Bull. Environ. Contam. Toxicol. (1990) 44:737–743

Bulletin of Environmental Contamination and Toxicology

Methyl Parathion Residue Retained in Fabrics for Functional Clothing Resulting from Use of Cationic Fabric Softeners in Laundering

Joan Laughlin and Roger E. Gold

University of Nebraska–Lincoln, Textiles, Clothing and Design, 234 Home Economics Building, Lincoln, Nebraska 68583-0802, USA

Human exposure to pesticides continues to be a problem for agricultural and urban workers who mix and apply these chemical tools. Dermal contact has been shown to account for 87 percent of the total human exposure to pesticides (Gold *et al.* 1988; Maibach *et al.* 1971; Wolfe *et al.* 1975). The importance of protective clothing is recognized; however, Wicker *et al.* (1979) reported that contaminated work clothing may act as an occlusive dressing facilitating dermal absorption of organophosphate insecticides. Lavy *et al.* (1983) found that individuals who were wearing obviously contaminated clothing showed greater levels of exposure than did other workers. Thus, refurbishment is an essential and critical part of continued safety. Completeness of pesticide removal in laundering is essential if the garment is to be worn again.

An important textile finish is a fabric softener. With machine washing, laundered clothing was becoming "hard" to the feel, due to build up of salts on the fibers that were not being rinsed away in the automatic machine washing when relatively hard water was used. Fabric softeners, adsorbed during the final rinse, add softness due to an interfiber lubricating effect (Davidsohn and Milwidsky 1978). Fabric softeners are cation-active, surface-active compounds, usually amine salts, quarternary ammonium (Egan 1978) or pyridinium derivatives (Trotman 1984). Quarternary ammonium salts are also used as emulsifying agents where adsorption of the emulsifying agent onto the substrate is desirable (e.g. insecticidal emulsions) (Maibach *et al.* 1971). Given the lipophilic fabric softener, an emulsifiable concentrate pesticide may be miscible in this auxiliary.

It has been reported that subsequent washing of clothes treated with fabric softener does not remove the softener already adsorbed on the fiber (Davidsohn and Milwidski 1978). "Softener build-up," refers to this phenomenon, such that as softness increases moisture, absorbency decreases. Repeated uses of high concentrations of fabric softener may render a fabric moisture repellent and affect pesticide soiling.

Send reprint request to J Laughlin at above address.

Laughlin *et al.* (1988) reported that single application of fabric softener did not affect chlorpyrifos absorption at initial contamination. A trend was observed for increased after-laundering pesticide residue when fabric softener had been used in the laundering prior to contamination. Given the potential for fabric softener "build-up," this study was undertaken to ascertain whether cationic surfactant (fabric softener) as a laundering auxiliary contributed to absorption of contamination and retention of methyl parathion residue after refurbishment.

MATERIALS AND METHODS

In a factorial design, three laundering procedures (with and without fabric softener, and with fabric softener except every fifth cycle), eleven levels of laundering (0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50 cycles) and two fabric finishes (unfinished and soil repellent finished) were studied. All work was replicated a minimum of three times.

Cotton/polyester (50/50) poplin was used in the study. Fabrics were 210 g/m^2 with a count of 480 x 200. Treatments included: (Tx_a) laundered 0, 1, 2, 3, 4, 5, 10, 20, 30, 40, and 50 times without a cationic fabric softener in an automatic home washer; (Tx_b) laundered with a rinse-added fabric softener in each laundering cycle; or (Tx_c) with the fabric softener except for each fifth laundering (5, 10, 15, 20, 25, 30, 35, 40, 45 and 50). After the requisite number of launderings, specimen lots were divided into paired sets. One specimen of each paired set was left unfinished (UN); the other specimen received a 1.0% add-on of fluorocarbon soil repellent finish (SR).

Laundering was done with nonionic, heavy duty liquid detergent with concentration of wash liquor as specified on the product label. A cationic rinse-added fabric softener was used as per manufacturer's recommendations. Municipally-supplied water (171 p.p.m. mineral content) was used at 47-49°C for washing and rinsing.

