

Laundering Protocols for Chlorpyrifos Residue Removal from Pest Control Operators' Overalls

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Improper laundering of pest control operator (PCO) overalls may allow dermal absorption of pesticides during subsequent wearings and significantly increase the period of exposure (Stone and Stahr 1989). Transfer of organophosphate (OP) residues may occur to other clothing (Finley *et al.* 1974) or to the appliance (Laughlin *et al.* 1981) during laundering. Chlorpyrifos is difficult to remove from fabric and a chlorine bleach pretreatment has been recommended to reduce residue levels to 0.03% (Perkins *et al.* 1992). However chlorine bleach affects color-fastness and durability although this has been shown to be an acceptable trade-off for PCOs (Perkins *et al.* 1996). Chlorine bleach pre-treatment takes advantage of the oxidative degradation of OP pesticides, including chlorpyrifos and fenthion, by halogens and other oxidants. Kim *et al.* (2000) found 82–100% conversion to the bioactive oxon within a few seconds using Br₂ in acetonitrile. OP pesticides have been shown to degrade readily in the presence of aqueous chlorine and ozone (Okumura 1992) and in the presence of hydrogen peroxide (Fang *et al.* 2004). Although more biologically active than its chlorpyrifos precursor, the chlorpyrifos oxon is less stable and rapidly degrades *in vivo* to 3,5,6-trichloro-2-pyridinol which is considered to be relatively non-toxic (Hanley *et al.* 2000).

This work was undertaken at the behest of, and in cooperation with Dow AgroSciences New Zealand Ltd., who were concerned that their current, recommended laundering protocols did not take account of developments in pesticide formulations and of modern laundering practices and detergents in the Australian- Pacific region.

MATERIALS AND METHODS

Three Dow AgroSciences formulations, which contained chlorpyrifos as the active ingredient, were tested. These were Dursban® PC Termiticide and Insecticide (Dursban PCT), Dursban® Micro-Lo Termiticide and Insecticide (Dursban Micro-Lo) and Empire® Insecticide (Empire). The Dursban PCT and Dursban Micro-Lo formulations are both emulsifiable concentrates but the latter contains some 10% less chlorpyrifos than the former and also forms emulsion droplets in water that are significantly smaller than the Dursban PCT formulation. Empire is a

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capsule suspension formulation. For purposes of comparison another organophosphate pesticide, fenthion, in the form of Baytex® 550 Insecticide spray (Fenthion) and a synthetic pyrethroid, permethrin, in the form of Perigen® 500 Timber and Residual Insecticide (Permethrin), were used; these are both emulsifiable concentrates. Weight percent of active ingredient was determined by high performance liquid chromatography (HPLC) on Zorbax ODS (7µm, 150mm x 4.6mm) eluted with acetonitrile:water:acetic acid (82:17.5:0.5; 1.0 mL min⁻¹) and with UV detection at 300nm.

Washing trials were conducted with a newly-purchased Fisher & Paykel® 5.5 kg top-loading automatic washing machine. Two different types of King Gee® PCO overalls in common usage were purchased new for the study. These were a 50% polyester/50% cotton overall and a 100% cotton overall.

Squares of material (100cm²) were sprayed with formulation, which had been made up according to the label directions, and allowed to air dry (120 min). The weight of formulation applied was determined by weighing before and after spraying. Preliminary washing trials were carried out with Dursban PCT using 5 replicates of each type of overall, cotton and polyester/cotton, for each trial. For further washing trials with Dursban PCT 10 replicates of cotton overall were used. Detergents were used at the recommended label use rate; in the case of chlorine bleach, for which the active ingredient was sodium hypochlorite (31.5 g L⁻¹), the recommended label use rate was 0.25 cup (~60 mL) in 4.5 L.

For Dursban Micro-Lo, Empire, Fenthion and Permethrin the washing trials were restricted to cotton material and to those washing methods that had proved successful with Dursban PCT (10 replicates) or with a pre-soak in NapiSan® (5 replicates). Material was air-dried after laundering and before extraction of residual chlorpyrifos. NapiSan® is a registered trademark of Reckitt Benckiser and contains 25.5% w/w of sodium percarbonate as the active ingredient. NapiSan® was used at the recommended label use rate of 0.75 level lid (~30 g) in 7L.

