



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 16 1987

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#6E3425. Phosmet (Imidar®) on Pistachio.
Evaluation of Analytical Methods and Residue
Data. Accession #263587. RCB #1193.

FROM : Sami Malak, Ph.D., Chemist *Sami Malak*
Tolerance Petition Section III
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

TO : Hoyt L. Jamerson, PM #43
Emergency Response and Minor Use Section
Registration Support and Emergency Response Branch
Registration Division (TS-767)

and
Toxicology Branch
Hazard Evaluation Division (TS-769)

THRU : Charles L. Trichilo, Ph.D., Chief
Residue Chemistry Branch
Hazard Evaluation Division (TS-769)

The petitioner, IR-4, on behalf of the IR-4 National Director, Dr. R. H. Kupelian, and the Agricultural Experiment Station of California, requests the establishment of a tolerance for the cholinesterase-inhibiting residues of the insecticide, phosmet, N-(mercaptomethyl)phthalimide S-(O,O-dimethylphosphorodithioate) and its oxygen analog N-(mercaptomethyl)-phthalimide S-(O,O-dimethylphosphorothioate) in or on the raw agricultural commodity pistachio nuts at 0.1 ppm. This is a tolerance with regional registration for California only.

Pistachio is listed in 51FR11341,4/2/86 as a minor crop.

Permanent tolerances are established under 40CFR§180.261 for cholinesterase-inhibiting residues of the insecticide, phosmet, N-(mercaptomethyl)phthalimide S-(O,O-dimethylphosphorodithioate) and its oxygen analog N-(mercaptomethyl)-phthalimide S-(O,O-dimethylphosphorothioate) in or on a variety of commodities in the range of 0.1 to 40 ppm including nuts at 0.1 ppm.

The product and residue chemistry chapters of the Registration Standard for phosmet were issued on April 15, 1986.

Conclusions

1. The metabolism of phosmet in plants and animals has not been adequately elucidated. However, for the purpose of the proposed minor use of phosmet on pistachio grown in California, RCB concludes that the residue of concern consists of the parent compound phosmet, per se, and its oxygen analog as expressed in 40CFR§180.261. While data concerning plant and animals have been requested, these data should be addressed through the Phosmet Registration Standard or with future requests for tolerances on major crops.
- 2(a). For the purpose of this minor use on pistachio grown in the state of California, RCB concludes that adequate analytical methods are available for enforcement. The enforcement methodology for the proposed tolerance for residues of phosmet in/on pistachios is Method III listed in PAM II.
- 3(a). Additional data are needed to support the proposed concentrate sprays on pistachio. Alternatively, the petitioner is requested to revise Section B by deleting all references to the proposed concentrate sprays on pistachio and limit the rate to a maximum of 4 lb act/A in a minimum of 300 gallons of spray solution and use be limited to a dormant spray at the proposed rate and one foliar spray application at a maximum of 4 lb act/A/season and a 14-day PHI.
- 3(b). If a revised Section B is submitted as suggested in Conclusion 3(a) above and Conclusion 3(c) below and efficacy considerations permitting, RCB can conclude that the combined residues of phosmet and its oxygen analog in/on pistachio nuts will not exceed the proposed tolerance of 0.1 ppm.
- 3(c). The proposed grazing restriction should be revised to read: "Do not allow livestock to graze in treated areas or feed on cover crops from treated pistachio groves."
4. There are no feed items in the proposed use of phosmet on pistachio. Therefore, RCB concludes that there is no expectation of secondary residues of phosmet in/on meat, milk, poultry and eggs.
5. For compatibility with Codex, RCB can recommend that the tolerance expression for residues of phosmet stated in 40CFR§180.261, may be revised to read "the sum of N-(Mercaptomethyl)phthalimide S-(O,O-dimethyl phosphorodithio-ate) and its oxygen analog" instead of the current expression which reads "N-(Mercaptomethyl) phthalimide S-(O,O-dimethyl phosphorodithioate) and its oxygen analog." The PM should be informed of this.