Emulsifiable concentrate methyl parathion (MeP) [0,0 dimethyl 0-p-nitrophenyl phosphorothioate] was prepared at 1.25% (AI) field strength concentration. Two-tenths mL of MeP were pipetted onto the specimens using a programmable micropipette. After spiking, specimens were allowed to air dry at 18-22°C.

Following MeP contamination (spiking), specimens were Launder-Ometer laundered through one additional cycle of a 12 minute wash, 5- and 3-minute rinses, using 0.13% heavy duty liquid nonionic detergent distilled water at 60°C (Easley *et al.* 1982). Specimens were air dried prior to pesticide extraction and analysis.

Specimens were individually extracted in 100 mL of reagent-grade hexane on a mechanical shaker for 0.5 hours at 120 rpm. The extract was decanted and replaced by an additional 100 mL of hexane for a second shaking. At the end of the hour shaking time, the fabric specimen was removed and the two extracts were combined.

Extracts were analyzed on a Varian Vista 3400-2882 gas chromatograph with an electron capture detector. Separation was achieved on a 2 m x 2 mm glass column packed with 10% OV-101 on 80/100 mesh Chromosorb W-HP with nitrogen flow of 40 mL/min. Injection, detector, and oven temperatures were 250, 325, and 220°C, respectively. External standards procedure was used to quantitatively analyze the pesticide residue, and area counts and retention times were recorded. Total amount of MeP residue in each specimen was expressed in $\mu g/cm^2$. Recovery rate was determined at 96% and used to calculate average residues after treatment which were compared to initial contamination ($\mu g/cm^2$) and expressed as percent residue remaining (%).

The statistical analyses of data were based on computed $\mu g/cm^2$ of pesticide residue remaining in the fabric after treatment and as a proportion (%) that the after-treatment residue was of the initial contamination. Arc sine transformations were applied to the percent residue remaining, and statistical differences among the treatments were calculated using General Linear Model analysis to compute the F-statistics. Further examination of treatments means of those dependent variables which produced significant F-values were completed with LS Means procedures. Orthogonal contrasts were used to test for linear or quadratic relationships. For all analyses, a 0.05 probability level was the criterion of significance.

RESULTS AND DISCUSSION

Of particular interest was differentiation between laundering with and without fabric softener, as well as differentiation among laundering without fabric softener, with fabric softener each cycle, and with fabric softener except omitting its use each fifth cycle. Since this later contrast was not present until five laundering cycles had been completed, to facilitate orthogonal contrasts, data were grouped for analysis into one through five washing cycles and 10 through 50 washing cycles.

Specimens were laundered through 0, 1, 2, 3, 4, 5, 10, 20, 30, 40, or 50 laundering cycles and then spiked. Following spiking and air-drying (with no laundering), specimens were extracted to determine baseline levels of contamination. Since the SR finish inhibited absorption of the liquid, the head of the unabsorpted solution was rolled into a wash beaker. Initial contamination of the unlaundered (0 cycles) specimens was 8.1 $\mu g/cm^2$ for SR and 40.6 $\mu g/cm^2$ for UN specimens. There were significant differences in initial absorption due to finish of the specimen ($F=34.56$, $df=1,14$, $p \leq 0.05$). These findings are in agreement with earlier work that identified differences in chemical absorption due to functional textile finish (Laughlin *et al* 1986).

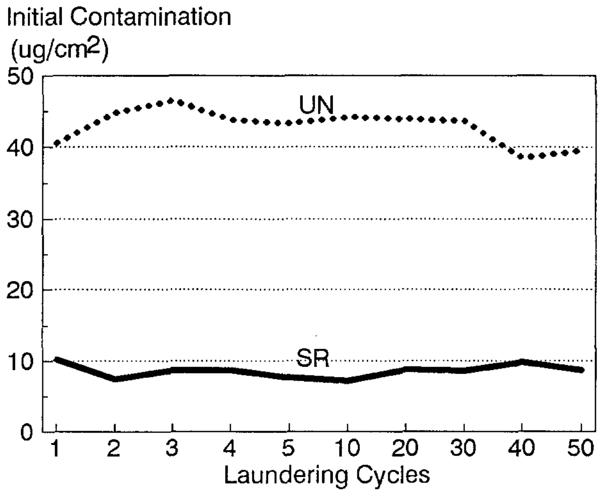

Figure 1. Initial contamination of fabric specimens pre-laundered 0 through 50 times with fabric softener.

