voltage of 10 kV, a working pressure of 1.5 T and condenser setting on 45% were used to maximise the X-ray yield. For consistency of analytical results EDS was calibrated on pure copper to obtain 4000 counts per second (cps) at above analytical conditions, which involved both specimen vertical position and condenser adjustments. Samples were X-ray microanalysed with an acquisition time of 60 seconds at 400 × magnification. Ken Moran software and hardware were used to manipulate the X-ray spectra.

Three readings at different locations were taken from each sample. Windows (ROI-region of interest) were set for spectral peaks corresponding to carbon, oxygen, aluminium, silicon, phosphorus, sulfur and chlorine. These readings were measured in cps. Other windows were set beside the base of the peaks to determine the background readings, which were then subtracted from the peak reading.

Classification of defects and statistical analyses. Defects were scored by the method developed by Canning [1, 2]. This method utilises a gridded template that allows for a 50% viewing of the contact prints and then counting the number of defects in each exposed cell. The types of defects found are summarised in Table 2 and illustrated in Figure 1.

Counts of surface defects from used gloves were not normally distributed (Kolmogorov-Smirnov Test), nor were variances equal (Levene Median Test). Transformation

Table 1. Codes for the agricultural origins of chemically protective gloves received in a glove exchange program.

Glove Code	Region	Agricultural enterprise	PVC n	NBR n
TF[a]	Tahune Fields	Mixed horticulture	19	16
OR	Huon Valley	Apple orchard	13	0
DP	Derwent Park	Sheep grazing	10	0
BG	Botanical Gardens	Ornamental horticulture	4	0
Total			46	16

[a]Tahune Fields is a diverse horticultural enterprise and employs several farm apprentices. Workers on this farm were encouraged to use a double gloving technique when using pesticides, wearing NBR next to the skin and PVC outside. Their gloves were kept in communal shelving and their individual histories were not known, although they were all washed in a washing machine with detergent after use.

Table 2. Taxonomy of the surface defects of chemically protective gloves observed at a magnification of 400 ×.

Surface defects	Description
Cavities	Concave forms such as holes, bubbles, pores and sink marks which may be regular or irregular in shape.
Convexities	Lumps and bumps which may be regular or irregular in shape.
Cracks	Parting of the surface structure and the formation of new surfaces.
Crazes	Very fine cracks usually forming enmeshed interconnected patterns; these cracks were not individually counted but given an absolute value - either it was crazed or it was not.
Slumps	Regular rolled semi-circular raised areas.
Smooth areas	An absolute value was given - either smooth or not.

of the counts failed to normalise most of them. Consequently the influences of glove material on each class of surface defect were investigated with Kruskal-Wallis One Way ANOVA on Ranks, using the statistical program SigmaStat™ [4]. The results of all pairwise multiple comparisons were determined with Dunn's Test since the sample sizes in the glove types were unequal.

The EDS results were more variable, and the data that were normally distributed were analysed with One Way ANOVA and the non-normal distributions were analysed as above. The all pairwise multiple comparison tests were either Student-Newman-Keuls Test or Dunn's Test. The data sets that comprised of two groups were analysed with a t-test for the normal distributions and a Mann-Whitney Rank Sum Test for the non-normal distributions.

Gas chromatography and mass spectrometry (GC-MS). Pesticide contamination in the lining of the PVC gloves was investigated by GC-MS methods. The middle finger was cut from two of the DP gloves and from two of the OR gloves. These gloves had been used for a variety of pesticides. One new glove was run as a control. Each finger was filled with distilled water to within 1 cm from the top. Distilled water, rather than a solvent was used to ensure minimal dissolution from the glove matrix. The glove finger was then pegged to a wire suspended across a

