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Removal of Organophosphorus, Organochlorine and Synthetic Pyrethroid Insecticides and Organochlorine Fungicides from Coverall Fabric by Laundering

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The removal of pesticide residue from fabric by laundering has been shown to be partially dependent on the water solubility of the formulation being used. Easley et al. (1983) showed that 2,4-D amine, which is readily water-soluble, is easily removed from fabric by laundering while the ester formulation, which is relatively non-soluble, is retained to a larger degree. Laughlin et al. (1985) studied three formulations of methyl parathion - emulsifiable concentrate, wettable powder, and encapsulated - and found that the emulsifiable concentrate was more difficult to remove than the other two formulations which were more water soluble. Laughlin et al. (1985) reported that dilute formulations of methyl parathion were much easier to remove than the concentrated pesticide which, even after ten launderings, left high residues of the insecticide; hence, where clothing has come into contact with highly toxic and concentrated pesticide, the clothing should be disposed of either by burning or burying. Spills of methyl parathion which had been diluted to field strength were adequately removed after three launderings. Easley et al. (1984) reported that clothing items worn during pesticide use should be laundered separately from the rest of the family wash to avoid transfer of pesticide to other clothing and that after laundering of pesticide-contaminated clothing, the machine should be put through an empty load cycle to minimize contamination of subsequent laundry. It was also reported that hot water (60^{o}) was more efficient in pesticide removal.

This paper describes the results of a study designed to compare different classes of insecticides and fungicides from the standpoint of laundering efficiency of treated fabrics.

MATERIALS AND METHODS

Fabric was cut into strips measuring 10 cm x 20 cm and the edges were sewn to prevent fraying. The strips were laid out on newspaper in a spray cabinet and sprayed using an overhead movable nozzle mounted in the cabinet. The nozzle was driven by an electric motor and pulley and spray pressure was provided by liquid carbon dioxide.

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Fabric strips consisting of 100% cotton, 17 x 26 threads per cm were laid out in a random block design, replicated four times, and sprayed with captan {3a,4,7,7a-tetrahydro-2- [(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione}, cypermethrin [cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate], endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide), and malathion [diethyl(dimethoxyphosphinothioyl) thiobutanedioate] at a rate calculated to deliver 10 ug/cm^2 in 0.45 ml water. The patches were allowed to air-dry and then placed into plastic bags and held for 5 and 52 hours before laundering. Laundering was carried out in a household General Electric (Talisman^R) washing machine. The single wash cycle was 15 min in length and was followed by a regular rinse cycle. The double wash cycle was a repeat of the single wash. Water temperature was 40^oC using a detergent of S-A-8 Plus Laundry Concentrate (AMWAY). Presoaking consisted of immersion in warm water to which an ammoniacal solution (Old Dutch^R) had been added at the rate of 155 ml/2L water; pre-soak was carried out for one hour prior to laundering. Unsprayed fabric strips (four replicates) were added to the treated strips in the washer to determine the extent of residue transfer from the single wash and also from the pre-soak and single wash.

Fabric strips consisting of 50% cotton and 50% polyester with 21 x 33 threads per cm were laid out in random fashion with four replicates in a block design and all were sprayed with diazinon {0,0-diethyl 0-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate}, dicloran (2,6-dichloro-4-nitrobenzenamine), dicofol {4-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)benzenemethanol}, and permethrin {3-phenoxyphenyl(1RS)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate} at a rate calculated to deposit 1 ug/cm^2 of each compound in 0.45 ml water. The patches were allowed to air-dry and then placed into plastic bags where they were held for 7 hours prior to laundering. Laundering was carried out in a household General Electric washing machine. The single wash cycle of 12 min was followed by a spin and double rinse cycle taking another 20-23 min. The double wash was a repeat of the single wash. Pre-soaking included immersion in warm water for one hour using detergent (SD-8 Plus laundry concentrate) followed by laundering cycles as above. Pre-spray was conducted using Amway Prewash Laundry Spray^R as prescribed on the container followed by laundering within 5 min as described above for single and double washes. Unsprayed patches were added to the pre-soaked and double/washed laundry to determine the amount of pesticide transfer via the laundry water.

Laundered and unlaundered patches were soaked in 250 ml dichloromethane for 16 hr (overnight); the solvent was decanted off as much as possible and the swatch and jar were rinsed with an additional 100 ml dichloromethane which was combined with the original extract. The extracts were evaporated just to dryness with rotary vacuum and residues were redissolved in 5.00 ml hexane. A measured portion (1.0 ml) of this extract was removed

for analysis of malathion and diazinon without further cleanup. The remainder of the extract was cleaned up on Florisil as described by Mills et al. (1972) and by Braun and Stanek (1982).