Residual chlorpyrifos was extracted from laundered fabric by shaking in hexane (30 min) and, in the case of Empire, glass beads were added to break up the capsules. Permethrin was similarly extracted with ethyl acetate. The extract was assayed by gas-chromatography with flame ionization detection (GC-FID) using an HP Ultra 2 cross-linked phenyl-methyl silicone fused silica capillary column (25m x 0.32mm x 0.52µm). The temperature gradient was 50°C + 50°C/min to 200°C + 10°C/min to 250°C; the final temperature was held for 13 minutes. Chlorpyrifos eluted at 7.96 minutes. Fenthion and Permethrin were also quantified by GC-FID, Fenthion with the same temperature program (7.98 min) and Permethrin isothermally at 250°C (13.32 min). Quantitation was achieved by comparing peak area to an external calibration curve. Calibration standards from 10-500µg/mL were constructed for each formulation; peaks less than 10µg/mL

were deemed to be non-detected. Multiple calibration standards were injected every ten samples. Mean results of different trials were compared by t-testing at the 95% confidence level. For all extractions of material and water duplicate spiked recovery standards (typical recovery 90-110%) and blanks were prepared.

For degradation trials insecticide formulation (5.00mL) and laundry additive (according to label use rate) were made up to 200 mL and held at 20°C except for two NapiSan® trials which were held at 50°C. Samples (20 mL) were analysed at 0, 3, 24, 48, 72 and 144 hours and, in the case of Dursban PCT and Fenthion, were extracted by mechanical shaking (30 min) with hexane (5.00 mL); in the case of Permethrin, extraction was with isooctane (5.00 mL) and sodium chloride solution (2 mol. L⁻¹, 5.00 mL). The Empire samples were homogenized before extraction with toluene (10.00 mL) and sodium chloride (2 mol. L⁻¹, 5.00 mL). Analysis was by GC-FID as detailed above.

In two trials for each pesticide the mass of pesticide in the wash water was determined and compared to a theoretical value derived from the mass applied and the residue on the material after washing. Extraction and analysis were as described above.

RESULTS AND DISCUSSION

The preliminary washing trials with Dursban PCT encompassed nine different regimes, which are listed (1-9) in Table 1, and which established that, under all regimes other than a 4 hour chlorine bleach pre-soak, polyester/cotton material retained significantly more residual chlorpyrifos than 100% cotton. This finding is contrary to Lillie *et al* (1981) but in agreement with Ko and Obendorff (1997). Further washing trials with Dursban PCT were restricted to 100% cotton material (10-12 in Table 1). Comparison of trials 1- 4 and 11 indicate that there is no significant difference in outcome between hot and cold washes and the quality of detergent used. Trial 10, in which detergent was omitted, demonstrated that detergent of some kind is essential. Repeated applications of Dursban PCT or exposure to sunlight before laundering both had significant deleterious effects upon removal of chlorpyrifos as did reducing the wash cycle time (trial 5). As expected (Perkins *et al*. 1992), the pre-wash soak (4h) in bleach caused a significant reduction in residual chlorpyrifos. The cold wash with Persil® concentrate was chosen as the baseline for testing the other formulations. In two trials with Dursban Micro-Lo, Table 2, trials 13 and 14, there was a significantly greater percentage of residual chlorpyrifos than occurred with Dursban PCT. In the case of Empire, Table 2, trials 17 and 18, there was a very marked reduction in the residual chlorpyrifos giving results comparable to the effect of a 4 hour chlorine bleach pre-soak.

Dursban PCT and Dursban Micro-Lo are both emulsifiable concentrates but the latter has smaller droplets and a higher proportion of surfactant than the former; either or both of these could result in greater penetration and adherence of chlorpyrifos to fabric. The capsule formulation is possibly prevented from

Table 1. Results of washing trials for overalls contaminated with Dursban PCT pesticide formulation.