Recommendations

RCB recommends against the requested permanent tolerance of 0.1 ppm for residues of phosmet, a cholinesterase-inhibiting insecticide N-(mercaptomethyl)phthalimide S-(O,O-dimethylphosphorodithioate) and its oxygen analog N-(mercaptomethyl)-phthalimide S-(O,O-dimethylphosphorothioate) in or on the raw agricultural commodity pistachio grown in California because of Conclusion #3(a), 3(b), and 3(c).

Notes to PM and Minor Use Officer

1. PM, please note RCB's suggested revision in the tolerance expression stated in Conclusion #5.
2. Minor Use Officer, the petitioner should be informed of the following guidance for orchard spray applications:

Guidance for Orchard Spray Application

As a guidance to any future orchard spray applications, the petitioner should incorporate one or more of the following concepts in their submissions as the means of instructing the users on how to vary the quantity of a.i./acre that is needed for different tree sizes.

Procedure 1. For High Volume (HV) Spray Applications to Orchards

Determine volume/A to spray orchard to run-off. Use so much active ingredient/ 100 gal and multiply this number by the volume/A to spray your orchard to runoff to determine the amount of active ingredient/A.

For Example:

Step 1: Use rate (determined by petitioner).....0.5 lb act/100 gal.

Step 2: To spray one acre of your orchard to run-off...300 gal/A.

Step 3: The amount of lb a.i./acre in 300 gal of water is 1.5 lb (0.5 lb act/100 gal x 300 gal/A).

Procedure 2. Estimation of Tree Row Volume (TRV) to Calculate the Gallons/A Needed to Spray to Run-off

Step 1: $43,560/\text{between-row spacing (ft)} = \text{feet of row/acre.}$

Step 2: $\text{Feet of row/acre} \times \text{tree height (ft)} \times \text{cross-row limb spread (ft)} = \text{cu ft of TRV/acre.}$

Step 3: Select one of the following numbers that best indicate the canopy density of each separate orchard or block:

0.70 gal/1,000 cu ft: Trees extremely open, light visible through entire tree, less than 15 scaffold limbs/tree or young tree.

0.75 gal/1,000 cu ft: Trees very open, 18 - 21 scaffold limbs/tree, light penetration throughout tree, healthy spurs within tree canopy.

0.80 gal/1,000 cu ft: Trees well pruned, adequate light in trees for healthy spurs throughout trunk and scaffold limbs, many holes in foliage where light can be seen through tree.

0.85 gal/1,000 cu ft: Trees moderately well pruned, reasonable spur population within canopy, tree thick enough that light cannot be seen through bottom two-thirds of tree.

0.90 gal/1,000 cu ft: Trees pruned minimally, spurs inside canopy are weak due to limited light, very few holes where light can be seen through the tree.

0.95 gal/1,000 cu ft: Little or no pruning, spurs dead or very weak in canopy, very little light visible through tree.

1.00 gal/1,000 cu ft: Tree totally unpruned, extremely thick, no light visible anywhere through tree canopy, trees more than 20 ft high.

Step 4:
$$\frac{\text{cu ft of TRV/acre (from Step 2)} \times \text{density (from Step 3)}}{1,000}$$

= gal of dilute solution to be applied/A.

Step 5: Using the volume of spray to run-off calculated in Step 4 above, calculate the lb a.i./acre using the formula of Procedure 1 (Step 3).

For Example: An orchard has rows spaced 25 ft apart, tree height is 20 ft, and cross row limb spread is 17 ft. The tree density is 0.85.

Step 1: $43,560 \text{ ft}^2 / 25 \text{ ft} = 1,742.4 \text{ ft}$

Step 2: 1,724.4 ft x 20 ft x 17 ft = 592.416 cu ft

Step 3: Density has been given as 0.85

scaffold limbs/tree or young tree.

Step 4: (592.416 x 0.85)/1,000 = 503.5 gal/acre

Step 5: Using the volume of spray to run-off calculated in Step 4 above, calculate the lb a.i./acre using the formula of Procedure 1 (Step 3).