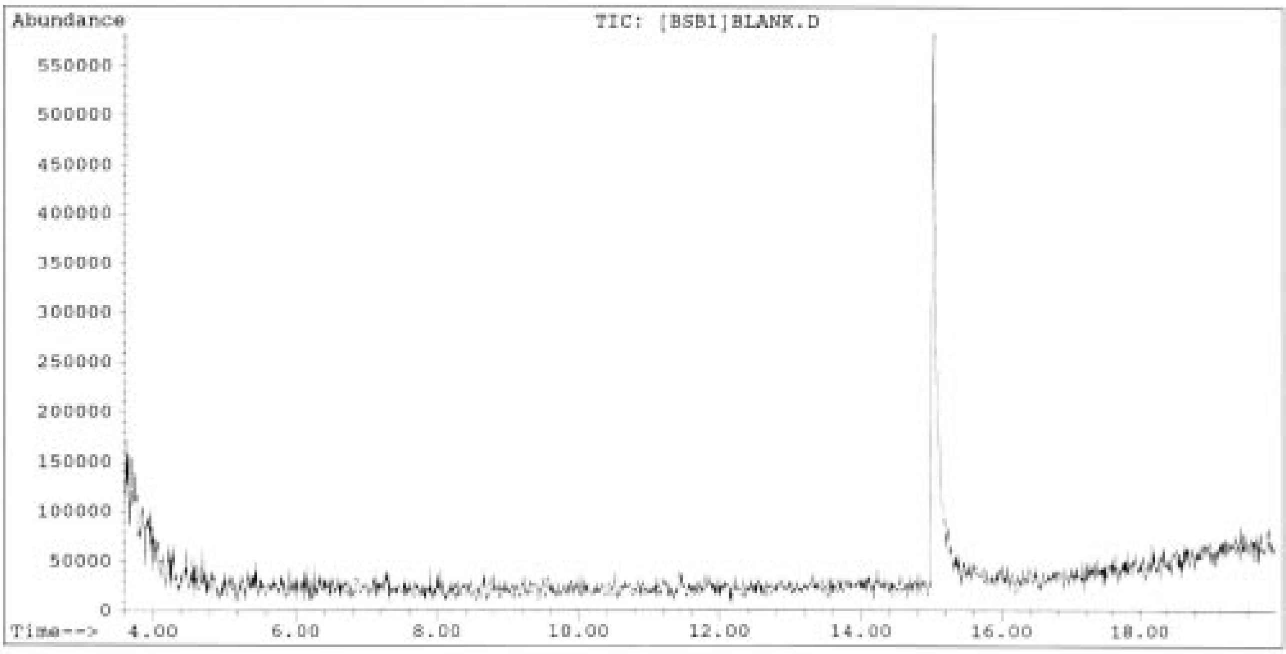

Figure 2. GC-MS spectra from the interior of a new PVC glove. The large peak at 14.6 minutes on the time line represents C22 enamide.

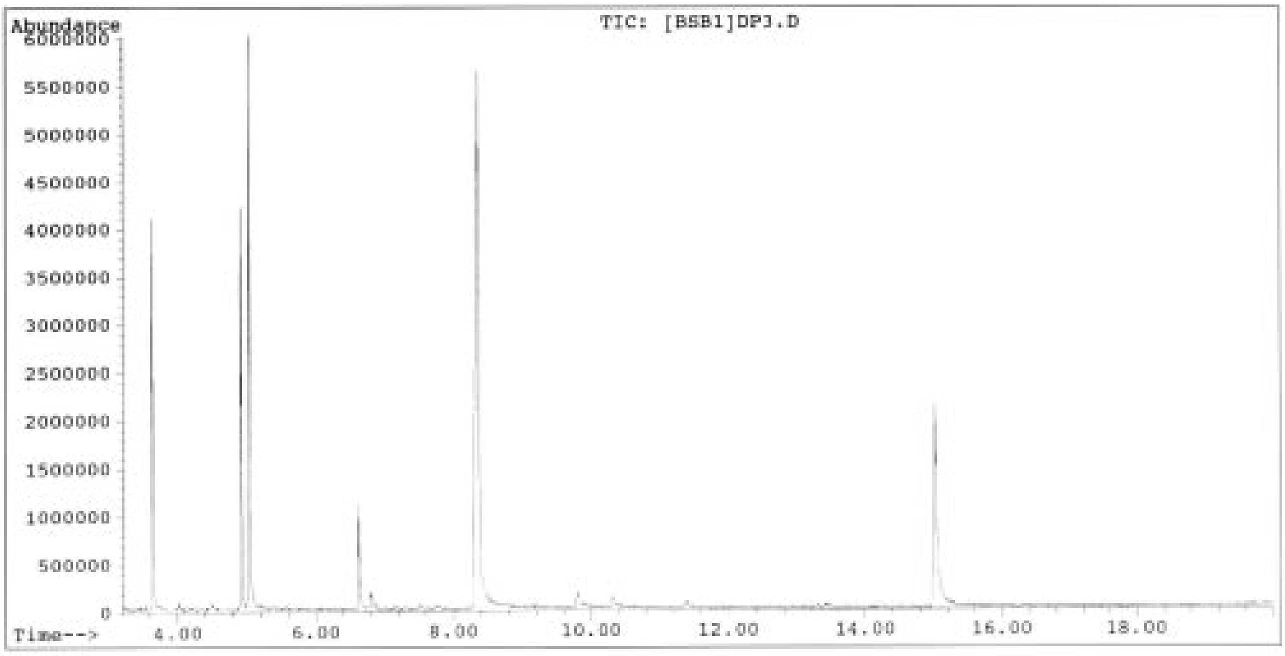

Figure 3. GC-MS spectrum from the interior of a DP3 PVC glove (in use for 3 years). The large peaks from 2–7 minutes on the time line represent glycol and at 8.2 minutes tetramisole.

sonicator filled with distilled water so that most of the finger was submerged but there was no possibility of the internal and external water being exchanged. The finger was then sonicated (50/60 Hz) for 5 minutes. A new pipette was used for each specimen to transfer the internal fluid to dedicated glass vials. Chloroform was used in the extraction process. An amount of 1 ml was placed in each vial for two hours and then 1 µl was injected into the GC.

