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Fluorescent Dye, Pesticide and Surfactant Penetration Tested in Simulated Spill. Part II. Nonwoven Fabrics as Barriers

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Fabrics that provide a barrier to pesticide penetration are in demand for usage in protective clothing. It is the dermal exposure to pesticides (Wolfe et al. 1966) that must be minimized. While field testing of protective apparel is desirable to examine certain aspects of performance there are limiting factors to such studies. Tests in the field are demanding in terms of time and money. Some of the variables that might have great impact on the workers' exposure may be difficult if not impossible to control.

Laboratory and spray chamber tests may be used to determine variations in performance of fabrics as barriers to penetration (Leonas et al. 1981, Raheel 1982). It should be noted that these tests also have limitations.

Tests have been done using spray chambers such as the one developed at the University of Tennessee (Leonas et al. 1987). A computerized spray chamber at Mississippi State University which has been used for testing allows control of spray pressure, atomizer spray and spray height, temperature and humidity (Ramaswamy and Boyd 1993). Fabrics that perform in this spray chamber testing as good barriers need to be tested in field trials since field exposure is a combination of spray and accidental spills of pesticide/pesticide formulations.

Pesticide spills have been simulated in the laboratory by dropping a known amount of the liquid onto fabric and analyzing the amount of pesticide collected on the collector layer (Laughlin and Gold 1990, Leonas and De Jonge 1986, Raheel and Gitz 1985, Shaw and Hill 1990). The findings of these studies are illustrative of pesticide penetration through garment that may occur during the workman's preparation to spray or clean up afterwards. It has been shown that application of external pressure and contamination at higher levels (Crouse et al. 1990) increase the severity of these tests and represents a worst case scenario.

The purpose of this research was to study 1) penetration of fluorescent dye and methyl parathion (MEP) in spill situations and, 2) effect of surfactant on the penetration of dye.

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MATERIALS AND METHODS

A fluorescent particle (FP) method and gas chromatography (GC) were used to predict the barrier performance of fabrics. Variations tested using the FP method were: dye only dissolved in water and then applied; dye and a surfactant dissolved in water and then applied; and dye dissolved in water and then applied to fabric which had been pretreated with a surfactant spray. The other variation which was tested, methyl parathion, was analyzed using GC.

Fabrics from S-208 southern regional project "Textile Fiber Systems for Performance, Protection and Comfort" were used. The nonwovens selected are those that are being used in making protective apparel or that have potential for use in such garments. The fabrics were Tyvek, Sontara and two weights of SMS and have been described previously (Ramaswamy and Boyd, 1993) and characterized (Wadsworth, et al. 1986). One Tyvek was corona treated which is added to improve its ability to absorb finishes. The repellent finishing process was performed using commercial equipment at North Carolina Finishing, Salisburg, North Carolina.

Fabrics were conditioned for 48 hours at 24° C prior to testing. Fabric assemblies consisted of test fabric, a collector layer of cotton knit and aluminum foil; samples were cut 8.9 cm^2. The collector layer was 100% cotton tee shirt knit.

Treatments to study penetration were: a) dye = basic sulfo-flavine (BSF) dye only; b) dye-surf = BSF dye and surfactant; c) dye-surf-surf = BSF dye and surfactant applied to surfactant treated fabric; d) MEP = methyl parathion (in formulation).

BSF dye was obtained from Organic Chemicals, East Providence, RI and is further described as Orco Acid Brilliant Sulfo Flavine F.F. The surfactant Triton X-100, contains <3% polyethylene glycol and is a product of Union Carbide Chemical & Plastics Technology Corporation. Methyl Parathion is O,O,-dimethyl O-para-nitrilephenyl phosphorothioate and a 4.O EC (emulsifiable concentrate) was used which is 43.3% active ingredient.

Eight fabrics were included for treatments a,b and d; the dye-surf-surf treatment was done on only two of the test fabrics. Four replications were made of each fabric for all treatments.