Procedure 3. Estimation of Gallons of Pesticide Spray Solution per acre to Spray to Run-off or LV Application at the Full Leaf Stage of Canopy Using the following Table

Tree height (ft) X Tree width (ft) ^b	Spray Type	Gallons Per Acre ^a												
		distance between tree rows (ft)												
		16	18	20	22	24	26	28	30	32	34	36	38	40
80	HV	152	136											
	LV	20 ^c	17 ^c											
100	HV	191	169	152										
	LV	25	22 ^c	20 ^c										
150	HV	256	254	229	208	191								
	LV	37	33	29	27	25								
200	HV	305	277	254	235	218						
	LV	39	36	33	30	28						
250	HV	346	317	293	272	254	238				
	LV	45	41	38	35	33	31				
300	HV	416	381	352	327	305	286	269	254	241	229
	LV	53	49	45	42	39	37	35	33	31	29
350	HV	445	411	381	356	334	314	296	281	267
	LV	57	53	49	46	43	40	38	36	34
400	HV	469	436	407	381	359	339	321	305
	LV	60	56	52	49	46	44	41	39
450	HV	490	457	429	404	381	361	343
	LV	63	59	55	52	49	46	44
500	HV	508	476	448	424	401	381
	LV	65	61	58	54	52	49
550	HV	524	493	466	441	419
	LV	67	63	60	57	54
600	HV	538	508	481	457
	LV	69	65	62	59

^a See text for full details of calculation. All values rounded to the nearest whole gallon. Based on standard dosage volumes of 0.7 gallon per 1,000 cu ft TRV for HV and 0.09 gallon for LV sprays. Trees which have a very dense foliar canopy may require slightly more spray volume than shown.

^b Where small trees are interplanted with large trees in the same row, use only the large tree dimensions.

^c LV applications of less than 25 gallons per acre are not generally recommended because of other factors affecting coverage.

^d Data not given because the combination of this tree size on this planting density is unlikely.

Reference: Unrath, C. R., and T. B. Sutton. North Carolina State University, Raleigh, NC 27695. Bulletin AG 37.

The amount of a.i./acre can be calculated by using the volume of spray to run-off per acre found in the table above into the formula used in Procedure 1 (Step 3) above.

Procedure 4. For Low Volume (LV) and Ultra-low Volume (ULV) Applications to Orchards

Take the amount of a.i./A for orchard calculated from Procedure 1; the TRV estimated from Procedure 2; or the full leaf stage of canopy table from Procedure 3; and add to X gal of water/A for LV applications or Y gal of water and/or other solvent/A. X and/or Y is (are) determined by petitioner to coincide with proposed use. Less active ingredient/A is normally required for LV and ULV applications. The lower amount of active ingredient/A, if proposed, should be stated as a fraction of the high volume rate. Residue data must be submitted for all uses proposed on the label. Therefore, LV and/or ULV applications will not be allowed if residue data is submitted for HV applications only.

DETAILED CONSIDERATIONS

Manufacturing Process

The details of the manufacturing process of phosmet were previously submitted and reviewed in the Phosmet Registration Standard, Appendix B (CBI), dated 4/15/86. We do not foresee any residue problems with impurities found in the technical material.

Formulation

The formulation proposed for use on pistachio is Imidan 50WP, a wettable powder containing 50% of the active ingredient. As per J. Akerman memo of 9/16/86, review of inert clearance for formulations is the purview of the Registration Division.

Proposed Use

Pistachio in California- For control of Navel Orange worm, Imidan 50%WP is recommended for use in the spring at 0.5-0.75 lb act/100 gallons of water as a full cover spray with a maximum of 4 lb act/A. Repeat application is also recommended to be made late in the season before hullsplit reaches 10%. There is a 14 day PHI. A grazing restriction is imposed which reads: "Do not graze livestock in treated pistachio groves."

The proposed grazing restriction should be revised to read:
"Do not allow livestock to graze in treated areas or feed on cover crops from treated pistachio groves."

Dormant Spray- For control of scale and peach twig borer infesting pistachio, Imidan 50WP is recommended for use at the rate of 0.5 lb act/100 gallons of water plus suitable spray oil as a full coverage spray.

For concentrate and semi-concentrate spray, the recommended rate is a minimum of 2 lb act/A. In either case, the maximum proposed rate should not exceed 4 lb act/A. Use is by ground equipment only.

The petitioner should be informed of the following guidance for orchard spray applications:

Guidance for Orchard Spray Application

As a guidance to any future orchard spray applications, the petitioner should incorporate one or more of the following concepts in their submissions as the means of instructing the users on how to vary the quantity of a.i./acre that is needed for different tree sizes.

