PERSISTENCE AND TOXICITY OF CHLORPYRIFOS-METHYL IN CORNMEAL[1]

Henry A. Highland, Richard A. Simonaitis, and Ronald E. Boatright[2]
Stored-Product Insects Research and Development Laboratory
Agricultural Research Service, U. S. Department of Agriculture
Savannah, GA 31403
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ABSTRACT

Chlorpyrifos-methyl-treated polymer film produced residues of the insecticide in cornmeal from small bags wrapped in the film for 3 months. Residues increased during 6 - 9 months storage of the bags in the film bundles, but decreased between 9 and 12 months. Residues persisted during 6 to 12 months storage in jars following 3 to 12 months of storage in the treated film bundles. In the cornmeal, the higher residues tested (ca. 9 - 16 ppm) remained toxic to adults of the red flour beetle, *Tribolium castaneum* (Herbst), for up to 52 weeks.

Key Words: Persistence of chlorpyrifos-methyl, chlorpyrifos-methyl residues, chlorpyrifos-methyl-treated film.

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INTRODUCTION

Chemical residues in packaged foods resulting from the use of treated, insect-resistant packaging has been a critical factor in the development and use of such packaging. The treatment is essential to prevent penetration of packages by boring insects and to help repel insects that enter through existing openings in the package. Highland et al. (1966) showed that treated packages can be used without the occurences of unsafe residues. In these investigations, composited samples of rice, dried milk, beans, or flour stored in treated paper bags contained 0.2 to 6.28 ppm of piperonyl butoxide, depending on the commodity and length of storage. These residues were well within the legal tolerance of 10 ppm (Anon 1975). These residues can be greatly reduced by a greaseproof paper barrier ply in the multiwall paper bags (Highland et al. 1972). Highland et al. (1984) also found that the same greaseproof paper is an effective barrier to the migration of permethrin from the outer treated ply of paper bags into CSM, a high protein, corn-based cereal. However, laboratory tests (results unpublished) have shown that greaseproof paper does not prevent the movement of chlorpyrifos-methyl from treated film into bags of dry pet food.

During investigations to develop chlorpyrifos-methyl-treated polymer films to protect small bags of cornmeal from infestation, chloryprifos-methyl residues were found in the cornmeal (Highland et al. 1984). This paper describes tests to determine the persistence of the residues and toxicity of the residues to the red flour beetle, *Tribolium castaneum* (Herbst).

[1] This papers reports the results of research only. Mention of a pesticide does not constitute a recommendation by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended.
[2] Research Entomologist, Research Chemist, and Biological Technician, respectively.

MATERIALS AND METHODS

The test packages as described by Highland et al. (1984) consisted of paper bags of cornmeal wrapped in chlorpyrifos-methyl-treated film.[3] There were 2 tiers of paper bags, each bag containing 0.9 kg of cornmeal, and closed with a wire tie. Each bundle contained 12 bags, and measured ca. 39.4 × 29.2 × 12.7 cm. The film contained either 377 or 1318 mg/m^2 of chlorpyrifos-methyl. Half the bundles were made with both ends of the sleeve of film heat-sealed, totally enclosing the bags, before the bundles were heated to 232C for 9 seconds. The other half of the bundles were left with open ends before passing them through the heat tunnel. The film on this type of bundle is frequently heated to shrink the film for easy handling of the bundle.

Previous tests of film treated with chlorpyrifos-methyl showed that the insecticide was released from the treated film, killing most of the insects in a simulated warehouse and used as a testing room. Therefore, the bundles were on pallets in a room (72.5 m^3) equipped with an exhaust fan that exchanged the air ca. 21 times per h. The fan operated continuously for the first 12 days, then for four 2-h periods daily for ca. 4 months, then for two 1-h periods daily for 2 months. Finally, the fans operated for two 0.25-h periods for most of the remainder of the test. Temperatures ranged from 21C to 32C, and relative humidity from 45% to 75%. The room was kept on 12L:12D photoperiods.

Samples were taken at 3-month intervals for one year for chemical analyses and subsequent toxicity tests. The samples were taken from one bag in the bottom and middle bundles of the 3-bundle stack. All samples were held at < 0C until the initial analyses were conducted after 3, 6, 9, and 12 months of storage. Subsequently, samples were held in jars with metal lids at 26.7 ± 1C for future chemical analyses and toxicity tests. Analyses were conducted according to the method described by Highland et al. (1984).

Toxicity tests were conducted with the cornmeal samples taken from the bags after 3, 6, 9, and 12 months of storage in the treated film bundles, then after intervals of 2 to 52 weeks storage in jars as shown in Table 2. Twenty-five 1- to 7-day old unsexed adult red flour beetles, *Tribolium castaneum* (Herbst), were confined on each of three samples of cornmeal for 7 days. The insects were then sifted from the cornmeal and counted as dead if no movement was discernible with the naked eye. Controls consisted of cornmeal taken from bags stored 3 months in untreated film bundles. The data were analyzed using Duncan's multiple range test at $P < 0.05$ level (Duncan 1951).