A Hewlett Packard (HP5890) gas chromatograph (GC) coupled to a Hewlett Packard (HP5970B) mass spectrometer

Table 3. Defects per unit area (median) on the surface of PVC gloves and inter-comparisons from various origins (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). The medians are shown with the 25th and 75th percentiles in brackets. Probabilities mean that the medians are significantly different, NS = not significant. TF: n = 190; OR: n = 130, DP: n = 100, BG: n = 40, new PVC: n = 50.

Defects	Origin	Median	Percentiles (25, 75)	Origin				
				TF	OR	DP	BG	New
Cavities	TF	2	(1, 3)					
	OR	4	(2, 7)	<0.05				
	DP	5	(3, 8)	<0.05	NS			
	BG	4	(4, 7)	<0.05	NS	NS		
	New	1	(1, 2)	NS	<0.05	<0.05	<0.05	
Convexities	TF	1	(0, 3)					
	OR	0	(0, 2)	NS				
	DP	2	(0, 4)	NS	<0.05			
	BG	0	(0, 0)	<0.05	NS	<0.05		
	New	2	(1, 3)	<0.05	<0.05	NS	<0.05	
Cracks	TF	0	(0, 0)					
	OR	0	(0, 1)	<0.05				
	DP	0	(0, 0)	NS	NS			
	BG	0	(0, 0)	NS	NS	NS		
	New	0	(0, 0)	NS	<0.05	<0.05	NS	

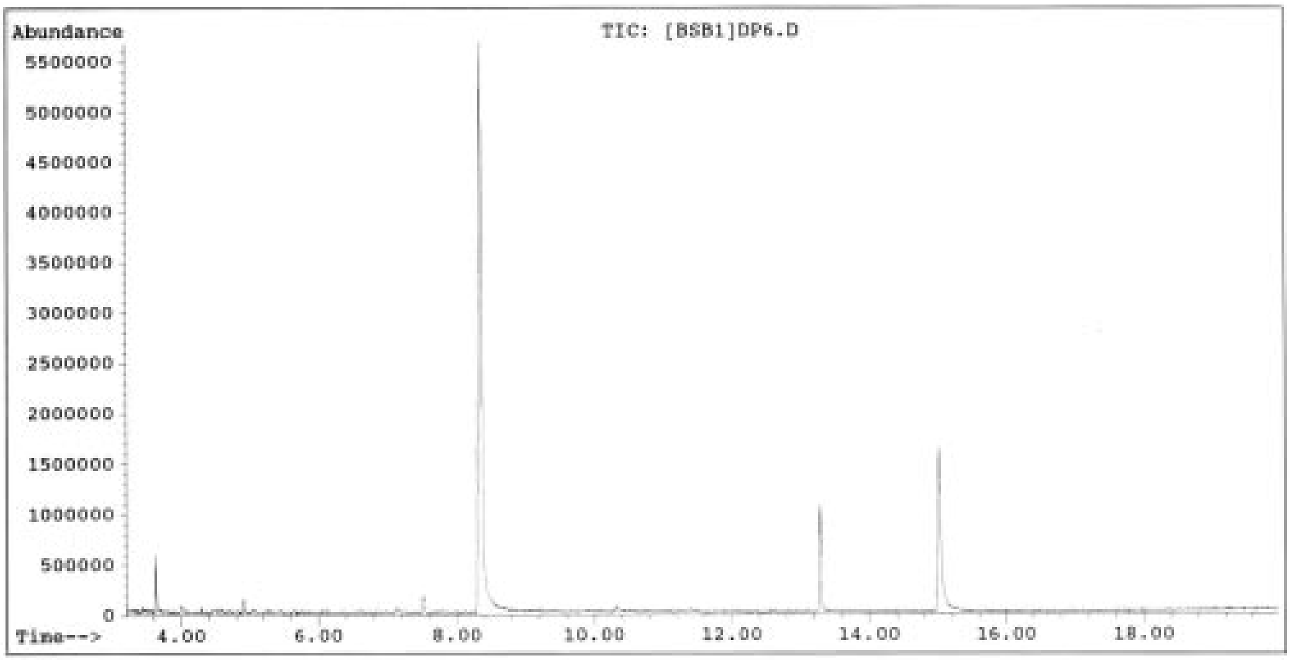

Figure 4. GC-MS spectrum from the interior of a DP6 PVC glove (in use for 4 years). The peaks on the time line represent glycol at 3.8 minutes, tetrasole at 8.2 minutes, plasticiser at 12.6 minutes and C22 enamide at 14.6 minutes.

(MS) was used with a 25 m (length) × 0.32 mm (ID) column with helium as the carrier gas. The GC oven temperature ranged from 50–150°C at 30°C per minute to 290°C at 10 minutes. The injector temperature was 260°C and the detector temperature was 290°C. The MS scan conditions were m/z 40–550, with 1.2 scans per second. Hewlett Packard Chemostation software was used. The spectra were matched against the Mass Spectral Library (MIST).