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Step 3: Select one of the following numbers that best indicate the canopy density of each separate orchard or block:

Step 3: Density has been given as 0.85

Step 4: $(592.416 \times 0.85)/1,000 = 503.5$ gal/acre

Step 5: Using the volume of spray to run-off calculated in Step 4 above, calculate the lb a.i./acre using the formula of Procedure 1 (Step 3).

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Nature of Residues

No new metabolism studies were submitted with this petition.

Plant and animal studies submitted and reviewed in connection with previous petitions (PP#4F1464 and PP#1E2565) have indicated that phosmet is considered a weakly systemic insecticide which can be absorbed and translocated after soil and foliar applications. Metabolism occurs primarily through oxidation and hydrolysis steps. A portion of the molecule is oxidized to its oxygen analog, imidoxon, and both compounds undergo hydrolysis to yield stepwise, hydroxymethylphthalimide, phthalimide, phthalamic acid, and phthalic acid. Decarboxylation may also occur with the formation of benzoic acid, p-hydroxybenzoic acid and benzimide....

TOX has not expressed concern over these metabolic products (see PP#1E2565).

The Phosmet Registration Standard (4/15/86) concluded that the available plant and animal metabolism data are not adequate. In plants, the metabolism is not adequately understood because: (i) the metabolites of phosmet have not been completely quantified or identified; (ii) metabolism studies exist for only one crop (cotton), and (iii) no data regarding the efficiency of extraction of ¹⁴C-residues from crops bearing weathered residues were submitted.

In animals, the metabolism studies are inadequate because residues were not characterized in tissues. The Registration Standard requested additional plant and animal metabolism data.

The metabolism of phosmet in plants and animals has not been adequately elucidated. However, for the purpose of the proposed minor use of phosmet on pistachio grown in California, RCB concludes that the residue of concern consists of the parent compound phosmet, per se, and its oxygen analog as expressed in 40CFR§180.261. While data concerning plant and animals have been requested, these data should be addressed through the Phosmet Registration Standard or with future requests for tolerances on major crops.

Analytical Methodology

An analytical method, WRC-72-46, is included with this petition. The method entitled: "Determination of Residues of Imidan® and Imidan Oxygen analog", is authored by B. J. Adelson and J. C. McKay of Western Research Center, dated September 7, 1972. The method is essentially the same as that described in connection with PP#4F1464, also listed in PAM II under Method III. The method is adapted for various crops including nut crops.

Briefly, Imidan and its oxygen analog are extracted from crop samples by blending with benzene and cleared up by a charcoal shake out. Acetonitrile-hexane partitioning is used to eliminate oils. Silica gel and charcoal column chromatography is used to clean up samples as appropriate. The determinative step is by the use of GC. Method sensitivity is reported at 0.05 ppm for either compound.

At the 0.05-1.0 ppm fortification levels of various plant commodities, recoveries were reported in the range of 68-101% for Imidan and 71-136% for its oxygen analog.

Sample chromatograms are included. Potentially interfering pesticides were shown to have different retention times.

For the purpose of this minor use on pistachio grown in the state of California, RCB concludes that adequate analytical methods are available for enforcement. The enforcement methodology for the proposed tolerance for residues of phosmet in/on pistachio nuts is Method III listed in PAM II.

Storage Stability

Phosmet storage stability in citrus, blueberries, and milo

are discussed in the Phosmet Registration Standard (4/15/86). The available storage stability data are sufficient to ascertain that residues of phosmet are stable in frozen plant commodities for up to one year.

In this petition, Stauffer Company submitted preliminary results of a two year storage stability study in plants utilizing alfalfa, almonds, apples, corn ears, oranges, peppers, potatoes, and soybeans. After one year of storage under -20°F , recovery from plant samples ranged from 0.076 to 0.104 ppm. At this time, RCB can make no conclusions on this study since detailed information were not available as to the fortifying agent (parent or its oxygen analog) and the level of fortification.

Storage stability data for animal commodities were cited by the Standard as an outstanding data gap. Since no feed items are involved in this petition, RCB will not raise an issue regarding the storage stability of phosmet in/on animal commodities.

