

US EPA ARCHIVE DOCUMENT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: FAP# 5H5080. Chlorpyrifos in food handling establishments. Evaluation of analytical methods and residue data.

DATE: JUL 28 1975

FROM: A. Rathman, Chemist, Chemistry Branch
Registration Division (WH-567)

TO: Product Manager No. 12 (F. Sanders)
and Toxicology Branch

THRU: Chief, Chemistry Branch *RJL 7/28/75*

THRU: Petitions Control Officer

Dow Chemical is proposing a food additive regulation to permit use of the insecticide chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate] in food handling establishments (including food service, food manufacturing and food processing establishments, such as but not limited to restaurants, grocery stores, bakeries, bottling plants, grain mills and canneries) where food and food products are held, processed, prepared or served. To assure safe use of the insecticide it shall be used in conformance with the label and labeling registered by EPA.

Pesticide tolerances have been established on a number of commodities at levels of 0.05-1.5 ppm, including tolerances for meat and milk (Sec. 180.342).

Conclusions

1. The fate of chlorpyrifos from the proposed premise use is adequately delineated; low level residues could result from either volatilization and/or spray drift. Additionally, the parent compound is the residue of concern.
2. We consider that adequate methods are available for regulatory purposes.
3. In a very limited number of instances low levels of residues may result in food as a result of the proposed crack and crevices and spot treatments. These cases of contamination of food products are more likely to result in food service establishments than in food manufacturing or processing establishments. We would not expect residue levels to exceed 0.01 ppm.
4. Although we do not consider it necessary for the petitioner to propose a numerical tolerance level, we believe the use should be circumscribed in any final regulation.

Recommendation

We recommend for the establishment of the proposed regulation contingent upon the following:

1. Revision of Section B as follows:

a. A statement should be included on the label that DDVP or pyrethrins are not to be used in combination with chlorpyrifos in food handling establishments. If the petitioner wishes to have a combination use registered, we will need data reflecting treatments of the mixed compounds. Additionally, the regulations for these compounds would have to note that combinations were acceptable for use in food areas.

b. Inclusion of a statement for spot treatments that any individual spot will not exceed 2 square feet.

c. Limit treatment to the nonfood areas of industrial, institutional and commercial buildings (page B6 of submitted "label copy") since any food areas in these establishments would be covered as food handling establishments. (See definition of food handling establishments FR 38 No. 105, 8/10/73, p 21685.)

2. Revision of Sec. F. We suggest the last sentence of the proposed regulation be changed to the following: To assure safe use of the insecticide, application shall be limited to spot and/or crack and crevice treatments only. The spray concentration shall be limited to a maximum of 0.5% active ingredient. For crack and crevice treatments, equipment capable of delivering a pin-stream of insecticide should be used. For spot treatments, a coarse low pressure spray should be used to avoid atomization or splashing of the spray. Contamination of food or food contacting surfaces should be avoided. Additionally, the regulation should be proposed for inclusion in Sections 123 and 561 of Title 21.

3. Clearance of the inerts (and the oil to be used in the oil-base spray) under Sections 123 and 561. The oil should be specified on the label.

Note: Considering the low levels [redacted] we would not expect a residue problem from these inerts and we defer to TOX on their clearance. We do suggest that information on the identification of [redacted] be obtained. Additionally, considering the levels of xylene and [redacted] in the formulations, some information should be obtained by the petitioner on the levels

Inert Ingredient Information is not Included

of these compounds that may result in foods. Identification of [redacted] should also be obtained.