RESULTS

PVC Defects

All the PVC gloves were supported by a knitted cotton matrix and manufactured in China with no brand name. There were two black gloves, which were from the BG group and the remainder were red. The defects on the

Table 4. Defects per unit area (median) on the surface of used PVC gloves and inter-comparison between different age groups (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). The medians are shown with the 25th and 75th percentiles in brackets. Probabilities mean that the medians are significantly different, NS = not significant. 2 months: n = 20, 1 year: n = 40, 2 years: n = 130, 3 years: n = 20, 4 years: n = 20, 5 years: n = 40.

Defects	Age	Median	Percentile (25, 75)	Age					
				2 months	1 year	2 years	3 years	4 years	5 years
Cavities	2 months	5	(4, 8)						
	1 year	4	(4, 7)	NS					
	2 years	3	(1, 6)	NS	NS				
	3 years	5	(3, 6)	NS	NS	NS			
	4 years	10	(8, 11)	NS	<0.05	<0.05	<0.05		
	5 years	4	(2, 7)	NS	NS	NS	NS	<0.05	
Convexities	2 months	4	(2, 6)						
	1 year	0	(0, 0)	<0.05					
	2 years	0	(4, 9)	<0.05	NS				
	3 years	0	(0, 3)	<0.05	NS	NS			
	4 years	3	(0, 5)	NS	<0.05	<0.05	NS		
	5 years	0	(0, 6)	<0.05	NS	NS	NS	NS	

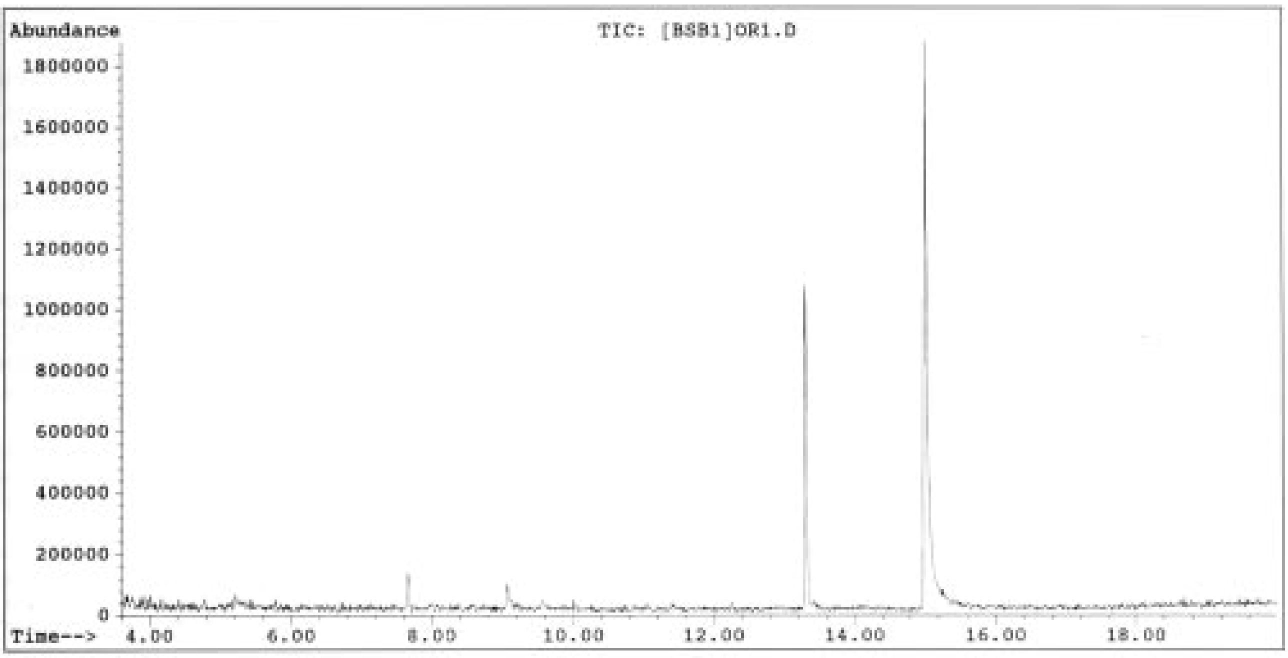

Figure 5. GC-MS spectrum from the interior of an OR1 PVC glove (in use for 2 years). The peaks on the time line represent carbaryl at 6.8 minutes, paclobutrazol at 8.8 minutes, plasticiser at 12.6 minutes and C22 enamide at 14.6 minutes.

black gloves were not as well defined as the red PVC and more difficult to focus upon, possibly due to being dipped in a final protective coating. However, the distributions of defects from these gloves were similar to the rest and therefore they were aggregated. Defects in PVC gloves from various origins are summarised in Table 3. PVC gloves were distinctive as they did not exhibit any slumps or crazing. There were only 7 cases of smooth areas in the aggregate samples and therefore did not warrant further statistical consideration. There were no cracks on the new PVC samples, but on used gloves there were differences between sources ($H = 24.6$, d.f. = 4, $p < 0.0001$). Cavities differed with origin ($H = 127.4$, d.f. = 4, $p < 0.0001$), and there were fewer cavities in new gloves. Convexities on PVC gloves differed between origins ($H = 44.1$, d.f. = 4, $p < 0.0001$).

