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Evaporative Dissipation of Methyl Parathion from Laundered Protective Apparel Fabrics

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Reduction of dermal exposure among mixer/handlers and applicators has prompted wide spread recommendations for protective clothing (Baker et al. 1979). However, recent investigations (Laughlin and Gold 1987) have confirmed that pesticide residues remain in these washable fabrics after laundering. Research has shown that residues from contaminated fabric can be transferred to clean fabric and, after the washing apparatus has been contaminated, to subsequent laundries (Laughlin et al. 1981). Measurable amounts of methyl parathion residues have been documented in the wash and rinse waters from laundering (Goodman et al. 1988). As the concentration of methyl parathion increased, removal became increasingly difficult. Full strength (54% A.I.) methyl parathion was not successfully removed even after 10 launderings (Laughlin et al. 1986). The recommendation was made to discard clothing that had been contaminated with highly concentrated pesticides. If the contamination occurred with a less concentrated solution, such as 1.25% A.I., a minimum of three launderings was need to sufficiently remove the residue (Easley et al. 1982).

Fluorocarbon soil repellent (SR) finishes on protective apparel fabrics decrease pesticide absorption; however, these finishes may hinder pesticide removal in laundering (Laughlin et al. 1986). Fluorocarbon polymers have very low surface tensions and therefore show very good oily soil repellency in air, but form high energy surfaces in water during fabric laundering, enabling hydrophobic soil dispersion in the aqueous wash medium (Das and Kulshreshtha 1979).

Laughlin and Gold (1987) reported significant reduction in MeP contamination in textiles held for periods up to six months, but with no laundering. They suggested that storage before or after laundering might assist in minimizing contaminating residues. Rather than recommendations to burn or bury protective clothing contaminated with highly toxic concentrated pesticides, after-laundering storage for periods of time and/or at temperatures

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that maximize the vaporization of the chemical may be an alternative. This work was undertaken to study these alternatives: 1) after-laundering dissipation of MeP residues in fabrics and 2) minimizing full strength MeP residues in fabrics through holding in moving air for six time periods.

MATERIALS AND METHODS

Fabric specimens were contaminated with pesticide, laboratory laundered, then held in one of four conditions for six time periods. In a 2 x 2 x 4 x 6 design, two fabrics (all cotton and 50 cotton/50 polyester), unfinished (UN) or fluoroaliphatic soil repellent (SR) finished were contaminated with 1.25% A.I. emulsifiable concentrate (EC) methyl parathion. Specimens were laundered, then held at a) 0°C, b) 20 ± 1°C, c) 20 ± 1°C plus air flow of 35.2 m.p.m., and d) 20 ± 1°C and 65 ± 2% R.H. for time periods of 24 hr, 48 hr, 72 hr, 168 hr (1 week), 720 hr (1 month) and 4,320 hr (6 months). Treatment fabrics were extracted immediately after air drying (control) and after laundering plus holding. A second phase of this study was conducted to determine whether holding at 20° ± 1°C plus air flow of 35.2 m.p.m. would be as effective for the concentrated (54% active ingredient) as it had been for the field strength (1.25% active ingredient).

Fabrics were an unfinished undyed 100% cotton poplin TestFabrics #407 and a 50 percent polyester/50 percent cotton poplin blend TestFabrics #7428. Fabrics were studied unfinished and finished with a fluorocarbon renewable soil repellent finish (Scotchgard*), applied at 1.0 percent (w/w) using procedures developed by Keaschall et al. (1986). Specimens, 8 x 8 cm, were randomly selected from yardages of fabric that had been stripped of warp sizing and softeners.

Methyl Parathion (MeP) (0,0-dimethyl 0-p nitrophenyl phosphorothioate [LD_{50} (mg/kg) oral=14, dermal=67]) dilutions were prepared at 1.25% (A.I.) field strength concentration from emulsifiable concentration formulation. For Phase II, the MeP was used at package strength (54% A.I.). Two-tenths ml were pipetted onto the center of the specimens. Following contamination and drying, specimens were laundered and evaluated, or were evaluated unlaundered. A 0.2 ml aliquot of MeP was placed in glass, allowed to air dry, and prepared in hexane as a baseline for determining recovery rate.

Specimens were LaunderOmeter laundered with a non-ionic heavy duty liquid detergent (0.13 percent). All specimens were laundered for 12 min (60°C) followed by two rinses of five and three minutes, respectively, in 49°C as per Easley et al. (1982).