It was appropriate to examine differences in contamination following the pretreatment of repeated laundering cycles (1, 2, 3, 4, 5, 10, 20, 30, 40, or 50). At initial contamination, there was no consistent effect of previous washing with or without fabric softener on pesticide absorption. Functional finish did impact initial contamination, with more MeP on unfinished specimens than on SR specimens (Figure 1); however, for UN it was noted that as laundering cycles increased, there was a trend for a decrease in MeP absorption. It was theorized that detergent residue or fabric softener left in the fabric was affecting subsequent absorption of pesticide. Orthogonal contrasts confirmed linear models (β=6.10, $p \leq 0.01$) rather than curvilinear, therefore failing to find significance in the apparent decrease in residue retention following 40 and 50 launderings. There was no significant difference between the two models in slope (α=2.669). The two lines were essentially the same, reflecting parallel responses although the residue was always larger for the UN specimens than for the SR specimens.

Laundering Following Spiking. Laundering reduced residues to 95-99% of the initial contamination. Greater after-laundering residues were found on SR functional finished specimens than on unfinished specimens. This held true for the comparisons among cycles 1, 2, 3, 4, 5 (Figure 2) and cycles 10, 20, 30, 40, and 50 (Figure 3). Earlier work had also noted that residue removal was more difficult from SR specimens than from UN specimens (Laughlin *et al.* 1986). While the effect of a fabric softener was not confirmed through F-statistics, a trend was observed for after-laundering residue to decrease as the number of cycles of laundering with or without a fabric softener increased (1, 2, 3, 4, 5 and 10, 20, 30, 40, 50) (Figures 2 and 3). It is possible

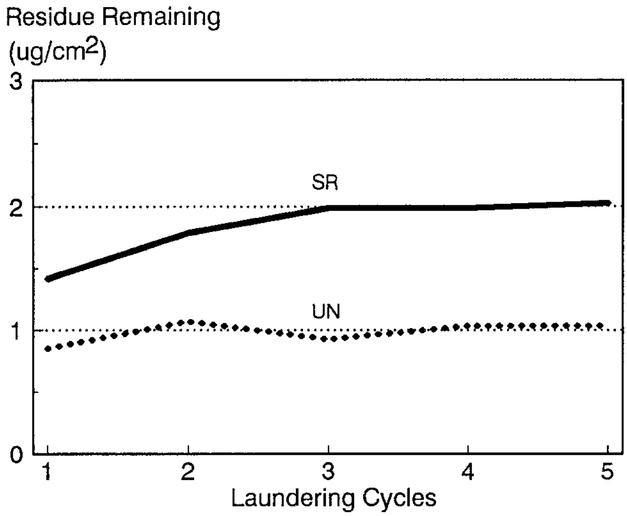

Figure 2. Residues of methyl parathion remaining after laundering (1-5 cycles).

that the decrease in residue retention after fabric had been laundered up to 50 times may be a function of detergent deposition in the fabric or may be a function of changes in fabric geometry such that soil removal is enhanced. From these data, it is apparent that there was no contribution due to presence or absence of fabric softener.

Analysis of variance established a main effect attributable to fabric finish. Visual inspection of graphic display of percent residue remaining per fabric finish was performed. It was readily apparent that greater percentages of initial contamination remained when specimens had an SR finish than when specimens were unfinished regardless of whether pre-laundering included or did not include a fabric softener.

When orthogonal contrasts were conducted, no linear (β=0.47), quadratic (β=0.22), nor cubic (β=0.04) relationships between number of pre-laundering cycles with or without fabric softener and amount of MeP residue remaining on contaminated fabric after one laundering were found. Based on these data, it was concluded that fabric softener, whether not used, used once, or used repeatedly with and without removal cycles, had no impact on residue remaining after laundering. SR finished fabric did limit MeP absorption at contamination, but pesticide removal was more difficult from SR fabrics. There was a slight, though not significant trend, for after laundering residues to decrease across the fifty pre-laundering cycles.

