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Qualitative and Quantitative Analysis of Diazinon in Fabric Exposed to Various Simulated Sunlight and Humidity Conditions

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Personal Protective Equipment (PPE) is commonly used by pesticide handlers/applicators to reduce dermal exposure to pesticides. In reusable fabrics, effective decontamination of garments after use reduces build-up that is caused by absorption of pesticides. Typically, laundering of contaminated garments is used to remove the pesticide residue. However, research indicates that percent not removed by aqueous extraction (laundering) ranged from 1% to over 42% (Nelson et al., 1992). Since pesticides break down when exposed to the natural environment, exposure of contaminated garments to sunlight may assist in reducing pesticide build-up in the fabrics. Previous studies on the effect of simulated light on pesticide reduction were conducted on fabric containing an impermeable microporous membrane laminated between two layers of fabric. Research conducted by Park et al. (1990) concluded that simulated weathering assisted in the breakdown of parathion and methyl parathion. Contrarily, Branson et al. (1988) reported that simulated weathering did not reduce the level of pesticide remaining in the laundered and unlaundered specimens. These latter researchers also stated that their finding might not be in agreement with Park et al. because of differences in black panel temperature. This study was designed to assess the effect of simulated sunlight and humidity on pesticide residue in Zonyl® finished fabrics that have potential for use in protective clothing.

MATERIALS AND METHODS

Fabrics were purchased from Testfabrics Incorporated, and Zonyl® (fluoroalkyl methacrylate polymer) finish applied commercially, according to specifications provided by DuPont. Fabric characteristics are given in Table 1. Emulsifiable concentrate (25% a.i.) of diazinon was used for the study to simulate an accidental spill. The percent active ingredient was verified by gas chromatography (GC) of acetone diluted concentrated formulation (performed in triplicate). Calibration of the GC detector was performed using analytical reference grade diazinon injected over the range of 0.005 ng to 5.00 ng on column. Concentration determinations were made using a least squares regression analysis of diazinon amount versus peak area.

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A three factorial experimental design was used for the study. The three factors were fabric, level of exposure, and exposure condition. Two sets (with three replications) of fabric specimens were tested for each combination. GC analysis was conducted to quantify the amount of pesticide remaining on fabric specimens. Backscattered electron imaging (BEI) on scanning electron microscope (SEM) was used to study the distribution of osmium labeled pesticide on specimen. The x-ray analysis assisted in confirming the presence or absence of osmium labeled pesticide.

Table 1. Physical characteristics of fabrics used for the study

Fiber Content	Weight (g/m^2)	Weave	Yarn Count/inch
Cotton (100 %)	187.5	Plain	100 x 50
Cotton/polyester (65/35 %)	190.9	Plain	119 x 65
Polyester (100%)	212.2	Plain	43 x41

A constant-volume micropipette was used to apply 0.1 mL of diazinon to 7 cm x 7 cm fabric specimens. Excess pesticide was removed from the surface after 10 min (Shaw and Hill, 1991). Atlas Ci-35 Weather-Ometer with 0.4 W/m^2 irradiance was used to expose the specimens. ASTM G26-90 (ASTM, 1984) test method was used to expose the fabrics to following conditions: 1) 85% humidity, all light cycle; 2) 30% humidity, all light cycle; 3) 85 % humidity, light and dark cycle; and 4) 30% humidity, light and dark cycle. For light and dark cycles 7.52 kJ/m^2 were alternated with 1 hr darkness until the desired exposure level was reached. This was done to simulate day and night conditions. Levels of exposure were 0, 10, 20, 40, and 80 kJ/m^2 for each fabric type. According to test specifications, the racks with no test specimens were covered with dummy specimens.

For one set, an orbital shaker was used to extract the diazinon in 50 mL acetone for 45 min. The procedure was repeated twice. A Hewlett Packard 5890 gas chromatograph equipped with a nitrogen/phosphorus detector (GC-NPD) and a 30 m x 0.32 mm id DB-5 (0.25 µm) fused silica capillary column were used to measure the amount of diazinon extracted from the specimens. The standard recoveries of diazinon ranged from 74 to 97 % . The above-mentioned procedure was used to analyze quantitatively test specimens and also to measure the transference of pesticide from test fabric to dummy specimens on the rack. To measure the transferred pesticide remaining in dummy fabric, 7 cm x 7 cm specimens were cut and analyzed at the end of the study. Mean, standard deviation (SD), analysis of variance (ANOVA), and least significant differences (LSD) were used to analyze the test specimens statistically.