MeP was double extracted from fabric specimens using two 100 ml aliquots of hexane as a solvent. The extracts were concentrated and analyzed on a Varian Vista 3400-2882 gas chromatograph with

electron capture detector and dedicated microprocessor. Separation was achieved on a 2 m x 2 mm glass column packed with 10 percent OV-101 on 80/100 mesh Chromasorb W-HP with a nitrogen flow of 40 ml/min. Injection, detector, and oven temperature were 250°C (482°F), 325°C (617°F), and 220°C (428°F) respectively. Total amount of MeP residue in each specimen was expressed in $\mu g/cm^2$. Recovery rate (97%) was used in calculating after-treatment residues. All work was replicated a minimum of three times.

The statistical analyses of data were based on computed amount of pesticide residue remaining in the fabric after treatment and as a proportion (percent residue remaining) that the after-treatment residue was of the initial contamination. Arc sine transformations were applied to the percentages, and SAS General Linear Model analysis was used to test for main effects and all interactions of the main effects. LS Means tests were performed to separate means where significant differences were observed. Orthogonal contrasts were used to establish linear and quadratic relationships. The decision level was $p \leq 0.05$.

RESULTS AND DISCUSSION

Initial contamination of the unlaundered specimens (controls) ranged from 21.79 to 50.31 $\mu g/cm^2$ MeP (Table 1). The initial contamination of the UN fabrics was significantly greater than the initial contamination of the SR fabrics ($F=29.38$, $df=1,10$, $p \leq 0.05$). There were no significant differences in initial absorption due to fiber content of specimens ($F=0.001$, $df=1,10$). These findings are in agreement with earlier work (Laughlin et al 1985).

Laundering significantly decreased the amount of MeP residue (Table 1). Generally, larger percentages of residue remaining after laundering were found for the SR specimens; however, the amount of initial contamination ($\mu g/cm^2$) had been lower for SR than for UN specimens. The SR specimens had absorbed less MeP at initial contamination and the amounts of pesticide remaining on the SR were greater than for the UN specimens. This finding is important as the critical concern in laundering studies is for lowering the post-laundering residues to the minimal amount possible.

For cotton, the amount of contamination on the SR finished specimens was significantly greater than the amount of contamination on the UN cotton. A similar difference was observed for the cotton-polyester blend specimens. The soil repellent finish inhibited soil removal in laundering.

Specimens that had been contaminated, laundered, and then held under one of four conditions for up to 4,032 hours differed in residues, with greatest differences attributable to the longest periods, and extremes in holding conditions. Both time and conditions of holding affected residues, with greatest residues in

Table 1. Methyl Parathion (1.25% A.I.) Residues Remaining in Specimens After Laundering.

Treatment	Initial Contamination	Holding Time (hours) 0	24	48	72	168	720	4032
		µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2
Cotton UN	49.61							
20°C		1.33	0.93	1.18	1.63	1.18	2.16	0.04
20°C/65% RH		1.02	0.90	0.03	0.93	0.65	0.22	0.12
20°C + air flow		1.49	2.01	1.12	1.10	1.39	0.30	0.04
0°C		0.85	0.95	1.07	0.94	1.31	0.74	1.88
Cotton SR	21.79							
20°C		3.63	3.18	2.54	1.51	2.43	1.55	0.85
20°C/65% RH		4.80	2.91	3.03	1.71	2.46	0.73	0.02
20°C + air flow		3.30	3.20	4.32	2.44	2.42	0.54	0.01
0°C		3.63	2.46	3.03	2.45	2.57	2.02	1.81
Cotton/PET UN	50.31							
20°C		0.35	0.31	0.36	0.30	0.21	0.10	0.03
20°C/65% RH		0.41	0.43	0.32	0.20	0.19	0.14	0.03
20°C + air flow		0.34	0.15	0.33	0.38	0.29	0.07	0.02
0°C		0.22	0.09	0.49	0.28	0.58	0.94	0.92
Cotton/PET SR	21.93							
20°C		3.63	4.06	3.90	2.31	2.73	3.80	0.03
20°C/65% RH		2.25	2.03	3.53	2.51	2.42	0.45	0.48
20°C air flow		3.18	4.88	3.74	3.73	1.48	0.44	0.02
0°C		3.72	3.97	3.24	3.16	2.83	2.58	4.78

specimens held at 0°C, and least residues after the longest time periods. Main effects of finish, holding, and time were found ($F=196.29$, $F=4.12$ and $F=9.94$ respectively) with interactions of these variables: fabric x finish ($F=15.68$), finish x time ($F=6.57$) and time x holding ($F=2.31$). Scrutiny of plottings for these interactions revealed the impact of finish (Figure 1 and 2).