Detailed Considerations

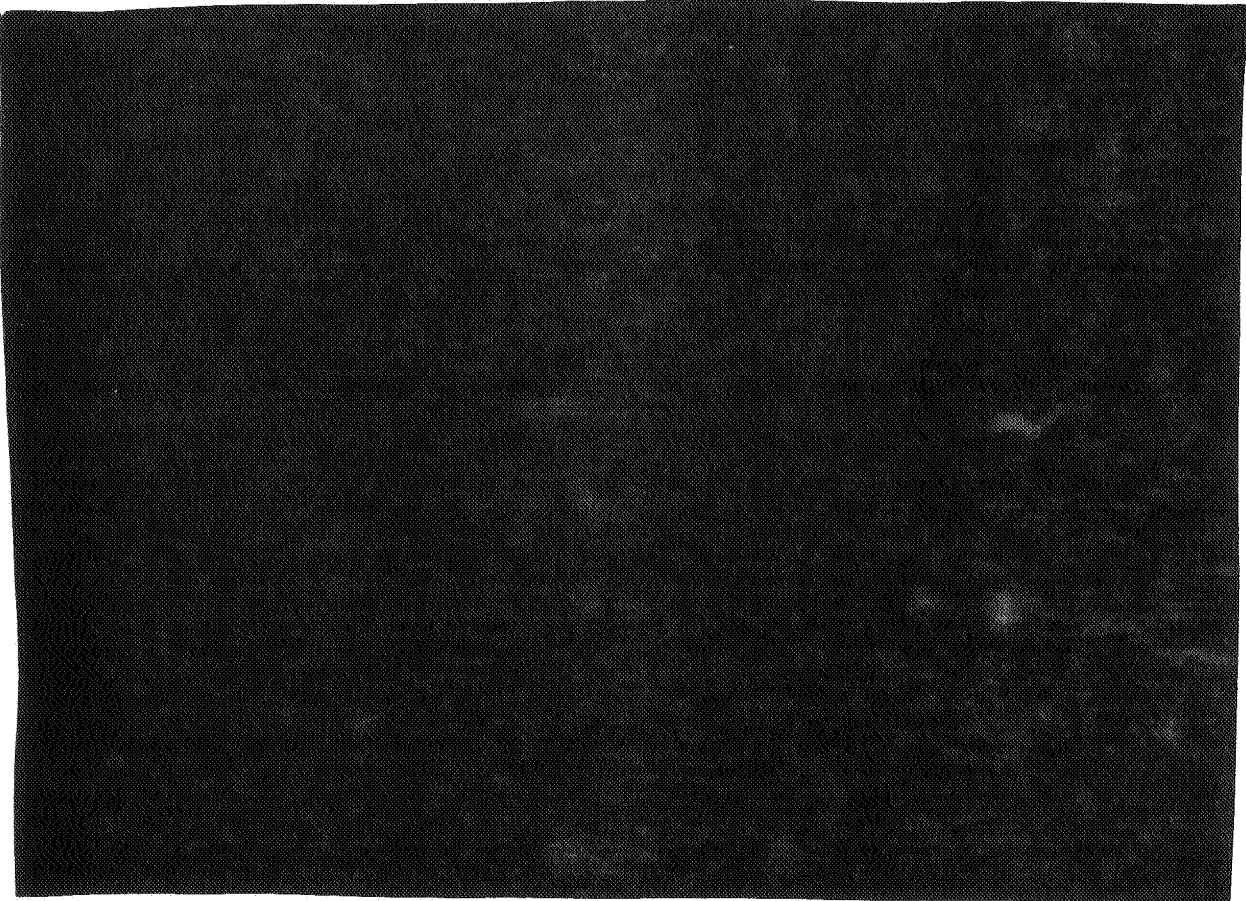
Formulation

The manufacturing process was discussed in the review of PP# 4F1445 (A. Smith memo of 5/3/74). The technical material is a minimum of 94% pure [redacted] of the technical product.

The compound is to be formulated as Dursban 2E (containing 2 lbs. chlorpyrifos/gal) and [redacted]. These products are formulated as follows:

Dursban 2E

Chlorpyrifos	22.4%
Xylene (mixture of o, m and p xylenes)*	42.1%



*C Teared under Sec 180.1001(c)

Inert Ingredient Information is not Included
Commercial/Financial Information is not Included

It should be noted that none of the inerts are cleared under Sections 123 and 561 for use in food handling establishments. We therefore defer to TOX concerning the clearance of these compounds. We do suggest that additional information be requested on the composition

[REDACTED] we would not expect a residue problem from these inerts. We do believe some information should be submitted on the levels of xylene and [REDACTED] that might result from these uses. Additionally, the petitioner is proposing the use of water-based or oil-based spray solutions; the oil to be used should be specified and clearance under Sections 123 and 561 be obtained.