The second set was used to study the pesticide distribution on the face and back of the control and contaminated specimens. Fabric strips were labeled with osmium tetroxide (OsO_4) vapors (Shaw, 1991). Tagged specimens from the front and back of the specimen were mounted on carbon stubs and carbon coated using Fullam carbon coater. A Joel JXA-840A SEM with a Tracor Northern 5500 series II energy dispersive analyzer was used to analyze the specimens. Specimens were analyzed at 100X and 500X magnifications using 30 kV probe current. BEI and x-ray analysis were used. The y-axis scale (VFS) was set at 4098 so visual comparisons of graphs could be made. X-ray analysis time was 20 seconds; the x-axis energy range was 0 to 20 Kev.

RESULTS AND DISCUSSION

Figures 1-4 show the percent diazinon remaining in the contaminated fabrics. The finish was effective in providing the barrier protection, and thus a very low percentage of diazinon residue remained in 0 kJ/m^2 exposure specimens (highest value was 2.07%). The amount of pesticide remaining in the fabric was reduced significantly after 10 kJ/m^2 of exposure for all four exposure conditions. The amount was further reduced in most specimens after subsequent exposure. There was no significant difference in the percent diazinon remaining after 20, 40, and 80 kJ/m^2 exposures to simulated sunlight. Statistically, the blend cotton/polyester fabrics had a higher percentage of residue remaining in the fabric than did the cotton and polyester fabrics (Table 3). GC results also indicate the amount of pesticide residue was higher in low humidity specimens. However, from a practical perspective, the percentage of pesticide remaining in the fabric was very low, and the statistically significant differences mentioned above were not different for practical purposes.

The SEM results were very interesting. The BEI of 0 kJ/m^2 exposure specimens indicated the presence of diazinon labeled with osmium tetroxide (bright areas), which was confirmed by the osmium peaks on x-ray analysis (Figures 5 top & 6). However, in specimens exposed to simulated weathering conditions, the pesticide mass was seen on BEI images, but the brightness decreased as level of exposure was increased from 0 to 20 kJ/m^2 (Figure 5). After 40 kJ/m^2 exposure, very few bright spots were seen. The absence of osmium was confirmed by x-ray analysis. This suggests that the pesticide formulation had degraded. To verify whether the active ingredient was being labeled, the additional fabrics specimens were contaminated as follows: 1) active ingredient (technical grade), 2) formulation, and 3) inert ingredient. The contaminated fabrics were exposed to 85 % humidity and the all light cycle and then labeled. The results of technical grade diazinon were similar to that of the formulation, whereas the inert specimens did not accept the osmium tetroxide label. As seen in Figure 6, the osmium peaks for 0 exposure of formulation and technical grade were high. Inert ingredient fabric specimens had no osmium peaks. However, after 40 kJ/m^2 exposure the x-ray analyses for technical grade and formulations show no high intensity peaks above background. This indicates that osmium tetroxide tagged the active ingredient, and after exposure to 40 kJ/m^2, the diazinon degraded.

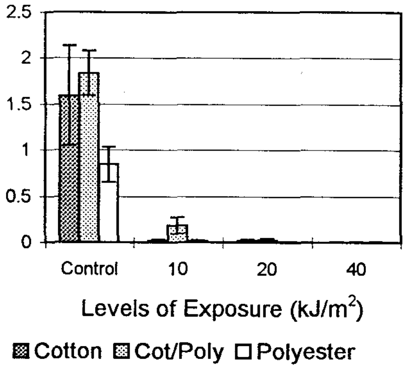


Figure 1. Percent diazinon remaining in control and fabrics exposed to 30% relative humidity, all light cycle

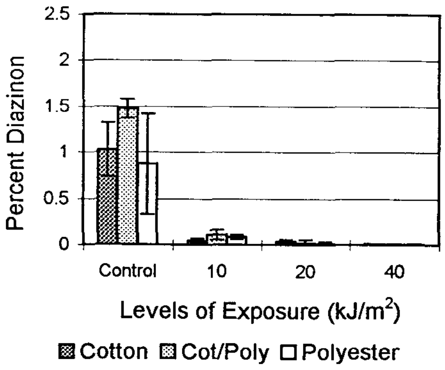


Figure 2. Percent diazinon remaining in control and fabrics exposed to 85 % relative humidity, all light cycle