The BSF dye was made in distilled water to obtain 1.5 percent active ingredient in water. The surfactant Triton-X-100 was included with dye to study effect of surfactant on penetration of dye. A concentration of 10 microliters surfactant per 10 ml water and dye solution was used. Pretreatment of the selected group of two fabrics involved spraying the surfactant solution onto the entire surface of fabric samples, air-drying samples and applying the dye solution.

Two hundred microliters of the dye, dye and surfactant or methyl parathion were applied to the fabric assemblies using a fixed volume micropipette. If there was an unabsorbed solution, it was rolled off after two minutes. Following contamination, fabric assemblies were allowed to air dry for two hours. This was similar to

contamination or spiking method used in other studies (Laughlin and Gold, 1990; Shaw and Hill, 1990).

After drying, contaminated samples for fluorometric assay were separated and the cotton knit layer was placed in a petri dish for extraction of the dye. Dye extraction was done using 40 ml of distilled water. An aliquot of the solution was read in a Turner 110 Fluorometer. Standard serial dilutions were used to obtain the BSF dye concentration. The collector layer was analyzed in this manner. Calculations were made (Smith et al. 1983) to obtain mean percent recovery from the collector layer.

GC analysis was also done on the collector layer only to determine amount of pesticide that penetrated through the fabric. Pesticides were extracted from collector layers by placing an individual layer of fabric in a 125 ml Erlenmeyer flask. Then 50 ml diethyl ether (pesticide residue quality - Burdick and Jackson Laboratories, Inc.) was added, shaken for one minute, and left for one hour with intermittent shaking. Ether was decanted into a 200 ml flask and fabric sample was rinsed twice with 25 ml portions of diethyl ether. Extracts and rinses were combined and evaporated to near dryness on N-Evap Concentrator (Organomation Associates, Inc.) under a gentle stream of nitrogen. The chromatograph used for MEP was a Hewlett-Packard 5890 Series II with HP 7673 auto injection, HP 3396A intergarter and electron capture detector. Injection temperature was 200°C, detection temperature 250°C and flowrate 68.6 ml/min HE. The column was HP-5: 30 m x .53 mm x .88 mm film.

Statistical treatment of the data was done using the General Linear Measures (GLM) model. Mean separation was done by Tukey's HSD method.

RESULTS AND DISCUSSION

The average recovery of dye from the cotton knit collector layer was 93.7 percent (Ramaswamy & Boyd, 1993). The summary of analyses from the four treatments (Table 1) shows the treatment with dye only and with dye and surfactant on fabric pretreated with surfactant were not significant. The amounts of dye recovered from collector layers under all fabric types in the dye treatment were negligible. For example, collector layers under SMS and Sontara had only 0.3% and 0.5% respectively. The dye-surf-surf treatment was limited to use on two fabrics, Sontara and the lighter weight SMS, both with repellent finish.

Table 1. Summary for GLM analyses of treatments

Source	F Value	Pr > F
dye	4.89	0.0002
dye-surf	4.86	0.0016
dye-surf-surf	0.04	0.8441
MEP	11.13	0.0001

When the dye-surf method of treatment was used, results were significant and negligible amounts of dye were recovered from the collector layer under fabrics. Two repellent finished fabrics - the heavier weight SMS and Corona treated Tyvek performed significantly better as barriers against the dye-surf.

Table 2. Percent recovery of dye-surf from collector layer under fabrics

Fabric Type	Percent	Tukey's ***
Tyvek (1.2 oz/yd^2)*	0.017	b
Tyvek (1.3 oz/yd^2)	0.038	a,b
SMS (1.8 oz/yd^2) RF**	0.027	b
SMS (1.8 oz/yd^2)	0.035	a,b
SMS (2.3 oz/yd^2) RF**	0.028	b
SMS (2.3 oz/yd^2)	0.061	a
Sontara (2.1 oz/yd^2) RF**	0.027	b
Sontara (2.1 oz/yd^2)	0.013	b

* Corona Treated
** Repellent finish
*** Means with same letter are not significantly different according to Tukey's HSD test.