Proposed Use

For use on indoor pests, general instructions specify a spray concentration of 0.25-0.5% active chlorpyrifos in either water or oil. The low rate is for light infestation and the high rate is to quickly reduce heavy infestations (or for control of certain insects). There is a note directing that where quick "knockdown" and/or "flushing action" is desired DDVP or pyrethrins may be added to the spray mixture. These compounds are not yet registered for spot treatment use in food areas of food handling establishments and although the label states that all use and handling precautions for these products should be followed, we believe that label should state that DDVP or pyrethrins are not to be used in combination with chlorpyrifos in food areas of food handling establishments. If the petitioner wishes to have a combination use registered, we will need data reflecting treatments of the mixed compounds. Additionally, the regulations for these compounds would have to state that combinations were acceptable for use in food areas.

Application of chlorpyrifos within food areas of food handling establishments including restaurants, grocery stores, bakeries, bottling plants, canneries and grain mills is to be made to control certain insects (such as cockroaches, ants, crickets, spiders and silverfish). Spot treatments to localized areas where the pests have been seen or are suspected of hiding or entering are to be made with coarse, low pressure sprays. Apply only enough spray to cover surfaces thoroughly using care to avoid unnecessary runoff. Areas that may be treated include dark corners of rooms and closets; along and behind baseboards; beneath and behind stoves, refrigeration units and similar food preparation areas and equipment; floor drains; and around plumbing and other utility installations.

Inert Ingredient Information is not Included

It is noted that spot treatment may encompass crack and crevice treatment by applying small amounts of spray directly into openings leading to voids and hollow spaces in walls, equipment legs and bases which occur at points between different elements of construction or between equipment and floors.

The spray is not to be introduced into the air or allowed to contact food or food-contacting surfaces.

Treatments may be made as needed but not more often than once every 7 days in restaurants and similar food service establishments or more often than once every 14 days in other types of food handling establishments. In case of emergency (call back) chlorpyrifos may be applied after 2 days from last treatment but emergency should be limited to once per month.

The directions for the spot treatment should contain the statement that any individual spot treatment must be limited to an area not to exceed 2 square feet.

Sec. B (page B6 of submitted label copy) also includes proposed labeling for the use of chlorpyrifos in food and nonfood areas of residential buildings including homes and apartment buildings and within industrial, institutional and commercial buildings including hospitals, stores, manufacturing plants and warehouses. The petitioner should be informed that a food handling establishment is defined as "an area or place other than a private residence in which food is held, processed, prepared and/or served." (FR 38 No. 105, 8/10/73, p. 21685). Therefore this section of the label should be revised to limit application to the nonfood areas of industrial, institutional and commercial buildings because any food areas in those buildings would be covered as food handling establishments.

Nature of the Residue

The fate of chlorpyrifos on plants from a field type of use was discussed most recently in our review of PP# 5G1595 dated 5/2/75.

Some of the information concerning the fate of chlorpyrifos on plants is applicable to the use under consideration here. The compound has been shown to be volatile and therefore we would expect contamination of food to result from both spray drift and volatilization.

Application of ¹⁴C ring-labeled chlorpyrifos to the surface

of growing corn and bean plants showed that a small amount of activity was absorbed into the plant. This absorbed activity was shown to consist primarily of 3,5,6-trichloro-2-pyridinol (TCP) in either free or conjugated form. To show that residues of TCP were not present as a result of the use in food handling establishments, analyses for TCP residues were performed on several samples taken from the treated areas. No detectable (less than 0.05 ppm) TCP residues were found in any of the samples that were analyzed for this compound.

We, therefore, consider the fate of chlorpyrifos from this use adequately defined, with the parent compound the residue of concern.

Analytical Methods

Residue data were obtained by the following methods for chlorpyrifos and TCP:

Chlorpyrifos - Dow's method ACR 73.4

Residues are extracted from the sample by blending with acetone. An aliquot is evaporated, taken up in hexane and the residue partitioned into acetonitrile. The acetonitrile is mixed with water and the residue is partitioned back into hexane. The residue is then cleaned-up on Florisil. Chlorpyrifos is then determined by gas chromatography using a flame photometric detector with a 526 m μ (phosphorus specific) filter. The method is modified slightly for some of the various substrates involved in this petition. Numerous samples were fortified at levels of 0.01-0.5 ppm with recoveries ranging from 60-135% (with the majority in the range of 80-110%). Blanks were all less than 0.01 ppm. We consider the practical limit of method sensitivity to be 0.01 ppm; residue levels of 0.005-0.01 ppm could be estimated but quantitation would be difficult. Any residue below 0.005 ppm would be essentially impossible to detect because of background noise.