Trial	Procedure	Percentage residual chlorpyrifos (95% confidence interval)	
		Polyester/cotton	100% Cotton
Preliminary Trials with Dursban PCT			
1	Cold wash ^a with Persil® concentrate	43.4 (37.1-49.7)	9.0 (7.3-10.7)
2	Hot wash ^b with Persil® concentrate	34.7 (30.7-38.7)	11.6 (10.7-12.5)
3	Cold wash with liquid Drive® concentrate	45.4 (36.6-54.2)	11.6 (8.9-14.3)
4	Cold wash with Drive® washing powder	43.8 (39.6-48.0)	11.7 (8.8-14.6)
5	Reduced cold wash with Persil® concentrate	56.4 (54.4-58.4)	16.8 (13.9-19.7)
6	Bleach soak (1.5h) prior to cold wash with Persil® concentrate	33.6 (23.6-43.9)	8.8 (6.4-11.2)
7	Bleach soak (4h) prior to cold wash with Persil® concentrate	10.7 (3.4-18.0)	3.7 (2.1-5.3)
8	Sunlight exposure prior to cold wash with Persil® concentrate	68.9 (46.8-100.0)	16.5 (13.2-19.8)
9	Repeated applications of Dursban PCT prior to cold wash with Persil® concentrate	35.1 (26.2-44.0)	13.1 (9.4-16.8)
Further Trials with Dursban PCT			
10	Cold wash with no detergent	-	22.2 (19.4-25.0)
11	Cold wash with budget (generic) washing powder	-	9.4 (7.5-11.3)
12	Water soak (4 h) prior to cold wash with Persil® concentrate	-	10.1 (8.0-12.2)

^a Wash cycle (15 min/ 14-15°C), Rinse cycle (5 min/ 14-15°C), spin cycle (5 min); ^b Same wash cycle at 60°C

adhering to the material by its polymer coating. Easley *et al.* (1982) found that residue levels were related to concentration of active material applied and certainly in the case of Empire the loading of active constituent is approximately half that of Dursban PCT and Dursban Micro-Lo. This generalization cannot be applied between different types of active ingredient since the Permethrin and Dursban Micro-Lo results were similar despite the latter having a use rate some four times higher than the former.

Table 2. Results of washing trials for overalls contaminated with Dursban Micro-Lo, Empire, Fenthion and Permethrin pesticide formulations.

Trial	Procedure	Percentage residual chlorpyrifos (95% confidence interval)
100% Cotton		
Trials with Dursban Micro-Lo		
13	Cold wash ^a with Persil® concentrate	14.6 (11.9-17.3)
14	Cold wash with Persil® concentrate	17.5 (15.6-19.4)
15	Overnight soak in Napisan® prior to cold wash with Persil® concentrate	1.1 (-0.2-2.4)
16	Overnight soak in Napisan® prior to cold wash with Persil® concentrate	1.3 (-0.4-3.0)
Trials with Empire		
17	Cold wash with Persil® concentrate	5.0 (4.7-5.3)
18	Cold wash with Persil® concentrate	4.7 (4.4-5.0)
Trials with Fenthion		
19	Cold wash with Persil® concentrate	28.3 (26.8-29.8)
20	Cold wash ^a with Persil® concentrate	31.2 (29.7-32.7)
Trials with Permethrin		
21	Cold wash with Persil® concentrate	14.5 (9.9-19.1)
22	Cold wash with Persil® concentrate	14.0 (7.5-20.5)
^a Wash cycle (15 min/ 14-15°C), Rinse cycle (5 min/ 14-15°C), spin cycle (5 min)		

Comparison of the means of the trials of Fenthion with that for Dursban PCT indicated that in the case of Fenthion considerably more residual material was present after laundering. Mass balance calculations for all the pesticides accounted for all the material applied either as residue or in the wash water ($100 \pm 10\%$) except for the two Dursban PCT trials and one Dursban Micro-Lo trial, which gave results of 60.0, 50.0 and 66.7% respectively. After the two Dursban PCT trials the washing machine was refilled and agitated for 5 minutes with no detergent. The water was sampled and analysed for chlorpyrifos but this was barely detectable. It is possible that some degradation had occurred although, as demonstrated below, chlorpyrifos is stable in alkaline detergent.