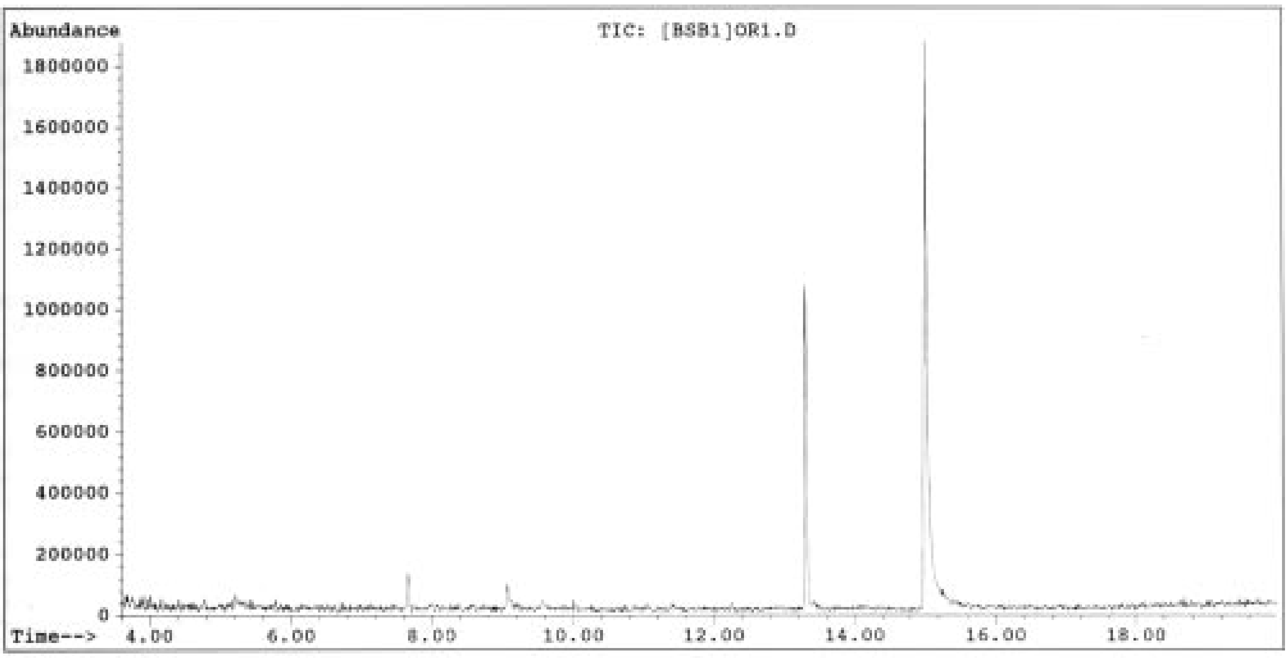

Figure 6. GC-MS spectrum from the interior of an OR13 PVC glove (in use for 2 years). The peaks on the time line represent plasticiser at 12.6 minutes and C22 enamide at 14.6 minutes.

The length of service (age) of the OR, DP and BG groups was known and therefore it was possible to examine the influence of age on the profile of defects. The age of the TF group was not known and therefore this group was excluded from the analysis. The two year old gloves formed the predominant age group (Tab. 4). The associations between the age of the gloves and the number of cracks were not significant ($H = 9.69$, d.f. = 5, $p = 0.0846$). There were differences between the number of cavities and the age of the gloves ($H = 31.1$, d.f. = 5, $p < 0.0001$), and convexities also differed strongly between age groups ($H = 47.2$, d.f. = 5, $p < 0.0001$). There was only one smooth area defect and this was located in the OR group.

PVC EDS

The PVC data were not aggregated, consequently BG B represents black PVC gloves from the Botanical Gardens and New B represents new black PVC gloves. All the other PVC samples are identified by their origins and the new red PVC are coded New R. The elements from the various origins are summarised in Table 5.

Red PVC gloves. The amount of carbon in PVC gloves differed between origins ($H = 22.7$, d.f. = 6, $p = 0.0009$). Oxygen concentrations also differed between origins ($H = 19.4$, d.f. = 6, $p = 0.0036$). Aluminium and silicon

Table 5. Elements as analysed by EDS (counts per second) on the surface of new and used PVC gloves. The left hand side of the table represents data from red PVC gloves. The medians, 25th and 75th percentiles are shown. Those with the same letters are not significantly different (Dunn's method following Kruskal-Wallis One ANOVA on Ranks). The right hand side of the table represents data from black PVC gloves, the means ± SE (standard error) and their differences are shown (t-test). Chlorine has the median and percentiles shown (Mann-Whitney Rank Sum Test).