RESULTS AND DISCUSSION

Chlorpyrifos-methyl residues persisted in the cornmeal for at least 18 months, at which time the tests were terminated (Table 1). Within 3 months the cornmeal from bundles with film containing 377 mg/m^2 of chlorpyrifos-methyl contained 4.09 - 4.54 ppm of the insecticide (Table 1). Residues in cornmeal from bundles wrapped with film containing 1318 mg/m^2 of chlorophyrifos-methyl ranged from ca. 9 to 24 ppm. There was no consistent difference between residues in cornmeal from open-end or sealed-end bundles. In the 3 periodic tests up to 9 months of

[3] Treated films supplied by Dow Chemical Company, Granville, OH.

Table 1. Chlorpyrifos-methyl residues in cornmeal from paper bags stored in treated film bundles followed by storage in glass jars; average of 3 replicates.

Chlorpyrifos-methyl content of film mg/m^2)	Bundle configuration*	Residue (ppm) in cornmeal after storage in Bag and Jar 3 mo	Bag and Jar 12 mo	Bag and Jar 6 mo	Bag and Jar 12 mo	Bag and Jar 9 mo	Bag and Jar 9 mo	Bag and Jar 12 mo	Bag and Jar 6 mo
377	S	4.09	2.37	4.71	2.91	3.91	2.50	2.68	2.66
377	O	4.54	–	4.45	2.14	4.61	2.41	1.63	2.67
1318	S	13.85	13.15	18.13	13.80	21.40	14.10	14.47	13.07
1318	O	16.68	9.19	24.20	14.23	20.28	9.89	13.64	15.97

* S – sealed ends; O – open ends.

Table 2. Mortality of red flour beetles exposed to residues of chloropyrifos methyl in cornmeal stored in bags from treated film (1318 mg/m^2) bundles, followed by storage in jars.

Bundles configuration*	Storage in jars (weeks)	Percent mortality after storage for† 3 mo	6 mo	9 mo‡
S	24/25	89.3 a	90.7 abcd	98.7 a
O		86.7 a	93.3 abcd	78.7 abcd
S	28	93.3 a	97.3 ab	89.3 abc
O		88.0 a	98.7 a	62.7 d
S	32	90.7 a	97.3 ab	97.3 ab
O		77.3 a	96.0 abc	68.0 cd
S	36	76.0 a	94.7 abc	88.0 abcd
O		70.7 a	94.7 abc	72.0 bcd
S	40	85.3 a	94.7 abc	
O		84.0 a	90.7 abcd	
S	44	86.7 a	81.3 d	
O		84.0 a	86.7 abcd	
S	48	88.0 a	85.3 bcd	
O		92.0 a	84.0 cd	
S	52	81.3 a	81.3 d	
O		68.0 a	86.7 abcd	

* S – sealed ends; O – open ends.

† Means followed by the same letter in each column are not significantly different at $P = 0.05$ level [Duncan's (1951) multiple range test].

‡ Cornmeal stored in bags 12 months produced 91 - 100% toxicity during 20 weeks storage in jars.

storage, residues in cornmeal in bundles with the higher treatment ranged from ca. 13.8 ppm to 24.2 ppm.

The extreme persistence of the residues is shown by the residues remaining after the cornmeal was removed from the bags and stored in jars at ambient temperatures. At least half (but generally more) of the residues persisted during 6 to 9 months storage in jars, following 3 to 12 months of storage in the bundles.

At 12 months the films originally containing 377 or 1813 mg/m^2 of chlorpyrifos-methyl contained only ca. 0.5 and 3.0 mg/m^2, respectively (Highland et al. 1984).

Cornmeal stored 3 months in bundles wrapped with film containing 377 mg/m^2 of chlorpyrifos-methyl produced almost no toxicity after aging 2 weeks in jars. The second generation adults appeared in these jars at 23 weeks, while in untreated check cornmeal second generation adults appeared in 10 weeks.

Highly toxic residues persisted in cornmeal from bundles wrapped with film containing 1318 mg/m^2 of chlorpyrifos-methyl, even after 52 weeks of storage in jars. From 68.0 to 81.3 percent of the insects died when confined on cornmeal stored 52 weeks in jars following 3 months storage in the bundles (Table 2). Similar results were obtained with cornmeal stored 48 to 32 weeks in jars after 6 and 9 months, respectively, of storage in treated bundles. Residues ranged from 9.19 ppm to 15.97 ppm in cornmeal stored for 6 or 9 months in jars, following 3 to

12 months' storage in the bundles. Thus, even after 18 months much of the chlorpyrifos-methyl remained in the cornmeal.

Similar results were reported by LaHue (1977) who found that ca. one-third of initial chlorpyrifos-methyl deposits on wheat were recovered after 1 year of storage. However, in his tests all *T. castaneum* died when confined for 21 days on wheat treated with as little as 3 ppm of chlorpyrifos-methyl, indicating a higher availability of the insecticide on wheat than on cornmeal.

The results of these tests indicate that high, persistent residues result from movement of chlorpyrifos-methyl from treated film wraps into bags of cornmeal. Such residues would preclude the use of this insect-resistant film as food packaging unless excessive residues were prevented.

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