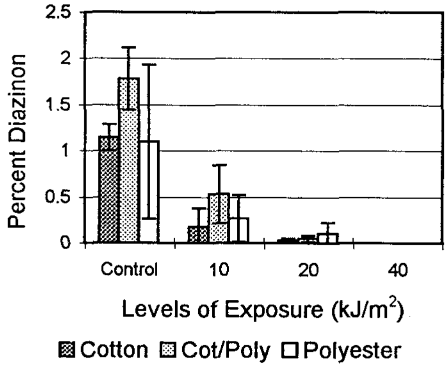


Figure 3. Percent diazinon remaining in control and fabrics exposed to 30% relative humidity, dark and light cycle

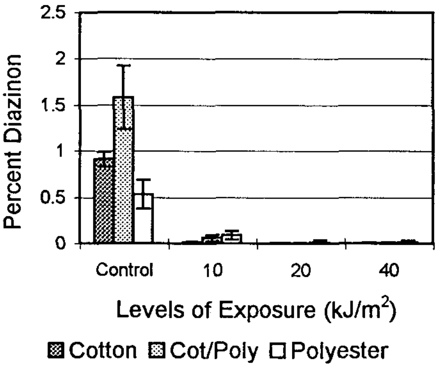


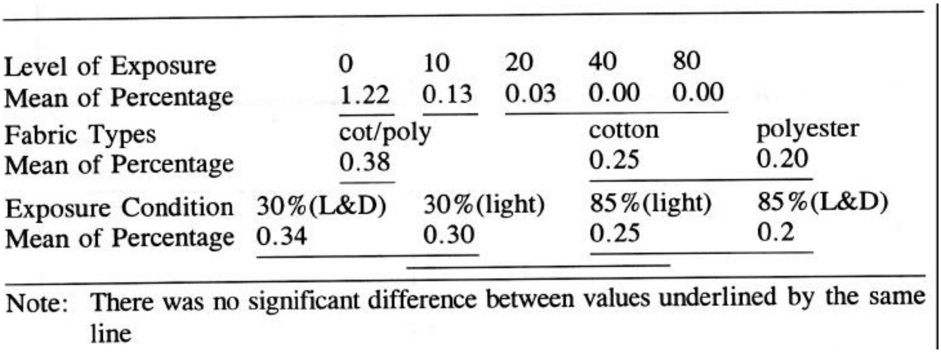
Figure 4. Percent diazinon remaining in control and fabrics exposed to 85% relative humidity, dark and light cycle

Table 2. Analysis of variance of percent diazinon remaining on fabrics

Source	d.f.	F-Value	Prob. > F
Level of Exposure	4	305.60[a]	0.0000
Fabric Types	2	16.57[a]	0.0000
Exposure Conditions	3	4.41[a]	0.0057
Level * Fabric	8	12.21[a]	0.0000
Level * Condition	12	2.54[a]	0.0052
Fabric * Condition	6	0.79	0.5780

[a] Significance at 0.05 level

Table 3. Least significant differences (LSD) pairwise comparisons of percent means



Level of Exposure	0	10	20	40	80
Mean of Percentage	1.22	0.13	0.03	0.00	0.00
Fabric Types	cot/poly			cotton	polyester
Mean of Percentage	0.38			0.25	0.20
Exposure Condition	30%(L&D)	30%(light)		85%(light)	85%(L&D)
Mean of Percentage	0.34	0.30		0.25	0.2

Note: There was no significant difference between values underlined by the same line