While some decrease in residue was noted at 168 hrs, LS Means showed declines were at 720 hrs and 4,032 hrs (Figures 1 and 2). When the condition of holding was 0°C, residues did not diminish over time. Orthogonal contrasts revealed a linear ($F=40.88$, $p \leq 0.05$) and quadratic relationship ($F=14.07$, $p \leq 0.05$) across time. The specimens held in moving 20°C air and at 20°C/65% RH retained much smaller residues at 720 hrs, while those held in ambient air required the extended time (4,032 hrs) before a significant decline in residue retention was experienced. Conditions of moving air or high humidity enhanced volatilization or dissipation. For all practical purposes only 0°C-held specimens differed in residues. Only minute amounts of residue remained at six months for the other three holding conditions.

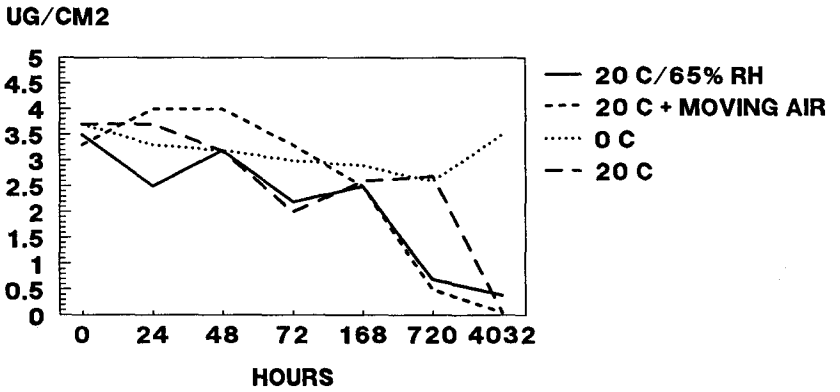

Figure 1. Interaction of the time of holding conditions on residues remaining on SR specimens after laundering fabrics contaminated with 1.25% A.I. methyl parathion.

When the interactions of fiber content, finish and time of holding as well as holding conditions were graphically displayed, it became readily apparent that the SR finished cotton/polyester blend had far less residues than the other fiber content/finish combinations. Furthermore, the holding condition contributing most to dissipation of residue was the presence of moving air at room temperature. Based on these data, if laundering is not feasible for certain items of protective apparel, holding for periods in excess of 4 weeks and preferrably up to 24 weeks at room temperature and in moving air can be pursued.

Since moving air at room temperature was so effective in dispersement of MeP residues from specimens contaminated with field strength (1.25% A.I.) pesticide, this one condition of holding on residues of package strength (54% AI) methyl parathion was studied. Laundering plus holding in moving air significantly reduced the concentrated (54% A.I.) MeP in the fabric specimens (Table 2). Analysis revealed main effects due to time and finish among the unlaundered specimens and these same main effects plus interaction effect of fiber content x time for the laundered specimens.

There were marked improvements at 720 hrs and 4,032 hrs, and the residues from specimens held these two time periods were significantly different from the shorter holding periods. At 4,032 hrs of holding, the laundered-plus-held specimens had residues similar to the level of contamination on specimens contaminated with field strength (1.25%) MeP, but unlaundered.

Unlaundered specimens had retained sizable quantities of MeP and may be biologically active (Laughlin and Gold 1987b). Scrutiny of graphic display of the interaction of fiber content of fabric, finish and time for the unlaundered specimens (Figure 3) and graphic display of interaction of fiber content and time for the laundered specimens (Figure 4) revealed the contribution of the

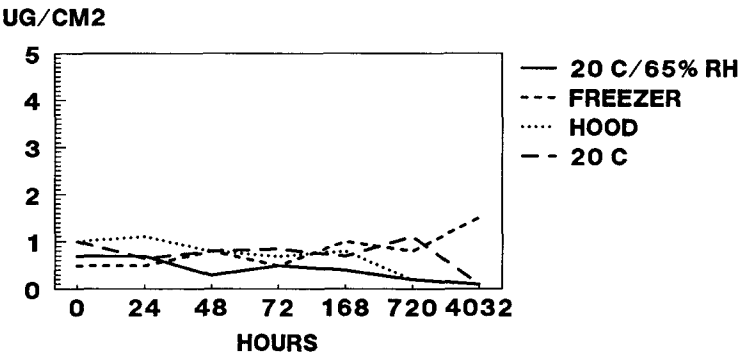

Figure 2. Interaction of the time of holding conditions on residue remaining on UN specimens after laundering fabrics contaminated with 1.25% A.I. methyl parathion.

Table 2. Residue of Package Strength (54% AI) Methyl Parathion in Specimens After Holding at 20°C with Air Flow.