Elements	Origins	n	Median	25%	75%		Black PVC	n		Mean ± SE	Differences of means
C	New R	12	6412	4358	7194	a	New B	12		4309 ± 171	3802
	BG	3	410	330	443	b	BG B	3		507 ± 46	
	DP	15	830	620	880	b				(t = 10.8, p < 0.0001)	
	OR	24	677	500	1006	b					
	TF	27	458	384	508	b					
O	New R	12	6071	4603	6925	a	New B	12		4038 ± 362	2104
	BG	3	1231	983	1365	b	BG B	3		1934 ± 177	
	DP	15	3482	2064	4253	ab				(t = 2.81, p = 0.0146)	
	OR	24	2278	1408	3178	b					
	TF	27	1105	978	1447	b					
Al	New R	12	387	321	450	a	New B	12		796 ± 166	–225
	BG	3	95	83	127	b	BG B	3		1021 ± 81	
	DP	15	610	235	820	ac				(t = -0.657, p = 0.5225)	
	OR	24	358	177	463	abc					
	TF	27	145	124	196	b					
Si	New R	12	535	427	566	a	New B	12		855 ± 43	89
	BG	3	192	154	233	ab	BG B	3		766 ± 89	
	DP	15	1604	562	2460	ac				(t = 0.941, p = 0.3640)	
	OR	24	848	562	1958	ac					
	TF	27	336	259	443	ab					
P	New R	12	0	0	0	a	New B	12		75 ± 15	–54
	BG	3	7	2	18	ab	BG B	3		129 ± 26	
	DP	15	76	8	101	b				(t = -1.66, p = 0.1213)	
	OR	24	10	0	39	b					
	TF	27	0	0	10	ab					
S	New R	12	391	333	456	a	New B	12		297 ± 15	200
	BG	3	69	61	88	b	BG B	3		97 ± 6	
	DP	15	180	71	224	b				(t = 6.55, p < 0.0001)	
	OR	24	351	167	611	ab					
	TF	27	83	64	124	b					
									Median	25%	75%
Cl	New R	12	30375	30055	32130	a	New B	12	33918	31471	38945
	BG	3	3080	2758	3350	b	BG B	3	3922	3374	3922
	DP	15	3513	2702	5174	b					
	OR	24	3299	1759	8740	b					
	TF	27	3699	3118	4167	b					

concentrations did not differ between origins ($H = 10.2$, d.f. = 6, $p = 0.1169$ and $H = 10.6$, d.f. = 6, $p = 0.1012$, respectively). Phosphorus concentrations differed between origins ($H = 15.3$, d.f. = 6, $p = 0.0179$). The New R and the BG B were not significantly different. Sulfur concentrations varied between origins ($H = 15.7$, d.f. = 6, $p = 0.0154$), as did chlorine ($H = 17.8$, d.f. = 6, $p = 0.0066$).

Black PVC gloves. New black PVC gloves were compared to used black PVC gloves from the BG group. The data passed the normality tests except for chlorine. Carbon concentrations differed between the two groups ($t = 10.8$, d.f. = 13, $p < 0.0001$). Oxygen varied also between the two ($t = 2.81$, d.f. = 13, $p = 0.0146$). Aluminium did not vary ($t = -0.657$, d.f. = 13, $p = 0.5225$), nor did silicon ($t = 0.941$, d.f. = 13, $p = 0.3640$). There were no differences for phosphorus ($t = -1.66$, d.f. = 13, $p = 0.1213$). Sulfur varied strongly between the two groups ($t = 6.55$, d.f. = 13, $p < 0.0001$). Chlorine differed between the two groups ($T = 6$, $p = 0.0115$).

PVC GC-MS

The spectrum of the rinsate from the new glove finger was relatively clean with one peak representing a C22 enamide. The DP 3 glove had a variety of large glycol peaks and second highest peak was tetramisole. There were several other peaks that could not be easily identified. DP 6 was generally similar, although there were different unidentified peaks and a plasticiser peak. OR 1 had a thermal artefact (an indicator for carbaryl), paclobutrazol and some unidentified peaks, which could have been related to pesticides. OR 13 was very similar to the control spectrum except for a plasticiser peak. The spectra are illustrated in Figures 2–6.

NBR Defects

There were two types of NBR gloves collected, Sol-Vex™ and MSA™, and both were unsupported by any fabric lining. As these gloves all came from the TF group, and were of uncertain age and therefore were categorised by type (Tab. 6).

Cracks on the NBR gloves differed by type ($H = 25.6$, d.f. = 3, $p < 0.0001$), as did cavities ($H = 59.5$, d.f. = 3, $p < 0.0001$). There were marked differences between types for convexities ($H = 103.8$, d.f. = 3, $p < 0.0001$) and for crazes ($H = 118$, d.f. = 3, $p < 0.0001$). Crazes were evident on the used Sol-Vex™ gloves and there were more convexities on the new gloves. Slumps varied between types ($H = 18.4$, d.f. = 3, $p = 0.0004$). Slumps and crazes were exclusive to the NBR gloves.

