Bull. Environ. Contam. Toxicol. (1990) 45:452–458

Bulletin of Environmental Contamination and Toxicology

Refurbishment of Nonwoven Protective Apparel Fabrics Contaminated with Methyl Parathion

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Dermal exposure to pesticides can normally be expected to be controlled by the use of protective clothing (Branson *et al.* 1986; Davies *et al.* 1980; Wolfe *et al.* 1976). Recent investigations have shown that, once contaminated, pesticide applicators' clothing is difficult to decontaminate through normal household laundering (Laughlin *et al.* 1985). Repellent finishes on apparel fabrics decrease pesticide absorption; however, these finishes may inhibit pesticide removal in laundering (Laughlin and Gold 1989b; Laughlin *et al.* 1986). Fluorocarbon polymers that are used for some repellent finishes 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, disenabling hydrophobic soil dispersion in the washiong solution (Das and Kulshreshtha 1979). Previous research has shown that significantly greater percentages of pesticide residue remain in woven cotton/polyester fabrics with a fluorocarbon, soil-repellent finish compared to those that were unfinished (Goodman *et al.* 1988; Keaschall *et al.* 1986; Laughlin and Gold 1988; Laughlin *et al.* 1986).

Nonwoven fabrics have been proposed as appropriate "barrier" fabrics for pesticide applicators' protective clothing. Staiff *et al.* (1982) concluded that even though spunbonded olefin nonwovens and cellulosic nonwovens treated with water-repellent finishes were penetrated by drifting pesticide sprays, these fabrics would provide more protection than usual work clothing. Nigg *et al.* (1986) concluded that a spunbonded-olefin, protective coverall reduced total dermal exposure by 40%.

The directions on the packages of coveralls made of spunbonded olefin state they can be machine laundered up to four times; yet no specific care instructions are provided. To date, very little information has been made available on the performance of repellent finished nonwoven fabrics and the new types of nonwovens being introduced into the market, particularly in reference to the effectiveness of laundering in removal of pesticide residues from these fabrics.

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MATERIALS AND METHODS

Six non-woven fabrics were studied: A=Tyvek 1422A*; B=Tyvek 1422R* (corona treated); C=Sontara, unfinished; D=Sontara, DuPont repellent finished (RF) supplied by the DuPont Company; E=Spunbonded/Meltblown/Spunbonded composite (S/M/S), unfinished and F=S/M/S, repellent finished (RF) provided by Kimberly-Clark Corporation.

To ascertain whether repeated laundering affected the repellency or absorbency and the air permeability of the nonwoven fabrics, the fabrics were laundered 0 (controls) 1, 2, 3, 4 or 5 times, then contaminated with methyl parathion and laundered one additional time or sampled for air permeability analysis. The factorial design was used as follows:

Baseline Contamination	After-Laundering Residues
Tx_0 - 0	CEx
Tx_1 - LCEx	LCLEx
Tx_2 - LLCEx	LLCLEx
Tx_3 - LLLCEx	LLLCLEx
Tx_4 - LLLLCEx	LLLLCLEx
Tx_5 - LLLLLCEx	LLLLLCLEx

where C=Contaminated, L=Launder, and Ex=Extract (hexane)

There were 10 specimens per treatment per replication and all work was replicated a minimum of three times.

Fabric characteristics (Table 1) were determined according to the procedures in ASTM D3779-79 and ASTM D1777-64 (ASTM 1988). Specimens (8 x 8 cm) were cut from the prepared fabrics using a plot diagram for random assignment to treatments.

Table 1. Fabric characteristics of regular and corona treated Tyvek* and of unfinished and repellent finished Sontara* and S/M/S fabrics.

	Tyvek*		Sontara*		S/M/S	
	1422A	1422R	UN	RF	UN	RF
Weight						
(oz/yd^2	1.22	1.12	1.90	1.97	1.65	1.61
(g/m^2)	47.53	42.72	70.02	71.84	61.69	60.33

Laundering was done in a General Electric, automatic, home-washing machine using AATCC Test Method 96-1980 R-1984, Washing Procedure II.E. (AATCC 1988) at 49° ± 1°C with a 4-lb, dummy load. A heavy duty, liquid detergent (nonionic and anionic surfactants) was used at 0.5 cup per 12 gal of water (0.13%) in the washing apparatus. One exception to this procedure occurred when the Sontara UN and the Sontara RF yardages did not survive the first wash cycle. In those two instances the planned research design was terminated after one wash cycle.