Malathion and diazinon were determined by gas chromatography with flame photometric detection (P-mode) using a 15 m x 0.53 mm fused silica column with 8 ml/min helium carrier gas. Oven temperature was programmed at 5°/min from 150°C with 0 hold time to a final temperature of 200°C.

Endosulfan, dicloran, and captan were determined by gas chromatography with constant current electron capture detection and isothermal operation at 190°C using a 1.8 x 2 mm i.d. column packed with 1.5% OV-17/2.0% OV-210 on Gas Chrom Q. Cypermethrin and permethrin were also determined by electron capture detection using the conditions described by Braun and Stanek (1982).

Recoveries were determined by applying 100 ug of each compound (in acetone) to similar-sized swatches, allowing the acetone to evaporate, and placing in a closed jar at ambient temperature for 6 hr; the compounds were then extracted and concentrated according to the above procedure. Recoveries ranged from 92% to 104% (2 replicates) and were acceptably close to 100% so that analytical results are not adjusted for recovery.

RESULTS AND DISCUSSION

Two laundering experiments were carried out in which two pesticides from each of four different chemical groups were chosen in an attempt to measure and compare the effectiveness of conventional laundering practices in removing these chemicals from treated fabrics. The four groups included organochlorine fungicides (OCF), organochlorine insecticides (OCI), organophosphorus insecticides (OPI), and synthetic pyrethroid insecticides (SPI); pesticides included in each group respectively were captan and dicloran, dicofol and endosulfan, diazinon and malathion, and cypermethrin and permethrin (Table 1 and 2).

Differences in extent of removal of pesticides by laundering were noted between the different groups and individuals within the groups. The OCF and OPI were more readily removed than the OCI and SPI. The mean overall removal (average of all laundering treatments) was captan - 100%, dicloran - 96.6%, malathion - 99.8%, diazinon - 97.7%, dicofol - 79.3%, endosulfan - 73.9%, cypermethrin - 76.6% and permethrin - 66.7%.

All laundering procedures removed captan to the maximum of 100%. Double washing was required for maximum removal of cypermethrin, diazinon, dicloran, and endosulfan and the removal of cypermethrin and endosulfan was significantly greater when the double wash was carried out within 5 hours of spraying; when left for 52 hour prior to laundering, pre-soaking and double washing was required before less than 10% of cypermethrin and endosulfan remained on the fabric. Dicloran and malathion exhibited only

small differences between single and double washings; with single washing dicloran and malathion were removed to the extent of 96.3% and 99.8%, respectively while double washing removed 97.9% and 99.7%, respectively. Double washing was significantly more effective in removal of cypermethrin, diazinon, and endosulfan than was the single wash. Permethrin and dicofol required pre-spray and double wash for best removal.

Combining non-treated fabric strips with the treated strips during the laundering operation resulted in significant transfer of the active ingredients to the non-treated fabric. The amounts ranged from 0% for captan to a high of 3.8% for dicofol when expressed as a percentage of the original deposit on the treated strips (Table 1 and 2).

Rigakis (1985) stated that the water solubility of the formulation was an important factor in the removal of pesticides from clothing. Research by Easley et al. (1983) and Laughlin et al. (1985) indicated similar correlations with different formulations of 2,4-D and permethrin. In this study, the authors attempted to correlate laundering efficiency with chemical groups. Table III lists the water solubility of the active ingredients used and reasonably good co-relation is obtained between water solubility vs. ease of removal from fabric by laundering. The fact that captan was so effectively removed is more likely due to its ease of degradation by hydrolysis rather than its solubility in water. Frank et al. (1983) calculated the half-life of captan to be less than 1 hour at 22°C at pH 8.5; under the conditions of this study with water at 40°C and pH 7.6, the absence of captan in all laundered fabric was more likely the result of hydrolysis rather than solubility.

Disappearance of diazinon, malathion, and dicloran is in good agreement with the reported solubilities. Easley et al. (1981) removed methyl parathion to a similar extent as diazinon while Lillie et al. (1981) also showed similar results for diazinon and malathion. The organochlorine and synthetic pyrethroid insecticides were the most persistent and this property is in good agreement with their low solubility in water. Finley and Rogillio (1969) made similar observations when comparing the removal of methyl parathion and DDT; methyl parathion was removed to less than 1% while DDT varied from 7.2% to 21.2% remaining depending on the laundering treatment and type of fabric.

In this study, the less soluble active ingredients were formulated as emulsifiable concentrates while the more soluble were formulated as wettable powders. Easley et al. (1983) and Laughlin et al. (1985) proposed that laundering efficiency was dependent on formulation type. This study indicates that water solubility of the active ingredient is also a factor and possibly formulation type and water solubility of the active ingredient are both factors.

Easley et al. (1982a, 1982b) reported that water temperatures of 49° to 60°C are required for efficient removal of methyl

Table 1. Removal of three insecticides and one fungicide from coverall fabric by normal household laundering procedures (Experiment 1).