The degradation pathway of chlorpyrifos is through the formation of 3,5,6-trichloro-2-pyridinol and this process is accelerated under alkaline or oxidative conditions (Racke *et al.* 1996). The degradation of chlorpyrifos to 3,5,6-trichloro-2-pyridinol was studied in the presence of a variety of potential pre-wash agents including water, chlorine bleach, alkaline detergent, acetic acid (0.05 mol L^{-1}) and sodium hydroxide (0.05 mol L^{-1}). With the exception of the chlorine bleach, none of the agents were any more effective than water alone, in which there was approximately 30% loss of chlorpyrifos over 144 hours. The efficacy of the chlorine bleach pre-treatment suggested that other oxidants might be as effective and therefore NapiSan® was trialled. This is a proprietary brand of soaking agent which contains sodium percarbonate as the active ingredient. Dursban PCT and Fenthion showed significant degradation in the presence of NapiSan® and, at 50°C , degradation over a 24 hour period was comparable to that of chlorine bleach, Fig. 1. Chlorpyrifos was degraded entirely to 3,5,6-trichloro-2-pyridinol, only a trace of the oxon was detected. Neither Empire nor Permethrin were degraded by NapiSan®, the former since it was protected by its polymer coating and the latter because it is stable to oxidative conditions and indeed was also found to be stable in the presence of acid and base pre-soaking agents. Overnight soaking in NapiSan® followed by a cold wash with Persil concentrate reduced residues of Dursban Micro-Lo to levels comparable with pre-soaking with bleach, Table 2, Trials 15 and 16. These results indicate that sodium percarbonate is a viable alternative to chlorine bleach as a pre-treatment for PCO overalls contaminated with chlorpyrifos or Fenthion. Sodium percarbonate has the advantage of avoiding the deleterious effects upon material of chlorine bleach.

In conclusion, the following protocols are recommended for PCO engaged in application of chlorpyrifos-containing formulations:

The overalls should be 100% cotton material and should be laundered as soon as possible after a single use by soaking for 24 hours in NapiSan® or some other formulation, which contains an equivalent amount of sodium percarbonate, at the recommended label-use rate and, at least initially, in hot water. After soaking the soak water should be discarded and the garment washed alone or with other similarly contaminated overalls. The wash (15 minutes minimum) can be cold but should have an appropriate water level and must include laundry detergent at the recommended label use rate. Despite the fact that Empire did not degrade in

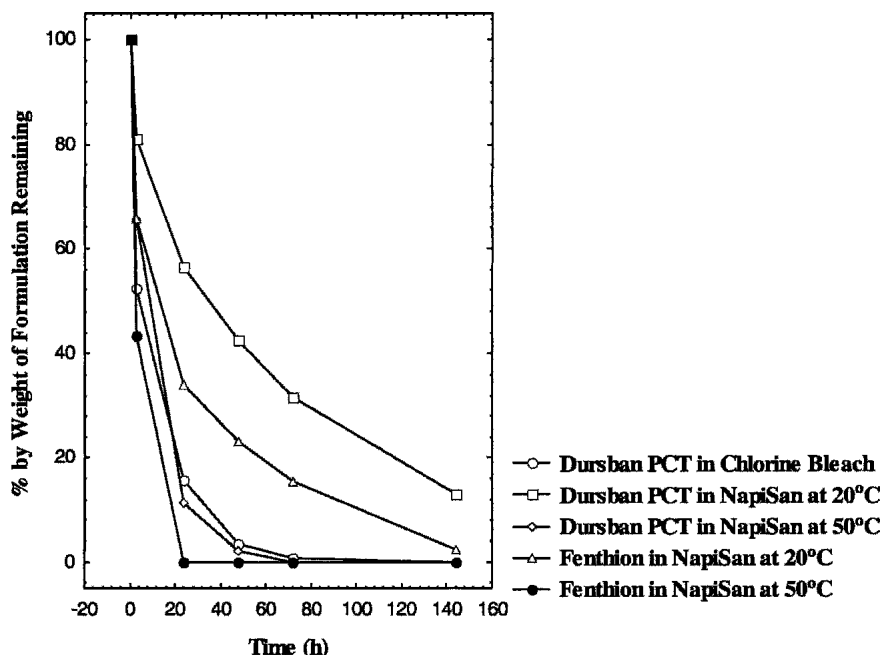


Figure 1. Degradation of Durban PCT and Fenthion in chlorine bleach and in NapiSan®.

NapiSan® we still recommend the pre-soak to deal with any chlorpyrifos released by physical fracture of the polymer coating.

This protocol can probably be safely extended to Fenthion formulations, but we cannot recommend it for pyrethroids, such as Permethrin.

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