In general, use of fabric softener in laundering is not a major factor in initial contamination or retention of methyl parathion. The findings of this study indicate that it may be used at the launderer's discretion without concern for adverse effects.

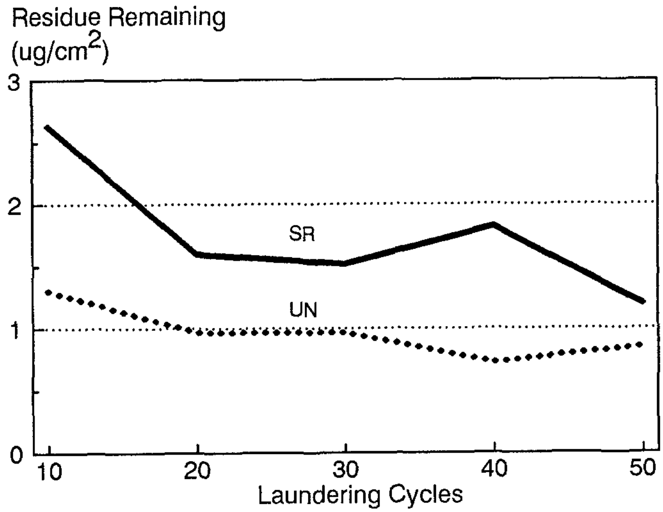

Figure 3. Residues of methyl parathion remaining after laundering (10-50 cycles).

Acknowledgments. We acknowledge the assistance of J Stonuey, D Clark and K Newburn. The work was funded in part by a grant from the Nebraska Pesticide Impact Assessment Program and the Nebraska Agricultural Research Division Project 94-015 and contributes to the North Central Regional Research Project NC-170 "Reducing Pesticide Exposure of Applicators Through Improved Clothing Design and Care. Journal Paper Number 8944, Nebraska Agricultural Research Division.

REFERENCES

Davidsohn A, Milwidsky BM (1978) Synthetic detergents. Wiley, New York

Egan RR (1978) Cationic surface active agents as fabric softeners. J Amer Oil Chem Soc 55:118-121

Easley CB, Laughlin JM, Gold RE, Schmidt K (1982) Detergents and water temperatures as factors in methyl parathion removal from denim fabrics. Bull Environ Contam Toxicol 28:239-244

Gold RE, Leavitt JRC, Holcslaw T, Tupy D (1982) Exposure of urban applicators to carbaryl. Arch Environ Contamin Toxicol 11:63-67

Laughlin JM, Easley CB, Gold RE, Hill RM (1986) Fabric Parameters and Pesticide Characterics that Impact on Dermal Exposure of Applicators. In Barker R, Coletta GC (eds) Performance of Protective Clothing ASTM STP #900, Amer Soc Test Mat, Philadelphia, pp 136-150

Laughlin JM, Lamplot JL, Gold RE (1988) Chlorpyrifos Residues in Protective Apparel Fabrics Following Commercial or Consumer Refurbishment. In Mansdorf SZ, Sager R (eds), Performance of Protective Clothing II ASTM STP 989, Amer Soc Test Mat, Philadelphia, pp 705-714

Lavy T, Mattice JD, Flynn RR (1983) Field Studies Monitoring Worker Exposure to Pesticides. In Seymour, KG, Pesticide Formulation and Application Systems: ASTM STP #745, Amer Soc Test Mat, pp 60-74
Maibach HI, Fieldman RJ, Milby TW, Serat WF (1971) Regional variation in percutaneous penetration in man. Arch Environ Contamin Toxicol 23:208-211
Rosen MJ (1984) Surfactants and interfacial phenomena. Wiley, New York
Wicker GW, Williams WA, Bradley JR, Gerthrie FE (1979) Exposure of field workers to organophosphorus pesticides: Cotton. Arch Environ Contamin Toxicol 8:433-440
Wolfe HR, Durham WF, Armstrong JF, Staiff DC, Comer, SW (1975) Exposure of apple thinners to parathion residues. Arch Environ Contamin Toxicol 3:257-267

Received August 22, 1989; accepted October 18, 1989.