NBR EDS

The NBR gloves were statistically analysed by their type. New MSA™ and new Sol-Vex™ were compared to their used counterparts (Tab. 7).

Table 6. Comparison of the number of defects per unit area on the surface of new and used NBR gloves from two manufacturers (Dunn's method following Kruskal-Wallis One Way ANOVA on Ranks). The medians are shown with 25th and 75th percentiles in brackets. Probabilities mean that the medians are significantly different, NS = not significant. Used Sol-Vex™: n = 110, New Sol-Vex™: n = 20, used MSA™: n = 50, new MSA™: n = 20.

Defects	Glove type	Median	Percentile (25, 75)	Sol-Vex	MSA	New MSA	New Sol-Vex
Cavities	Sol-Vex	0	(0, 0)				
	MSA	3	(1, 6)	<0.05			
	New MSA	2	(0, 5)	<0.05	NS		
	New Sol-Vex	1	(0, 3)	NS	NS	NS	
Convexities	Sol-Vex	0	(0, 0)				
	MSA	2	(0, 4)	<0.05			
	New MSA	2	(1, 2)	<0.05	NS		
	New Sol-Vex	2	(1, 3)	<0.05	NS	NS	
Cracks	Sol-Vex	0	(0, 0)				
	MSA	1	(0, 2)	NS			
	New MSA	1	(0, 3)	NS	NS		
	New Sol-Vex	0	(0, 0)	NS	<0.05	<0.05	
Crazes	Sol-Vex	6	(3, 10)				
	MSA	0	(0, 0)	<0.05			
	New MSA	0	(0, 0)	<0.05	NS		
	New Sol-Vex	0	(0, 0)	<0.05	NS	NS	
Slumps	Sol-Vex	0	(0, 0)				
	MSA	0	(0, 0)	NS			
	New MSA	0	(0, 0)	NS	NS		
	New Sol-Vex	0	(0, 2)	NS	<0.05	<0.05	

Table 7. Elements as analysed by EDS (counts per second) on the surface of new and used NBR gloves. The left hand side of the table represents data from Sol-Vex™ gloves. The medians, 25th and 75th percentiles are shown (Mann-Whitney Rank Sum Test). The right hand side of the table represents data from MSA™ gloves, the means ± SE and their difference are shown for aluminium (t-test).

		Sol-Vex™				MSA™				
Elements	Origin	n	Median	25%	75%		n	Median	25%	75%
C	New	6	3963	3621	4205	New	9	4703	2921	6732
	TF	15	141	119	334	TF	9	150	103	202
O	New	6	7023	6873	8877	New	9	3872	2251	5249
	TF	15	290	232	504	TF	9	438	389	686
								Mean ± SE	Difference of mean	
Al	New	6	311	228	1724	New	9	187 ± 33	76	
	TF	15	40	29	82	TF	9	111 ± 12	(t = 2.16, p = 0.0460)	
								Median	25%	75%
Si	New	6	1003	942	1063	New	9	3347	1708	4054
	TF	15	83	42	189	TF	9	257	191	371
P[a]	New	6	0	0	0	New	9	0	0	0
	TF	15	0	0	0	TF	9	5	3	40
S	New	6	3518	3018	4026	New	9	2659	2135	3153
	TF	15	123	57	179	TF	9	61	46	93
Cl	New	6	29639	29596	31379	New	9	5888	3794	6317
	TF	15	486	317	851	TF	9	239	148	513

[a]The mean for phosphorus from the Sol-Vex™ data = 0.77

Sol-Vex™ gloves. All the data failed the normality tests. There were marked differences for carbon between the two groups ($T = 110$, $p < 0.0001$). Aluminium differed between groups ($T = 108$, $p = 0.0012$). Silicon differed strongly ($T = 110$, $p < 0.0001$). There were no differences for phosphorus ($T = 57$, $p = 0.502$). Sulfur and chlorine differed strongly between groups ($T = 110$, $p < 0.0001$ in both cases).

MSA™ gloves. The only group to pass the normality test and equal variance test was aluminium. There were strong differences for carbon, oxygen, silicon, phosphorus, sulfur and chlorine ($T = 126$, $p < 0.0001$ for all). Aluminium varied between the groups but not as strongly ($t = 2.16$, d.f. = 16, $p = 0.0460$).

DISCUSSION

Used CPGs revealed a range of defects on the surface of the gloves. These defects could have a critical impact upon CPGs' efficacy, and as weathering progresses more defects can be anticipated. Defects that occur as a result of the manufacturing process can influence the barrier properties of CPGs. Many defects can give rise to crack propagation, which would enhance penetration of organophosphates and other pesticides. Depressed defects can harbour pesticides and other contaminants, which in turn may penetrate and/or permeate the entire glove matrix. In a supported glove the lining can act as a reservoir for pesticides and thus increase the potential for dermal exposure. Some contaminants can be abrasive and can cause physical damage to the gloves, and at the same time their properties may cause chemical damage.