Methyl parathion (0,0-dimethyl 0-p-nitrophenyl phosphorothioate) (MeP) dilutions were prepared at 1.25% (w/v) active ingredient from an emulsifiable-concentrate formulation. Specimens that had been subjected to 0, 1, 2, 3, 4 or 5 launderings were contaminated. A 0.2-mL aliquot of the 1.25% a.i. MeP solution was pipetted onto the center of the specimen. Contaminated specimens were allowed to air dry (18-22°C) for 4 to 6 hrs. Previous work had established no significant vaporization from textiles in 24 hr. (Laughlin and Gold 1989a). Following contamination and drying, specimens were laundered or were evaluated unlaundered.

Because air permeability is believed to be inversely related to barrier performance, this property was determined in Dr. Larry Wadsworth's Nonwovens Laboratory at the University of Tennessee according to ASTM Test Method D 737-75 (R-1980) Air Permeability of Textile Fabrics (ASTM 1988). A Model 4301 Gurley Permeometer was used to determine the differential pressure of each specimen (Wadsworth *et al.* 1988).

The research design of this experiment included laundering after contamination. Using procedures modified from AATCC 61-1980, (AATCC 1988) the accelerated method was used to simulate a single laundry cycle. A LaunderOmeter model LEF was used for the 12 min wash cycle at 60°C with a 0.13% nonionic and anionic heavy duty liquid detergent (Liquid Cheer*)[1] solution in distilled water followed by 5 and 3 min rinses at 40°C.

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

Extracts were analyzed with a Varian Vista 3400 gas chromatograph with 2882 data system using 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 a column nitrogen-flow of 40 mL/min. Inlet, detector, and column temperatures respectively, were 220, 325, and 220°C. Area counts and retention times for the specimens were recorded. Total amount of MeP residue in the specimen was expressed in $\mu g/cm^2$ and as a percentage of initial contamination.

The variables in this study included six fabric types, six levels of laundering and with or without an additional laundering (post-contamination) resulting in two 6 x 6 factorial designs impacting on two dependent variables, MeP residue and air permeability. General Linear Model (ANOVA) and Least-Squares Means tests were performed on the data to determine which main and interaction effects had a significant influence on the amount and percentage of pesticide residue remaining on the specimens after

[1]Use of product brand name does not imply endorsement.

laundering and the change in air permeability after laundering. For both analyses procedures, a 0.05 probability level was the criterion of significance.

The Sontara fabrics had the greatest mean air permeability (Table 2), with Sontara* RF somewhat higher than the Sontara* UN. This was approximately the same permeability reported by Wadsworth *et al.* (1988) for these fabrics; however this would be expected given that Wadsworth *et al.* (1988) reported that the greatest variability was at the middle of the roll of fabric, the site for selecting samples of the fabric that were studied at Nebraska. This fabric was greatly affected by one laundering cycle; therefore a 300% increase in permeability was noted after one laundering and no observation was recorded for air permeability for subsequent laundering cycles. The S/M/S fabrics (1.8 oz/yd^2) had the lowest air permeability, and the unfinished Tyvek had no measurable air permeability.

Table 2. Air permeability of regular and corona treated Tyvek* and of unfinished and repellent finished Sontara* and S/M/S fabrics.

	Tyvek*		Sontara*		S/M/S	
	1422A	1422R	UN	RF	UN	RF
Air Permeability ($ft^3/min/ft^2$)	0.00	1.4	52.3	68.9	19.7	11.2
Laundering Cycle						
1 ($ft^3/min/ft^2$)	2.8	2.7	177.4	118.1	20.1	14.6
2 ($ft^3/min/ft^2$)	3.5	3.0			22.2	13.4
3 ($ft^3/min/ft^2$)	3.3	3.1			20.7	13.1
4 ($ft^3/minft^2$)	3.5	3.3			19.3	14.0
5 ($ft^3/min/ft^2$)	3.5	3.9			20.1	15.1

Laundering altered air permeability. Significant differences were observed due to fabrics ($F=298.43$, $df=5$, $p \leq 0.05$) and due to laundering cycle ($F=4.55$, $df=5$, $p \leq 0.05$); but there were no interactions of fabric with laundering cycle. As fabrics were laundered, air permeability increased slightly with the greatest change occurring after the first laundering cycle. This may be attributable to distortions in fabric geometry or due to removal of the functional finish on the RF specimens.

Initial contamination was significantly lower on the fabrics with the repellent finish than on the unfinished fabrics (Table 3). Statistical analysis revealed a main effect due to fabric ($F=13.03$, $df=5$, $p \leq 0.05$) and a main effect due to prior laundering cycle in amount of residue absorbed by specimens, but

Table 3. Amount of methyl parathion on specimens laundered 0, 1, 2, 3, 4, or 5 times before contamination.