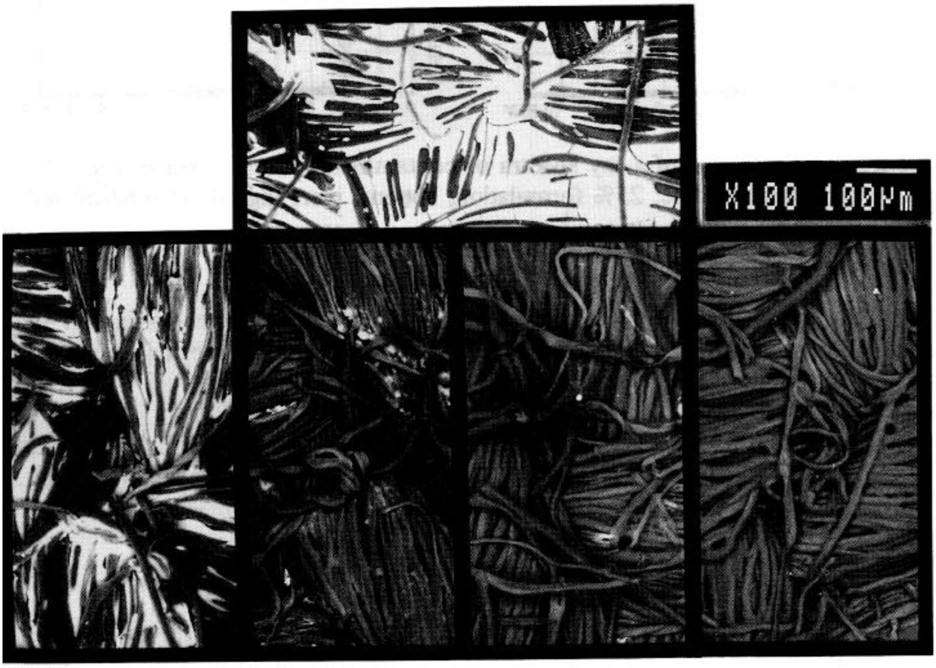


Figure 5. Backscattered electron images of contaminated fabric surfaces (top: 0 kJ/m^2; bottom, left to right: 10, 20, 40 & 80 kJ/m^2)

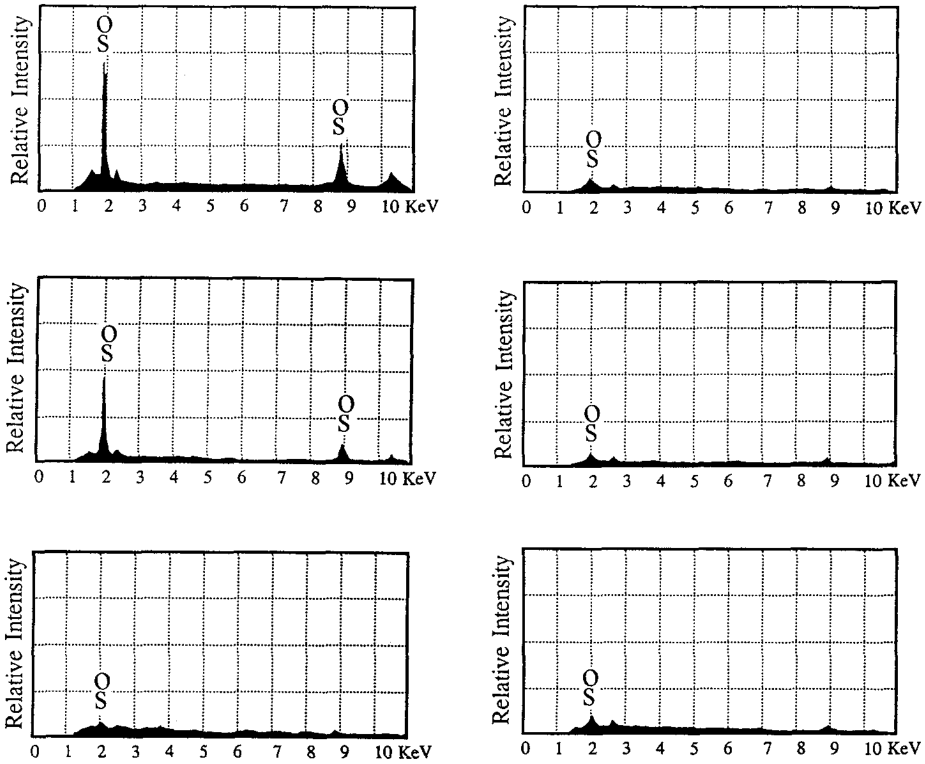


Figure 6. Comparison of x-ray spectra of contaminated fabric surface (top: 95 % active ingredient; middle: 25% formulation; bottom: inert ingredient 0 kJ/m^2 left, 40 kJ/m^2 right)

The results of this study show that exposure to sunlight may assist in the decontamination of pesticides in textile materials. Additional work is needed in this area to study the fate of pesticide after photodegradation.

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