Laundering Procedure	Total Wash Time (min)	%Residue Remaining in Fabric (mean±SD) Captan OCF[1] (80 WP Captan)[2]	Cypermethrin SPI (250 EC Cymbush)	Endosulfan OCI (400 EC Thiodan)	Malathion OPI (25 WP Malathion)
1. Treated Strips	0	100±10	100±11	100±10	100±10
A. No Washing		(1450 ug)[3,4]	(2150 ug)	(1925 ug)	(2088 ug)
B. Air dried for 5 hours					
one wash	30	0	18.4± 5.8	25.4± 6.9	0.24 ±0.03
two washes	60	0	2.9± 3.2	5.0± 3.8	0.026±0.005
presoak - one wash	90	0	25.7± 2.9	29.4± 2.1	0.046±0.011
presoak - two washes	120	0	20.2± 8.9	24.9±11.	0.029±0.023
C. Air dried for 52 hours					
one wash	30	0	35.0± 6.5	42.6± 6.6	0.74 ±0.16
two washes	60	0	38.6± 8.6	35.7± 7.9	0.043±0.022
presoak - one wash	90	0	34.4±12.1	36.0± 6.5	0.050±0.008
presoak - two washes	120	0	12.2± 9.4	10.0± 5.1	0.031±0.003
2. Untreated Strips					
one wash	30	0	0.23± 0.20	0.68±0.22	0.17 ±0.06
presoak - one wash	90	0	0.40± 0.16	0.86±0.18	0.012±0.001
Limit of detection		<1.0 ug[4]	<1.0 ug	<0.2 ug	<0.5 ug

[1]OCF - organochlorine fungicides, SPI - synthetic pyrethroid insecticide, OCI - organochlorine insecticide, OPI - organophosphorus insecticide.
[2]80 WP = 80% wettable powder, 250 EC - 250 g/L emulsifiable concentrate, 400 EC - 400 g/L emulsifiable concentrate, 25W - 25% wettable powder.
[3]Captan likely degraded in solution before spraying carried out.
[4]ug per 200 cm^2 of fabric, initial concentration.

Table 2. Removal of three insecticides and one fungicide from coverall fabric by normal household laundering procedures (Experiment 2).

Laundering Procedure	Total Wash Time (min)	%Residue Remaining in Fabric (mean±SD) Diazinon OPI[1] (50 WP Diazinon)[2]	Dicloran OCF (75 WP Botran)	Dicofol OCI (187.5 EC Kelthane)	Permethrin SPI (500 EC Ambush)
1. Treated Strips	0	100±12	100±14	100±11	100±13
A. No Washing		(286 ug)[3]	(160 ug)	(178 ug)	(143 ug)
B. Dried for 7 hours					
one wash	35	3.5±1.1	3.7±0.1	18.0±1.7	44.8±2.8
two washes	70	0.9±0.2	2.1±0.2	14.6±2.5	33.6±5.6
presoak - one wash	95	3.9±1.1	4.3±0.6	35.4±3.9	44.1±7.0
presoak - two washes	130	0.8±0.1	4.1±0.4	33.1±6.7	44.1±7.7
prespray - one wash	40	3.4±0.4	3.7±0.8	12.4±1.3	21.0±5.6
prespray - two washes	75	1.4±0.3	2.4±0.3	10.7±1.3	11.9±4.9
2. Untreated Strips					
presoak - two washes	130	0.2±0.1	0.6±0.1	3.8±0.4	2.9±0.1
Limit of detection		<0.1 ug	<0.1 ug	<0.5 ug	<0.5 ug

[1]OPI - organophosphorus insecticide, OCF - organochlorine fungicide, OCI - organochlorine insecticide, SPI - synthetic pyrethroid insecticide

[2]50 WP - 50% wettable powder, 75 WP - 75% wettable powder, 187.5 g/L emulsifiable concentrate, 500 EC - 500 g/L emulsifiable concentrate

[3]ug per 200 cm^2 of fabric, initial concentration.

parathion from denim fabric and that heavy duty liquid detergents performed better than dry detergents; in this study the dry detergent at a lower temperature appeared to work well. Kim et al. (1986) reported that alcohol as a pre-treatment to laundering did not work well but that perchloroethylene was effective. In this study the removal of the more insoluble pesticides was enhanced by pre-soaking and further enhanced by a pre-spray treatment.

When non-treated fabric strips were included in the wash during the laundering of the treated strips, significant levels of the organochlorine and synthetic pyrethroid insecticides were transferred from the treated material to the untreated; transfer of diazinon and malathion was considerably less and co-relation with water solubility is again indicated. These results support earlier findings by Easley et al. (1984) which led to the conclusion that pesticide-contaminated clothing should be laundered separately from the rest of the family wash.

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