	Laundering Cycle					
Specimen	0 $\mu g/cm^2$	1 $\mu g/cm^2$	2 $\mu g/cm^2$	3 $\mu g/cm^2$	4 $\mu g/cm^2$	5 $\mu g/cm^2$
Tyvek 1422A	19.0	40.6	38.0	40.4	39.6	39.6
Tyvek 1422R	30.5	37.7	40.8	38.0	40.7	37.8
Sontara, UN	36.0					
Sontara, RF	10.3					
S/M/S, UN	36.5	37.4	37.0	39.6	43.8	36.3
S/M/S, RF	14.5	27.3	27.1	29.6	37.5	38.7

no interactions. The differences were attributable to the repellency of the RF specimens.

Laundering before contamination significantly reduced the ability of these repellent finished non-wovens to limit pick-up of the chemical. For the S/M/S, the amount of MeP on the specimens that had been laundered once before spiking was double the amount on the unlaundered specimens. As laundering cycles increased, the functional finished specimen exhibited absorbency more like the unfinished fabric. Clearly, laundering reduces the repellency of these nonwoven fabrics, and should be avoided.

One laundering after spiking significantly reduced the levels of contamination (Table 4). A main effect attributable to fabric type ($F=70.32$, $df=5$, $p \leq 0.05$) was observed in residue retained, but there was no effect attributable to laundering cycle ($F=0.62$, $df=5$) and no interactions. Fabric differences can be observed on two levels; the S/M/S fabrics retained less residue after the additional laundering-after-contamination, and the RF specimens effectively limited contamination and thus exhibited lower after-laundering residues, at least through the first two laundering cycles. The corona treatment of Tyvek* is performed to improve

Table 4. Residue of methyl parathion on specimens after laundering.

	Laundering Cycle					
Specimen	0 $\mu g/cm^2$	1 $\mu g/cm^2$	2 $\mu g/cm^2$	3 $\mu g/cm^2$	4 $\mu g/cm^2$	5 $\mu g/cm^2$
Tyvek 1422A	1.6	2.3	2.1	1.6	1.8	7.3
Tyvek 1422R	1.1	0.9	1.1	1.2	1.9	1.7
Sontara, UN	0.1					
Sontara, RF	0.1					
S/M/S, UN	0.6	0.5	0.3	0.3	0.4	0.4
S/M/S, RF	0.1	0.2	0.3	0.4	0.3	0.3

its ability to absorb finishes, and actually makes the fabric more hydrophilic (Wadsworth *et al* 1988). In this study, corona-treated Tyvek* had lower MeP residue after laundering than did untreated Tyvek*.

Residues were lower in nonwoven-fabric specimens with a repellent finish than in the unfinished fabrics; however, when the RF specimens had been laundered before contamination, no meaningful differences were observed in the specimens. Residues retained after laundering in specimens that had been contaminated following prelaundering cycles of 1, 2, 3, 4, 5 and no laundering (0) were 0.88, 0.97, 0.83, 1.11, 1.03 and 0.88 $\mu g/cm^2$, respectively. Earlier work with woven-cotton/polyester fabrics had revealed that residue removal by laundering was more difficult when fluorocarbon-finished specimens were compared to unfinished fabrics, but this was not true for these nonwoven fabrics.

Based on these data, the Sontara fabrics offered the greatest barrier to MeP absorption; however, these spunlaced nonwovens are not intended to be laundered, and in fact, did not survive one laundering cycle. Repellent finishes on nonwoven fabrics limited absorption of MeP pesticide; but laundering before exposure to pesticides decreased the effectiveness of the functional finish to limit pesticide pick-up.

As laundering cycles increased, the functional finish exhibited absorbency similar to the unfinished fabric. Clearly laundering reduced the repellency of the nonwoven fabrics and should be avoided; however, there was no contribution of the repellent finish to greater amounts of residue remaining in the laundered nonwoven fabrics as had been observed in woven cotton and cotton blend fabrics in earlier work. A home application of repellent finish might be warranted after each washing, but bears further evaluation before further recommendations can be made.

Acknowledgments. Published as Journal Series Number 9125, Agricultural Research Division, UN-L. Funded in part by the Nebraska Project 94-014 and the Southern Project S-208 Textile Fiber Systems for Performance, Protection and Comfort. Appreciation is extended to Du Pont Co. for the "Sontara*" and "Tyvek*" fabrics and to Kimberly Clark for the S/M/S fabrics.

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Received December 15, 1989; accepted February 8, 1990.