PVC

Cavities were intrinsic to the glove surface because they were present in the new gloves. The distribution of cavities increased when PVC gloves had been in service. This phenomenon correlated with the length of service and therefore the type of work and environmental exposure were likely to be contributing agents.

Convexities were a conspicuous feature of the new gloves. All the used groups except DP were different from the new group. This finding was supported by the aged group analysis where the two month old gloves had more convexities than the older gloves. A tentative conclusion from these findings is that the convexities may be eroded with use. If this is the case there will be a loss of the surface integrity, making it more susceptible to penetration.

No cracks were found on the new PVC gloves and it can therefore be assumed that cracks were caused by working conditions. Apart from the OR group differing significantly from the TF group there were no differences between the used groups. Very few cracks were found on the PVC gloves, which seem to be quite resistant to cracking.

Smooth areas were a significant characteristic of the new gloves, which are due to the manufacturing process. These areas on the used gloves may be a function of the permeation process and could be the upper part of a larger convexity.

PVC EDS

Carbon, oxygen, aluminium, silicon, sulfur and chlorine were constituents of the new PVC gloves. While there were compositional differences between the groups these may have been due to occlusion by contaminants and variations in the manufacturing process. Phosphorus was not integral to the new red PVC gloves but was a component of the black PVC. Phosphorus was highest in the DP group followed by the OR group, it therefore seems likely that its presence was due to the retention of organophosphate insecticides. The lower levels in the TF group in both types of gloves may be related to their care, which involved after use washing in a washing machine with a common detergent, thus the pesticides may have been washed off or considerably diluted.

Sulfur was a component of the new gloves, which was depleted with use. Sulfur based pesticides (diazinon and Nilverm®) were used by the DP group.

GC-MS

The GC-MS results revealed that pesticides are retained in the glove matrix, which supports the findings of Maddy *et al.* [5]. As anticipated, the spectrum from a sample taken from the new glove was fairly clear. Because water did not dissolve much of the glove matrix it does seem to be an effective agent for this purpose, even though it was found that many of the pesticides were not highly water soluble. The glycol peaks in DP 3 may be associated with pesticides. The tetramisole originated from a sulfur based sheep/cattle drench (Nilverm®). The thermal artefact in OR 1 is associated with carbaryl, which decomposes in the GC column. Paclobutrazol is a component of a growth inhibitor found in products such as Cultar® and Clipper®.

GC-MS is a proven effective method for assessing pesticide retention. However, it cannot be determined whether or not the pesticide permeated, penetrated, was transferred through cleaning practices or was spilled inside the glove. The sulfur found on the exterior of the DP gloves (by the EDS method) was probably related to the Nilverm® observed by the GC-MS method and therefore permeation and/or penetration were the probable modes of transmission.

NBR

The results imply that cavities are the product of the manufacturing process for MSA™ gloves (not for Sol-Vex™), and not a defect caused by use. New MSA™ gloves had a more textured surface on the predetermined sampling areas.

Convexities were a dominant feature of the new gloves and are therefore assumed to be associated with the manufacturing process. The used MSA™ gloves retained some convexities, but the Sol-Vex™ ones did not. This is similar to the PVC result and a similar conclusion may be drawn.

There were no differences in the distribution of cracks between the new types of gloves. However, there were significant differences between the new Sol-Vex™ and both the new and used MSA™, with the used MSA™ having the greater frequency of cracks. It is therefore assumed that cracking was related to working conditions.

The used Sol-Vex™ gloves were the only type of CPGs to exhibit crazing. This may have been due to weathering. Crazing is not regarded as true material failure, although it can lead to the propagation of larger cracks. Slumps were primarily a characteristic of new Sol-Vex™ gloves and were most likely a result of the dipping and drying cycles during the manufacturing process.

NBR EDS

Carbon, oxygen, aluminium, silicone, sulfur and chlorine were constituents of both types of new NBR gloves, except phosphorus, which was only found in the MSA™ gloves. The concentration of sulfur was much higher in both types of new gloves than the used gloves, therefore it seems that sulfur is lost with use.

It was hoped that phosphorus and sulfur would act as distinct markers for some pesticide contamination, but this was not the case and it seems that generally there is a loss of sulfur and an increase in phosphorus, but not at significant levels, after use with both types of gloves.

CONCLUSION

A new method for classifying surface defects on CPGs has been developed and used to ascertain their distribution by extensive statistical analyses. This work is complementary to other methods of CPG testing and provides new insight about the flaws in the materials that are a result of the manufacturing process and those that occur from agricultural use. Further elucidation of the relationship between defect size and risk of potential dermal exposure would require strength testing, defect identification and measurements in combination with degradation and permeation testing. It is therefore recommended that such research be instigated. There should be a reassessment of the efficacy of CPGs, and protocols for their use and care in agricultural situations developed to provide a safer environment for those working in the agricultural sector.

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