When Methyl Parathion was applied to fabrics, analysis of the collector layer showed the repellent finished SMS (both weights), Sontara and Corona treated Tyvek were different from the unfinished variation for each. The repellent finish and Corona treatments would appear to have added to the barrier properties of these fabrics in a spill situation.

Table 3. Percent recovery of MEP from collector layer under fabrics

Fabric Type	Percent	Tukey's***
Tyvek (1.2 oz/yd^2)*	0.065	b
Tyvek (1.3 oz/yd^2)	36.398	a
SMS (1.8 oz/yd^2) RF**	0.320	b
SMS (1.8 oz/yd^2)	13.588	a,b
SMS (2.3 oz/yd^2) RF**	0.425	b
SMS (2.3 oz/yd^2)	13.218	a,b
Sontara (2.1 oz/yd^2) RF**	0.085	b
Sontara (2.1 oz/yd^2)	21.148	a,b

* Corona treated
** Repellent finish
*** Means with same letter are not significantly different according to Tukey's HSD test.

Use of a fluorescent dye in the simulation of a spill on fabrics gave results that would lead to the same conclusion as when it was used in a spray chamber (Ramaswamy and Boyd, 1993). The dye can be used only as a predictor of fabric

barrier performance. In this spill study, the repellent finish did improve barrier performance. Presence of a surfactant with dye or as pretreatment for fabric seemed to have little or no effect on penetration. Additional testing is needed in field settings.

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REFERENCES

Crouse JL, De Jonge JO, Calogero F (1990) Pesticide barrier performance of selected nonwoven fabrics in laboratory capillary and pressure penetration testing. Tex Res Journal, pp 137-142

Leonas KK, De Jonge JO (1986) Effect of functional finish barriers on pesticide penetration. In: Barker RL, Coletta GC (eds) Performance of Protective Clothing, ASTM STP 900, America Society for Testing and Materials, Philadelphia, PA, pp 177-186

Leonas KK, De Jonge JO, Duckett KE (1981) Development and validation of a laboratory pesticide spray system for fabric penetration evaluation. In Mansdorf S.Z., Sager R., Nielson AP (eds) Performance of Protective Clothing: Second symposium, ASTM STP 989, American Society for Testing and Materials, Philadelphia, PA, pp 660-670

Leonas KK, Easter EP, De Jonge JO (1989) Effect of fabric characteristics on pesticide penetration through selected apparel fabrics. Bull Environ Contam Toxicol 43:231-2

Laughlin J, Gold RE (1990) Refurbishment of nonwoven protective apparel fabrics contaminated with methyl parathion. Bull Environ Contam Toxicol 45:452-458

Raheel M, Gitz EC (1985) Effect of fabric geometry on resistance to pesticide penetration and degradation. Arch Environ Contam Toxicol 14:273-279

Raheel M, Resistance of selected textiles to pesticide penetration and degradation. Jour Environ Health 49:214-219

Ramaswamy GN, Boyd CR, (1993) Fluorescent dye and pesticide penetration tested in a computerized spray chamber. Part I. Nonwoven fabrics as barriers. Bull Environ Contam Toxicol 51:341-348

Shaw A, Hill KR (1990) Variability in Sorption of Diazinon through microporous fabrics. Bull Environ Contam Toxicol 45:500-506

Smith DB, Plummer DD, Harris FD, Pickett EE (1983) Recovery of fluorescent tracer dyes. Transactions ASAE, pp 1308-1311

Wadsworth LC, Easter EP, Lin YQ (1988) A study of nonwoven fabrics in providing repellency and performance. The First International Symposium on the Impact of Pesticides, Industrial and Consumer Chemicals on the Near Environment. Sponsored by USDA-CSRS and the University of Georgia, Symposium Proceedings, pp 137-153

Wolfe HR, Armstrong JF, Durham WF (1966) Pesticide exposure from concentrate spraying. Arch Environ Health 13: 340-344