	Unlaundered	Laundered
	µg/cm^2	µg/cm^2
Cotton		
UN		
0	6,117.0	313.7
24	14,491.0	436.8
48	8,600.0	310.0
72	5,410.0	214.9
168	5,526.0	173.0
720	821.0	75.6
4032	2.0	41.4
SR		
0	1,908.0	314.4
24	3,182.0	271.0
72	1,786.0	225.2
168	2,009.0	269.0
720	693.0	120.0
4032	3.0	68.7
Cotton/Polyester		
UN		
0	8,107.0	1137.9
24	5,663.0	1024.1
48	4,269.0	1031.0
72	7,303.0	1055.1
168	5,433.0	1778.4
720	591.0	194.7
4032	6.0	37.4
SR		
0	2,495.0	1012.3
24	2,237.0	1649.6
48	2,938.0	368.7
72	1,779.0	608.5
168	2,203.0	434.0
4032	2.0	44.7

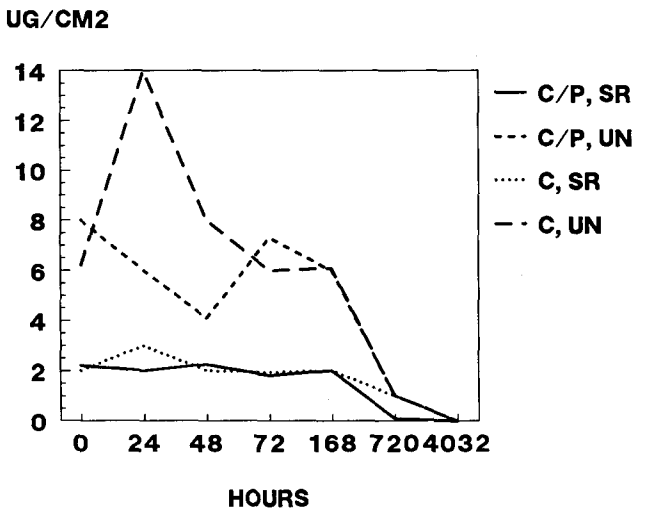

Figure 3. Interaction of fabric with finish with time of holding for amount of MeP residue on unlaundered specimens contaminated with package strength (54% A.I.) methyl parathion and held at room temperature in moving air.

fluorocarbon finish in limiting pesticide absorption at initial contamination. With less pesticide present, dissipation over time was more complete. However, when the specimen had been laundered before being held, the contribution of the functional finish was less important. Cotton/polyester blend fabric specimens retained greater quantities of MeP than did all cotton fabric specimens. Storage of laundered garments at 20°C with air flow and/or at higher humidity levels will assist in dissipating residues. Fabric finish played a two-fold role in the study. First, the functional finish limited initial contamination and secondly, it was an inhibitor to residue removal during laundering.

Recommendations from these data include using a functional finish to limit methyl parathion absorption at initial contamination, and post-laundering holding of apparel in moving air for several days for field strength contamination and longer times for package strength contamination. The greatest benefits of these findings may be in the event of industrial and/or aerial applicator accidents, recognizing that expensive and difficult-to-replace protective apparel (such as firefighters turn-out coats) might experience residue reduction through airing following refurbishment or airing alone rather than discarding. Additional work with other pesticide classes and formulations is needed prior to widespread dissemination of these recommendations.

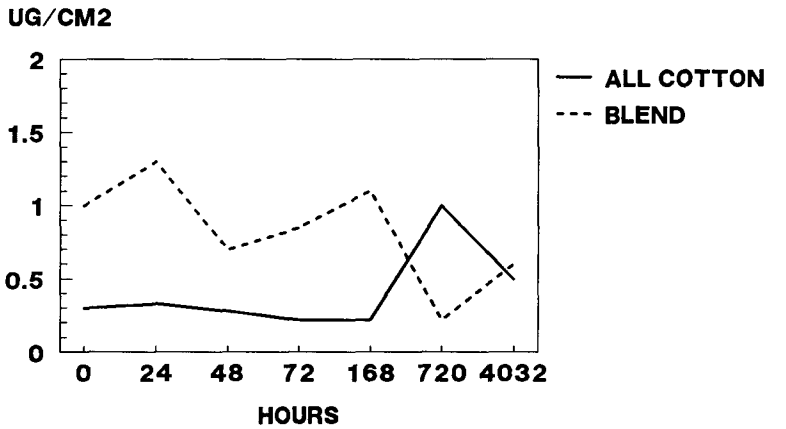

Figure 4. Interaction of fiber content and time for amount of MeP residue on laundered specimens contaminated with package strength (54% A.I.) methyl parathion and held at 20C with air flow.

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