TCP - Dow's method ACR 71.19R

The method involves heating the sample with 10% sodium hydroxide in methanol and extracting by blending and shaking. (Any chlorpyrifos present is hydrolyzed to TCP so that the analysis is for total TCP. Duplicate samples must be analyzed for chlorpyrifos. The TCP is then determined by difference. The hydrolysis step also releases any TCP present in a conjugated form.) An aliquot of the methanol is evaporated to near dryness and taken up in water. After the addition of HCl and NaCl, the TCP is extracted into benzene. The benzene phase is chromatographed on the acidic

alumina column using ethyl ether/pH 6.5 buffer mix. The ether eluate is partitioned with sodium bicarbonate which is acidified and the residue partitioned into benzene. The benzene phase is treated with BSA (N,O-bis(trimethylsilyl) acetimide) to form the pyridinol trimethylsilyl derivative, which is determined by ECGC. Blanks were less than 0.05 ppm with recoveries averaging 74% at a fortification level of 0.1 ppm.

These methods are essentially the same as methods successfully tested by AMS for residues of chlorpyrifos and TCP in meat (PP# 3F1306) and TCP in bananas (PP# 3F1370). Therefore, we conclude that the method is adequate for regulatory purposes. It should be noted that TLC and the determination of p-values of chlorpyrifos are available as confirmatory techniques.

Residue Data

Residue studies were conducted in two cafeterias, a restaurant, supermarket, bottling plant, bakery, grain mill and a cannery. These establishments are representative of food service, manufacturing and processing.

The two cafeterias were treated with an aqueous spray containing 0.5% active chlorpyrifos. Each cafeteria was sprayed twice (14 day interval between applications) with treatment reflective of typical spot treatments in both food and nonfood areas of these establishments. Samples were taken immediately after each treatment and at 1, 7 and 13 days after each treatment. Samples consisted of complete meals and several individual foods that were close to the spraying and not covered. These included lard, potato salad and pineapple upside-down cake. These items were 1-3 feet from treated areas.

The restaurant was given three separate spot treatments, the first two with a 0.5% water-base spray and the third with a 0.5% oil-base spray. The second treatment was 2 days after the initial treatment and the third treatment was 7 days after the initial treatment. Samples consisted of complete meals for three consecutive meal periods beginning with the first meal period after each treatment.

The supermarket, bottling plant and bakery were also given three separate treatments, all with a 0.5% water-base spray. As in the restaurant, the second treatment was made 2 days after the initial treatment; however, the third treatment was made 14 days after the initial treatment. Samples were taken immediately after the first and second treatments and immediately before and after the third treatment. The samples from the supermarket

consisted of representative exposed and packaged foods which were in the area of the spraying. Samples from the bottling plant and bakery consisted of the final commercial product.

The grain mill and the canning plant were given two separate spot treatments with a 0.5% water-base solution. Samples (flour and meal from the mill and canned potatoes and peppers from the canning plant) were collected immediately after each treatment as well as 2 and 14 days after each treatment.

Of the nearly 300 samples analyzed, only seven contained what we consider to be real residues, one of the seven contained a quantifiable level of 0.01 ppm. It should be noted that essentially all the samples containing a residue were collected from the food service establishments (restaurant and cafeterias) where food is more likely to be exposed during spraying. It should also be noted that the sprays used in these tests except for the initial treatment of each cafeteria were fine sprays which would tend to maximize the possibility of food contamination because of atomization of the spray. The label calls for a course spray to be used.

The data obtained from these tests show that only in a very few cases would residues be present in food items from the proposed spot treatment in food handling establishments. The chances of these residues in food is greatest in food service establishments with levels ranging up to 0.01 ppm on occasion; however residues would not be present in food for consumption on a continuous basis. As a result, we do not consider it necessary for the petitioner to specify a numerical tolerance level in any final regulation. However, we believe the use pattern should be circumscribed in the regulation.



A. RATHMAN