Residue Data

Residue data submitted reflect nine field trials from the state of California representing three different locations. In all but one trial, phosmet was applied at the rate of 4 lb act/A in 100 gallons of spray (1X). Only one trial received two applications, each at 4 lb act/A in 100 gallons of spray for a total of 8 lb act/A/season.

Residue of phosmet ranged from non-detectable (<0.05 ppm) to 0.08 ppm reflecting 0-day to 38 day PHI's. The highest residue of 0.08 ppm reflects 1X rate and 0-day PHI. The next highest residue was 0.07 ppm reflecting two applications at 1X rate and 21 day PHI (the proposed PHI is 14 days).

Residue of phosmet's oxygen analog were all non-detectable (<0.05 ppm) reflecting 0.5 to 1X rates and 0-day to 38-day PHI.

No data were submitted to support the proposed dormant spray.

Phosmet is considered a weak systemic insecticide which can be absorbed and translocated after soil and foliar applications. We note, however, that the bulk of the residues from the proposed foliar application remain on the hulls. Residues of the parent, per se, on the hulls ranged up to 17.1 ppm while the corresponding samples showed no detectable residues in/on pistachio meat. None of the samples showed detectable residues of phosmet's oxygen analog (<0.05 ppm).

No data were submitted to support the proposed concentrate sprays. Additional data are needed to support the proposed concentrate sprays on pistachio. Alternatively, the petitioner is requested to revise Section B by deleting all references to the proposed concentrate sprays on pistachio and limit the rate to a maximum of 4 lb act/A in a minimum of 300 gallons of spray solution and use be limited to a dormant spray at the proposed rate and one foliar spray application at a maximum of 4 lb act/A/season and a 14-day PHI.

With a revised Section B as suggested above and provided efficacy considerations permitting, RCB can conclude that the combined residues of phosmet and its oxygen analog in/on pistachio nuts will not exceed the proposed tolerance of 0.1 ppm.

Meat, Milk, Poultry and Eggs

There are no feed items in the proposed use of phosmet on pistachio. Therefore, RCB concludes that there is no expectation of secondary residues of phosmet in/on meat, milk, poultry and eggs.

Other Considerations

An International Residue Limit Status sheet is attached. There is a Codex tolerance of 0.1 ppm for the sum of phosmet and its oxygen analog in/on tree nuts. No Canadian or Mexican tolerances are currently established for phosmet in/on pistachio nuts.

For compatibility with Codex, RCB can recommend that the tolerance expression for residues of phosmet stated in 40CFR§180.261, may be revised to read "the sum of N-(Mercaptomethyl)phthalimide S-(O,O-dimethyl phosphorodithio-ate) and its oxygen analog" instead of the current expression which reads "N-(Mercaptomethyl) phthalimide S-(O,O-dimethyl phosphorodithio-ate) and its oxygen analog." The PM should be informed of this.

Attachment 1: Codex Sheet (one page).

cc: RF, Circu, S. Malak, SF (phosmet or Imidan), PP#
6E3425, TOX, EAB, EEB, RD (PM #43), and PMSD/ISB.
RDI: P.V. Errico: 4/15/87: R. D. Schmitt: 4/15/87.
TS-769C:RCB:CM#2:RM814A:S.Malak:X557-4379:10/7/86.

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Phosmet (Imidan)

PETITION NO. 6E3425

CCRR NO. 103

REVIEWER Sami Malak

CODEX STATUS

CODEX COORDINATOR F. Ives 8/21/1986
Fred Ives Date

NO CODEX PROPOSAL
Step 6 or Above

Proposed U. S. Tolerances
Residue: Parent compound, phosmet, N-(mercaptomethyl)phthalimide S-(0,0-dimethylphosphorodithioate) and its oxygen analog, N-(mercaptomethyl)phthalimide S-(0,0-dimethylphosphorothioate).

Residue : (if Step 9):

Sum of phosmet and its oxygen analog

<u>Crop(s)</u>	<u>Limit (mg/kg)</u>
<i>Tree nuts</i>	<i>0.1 (shell free)</i>

<u>Raw Agricultural Commodities Under 40CFR§180.261</u>	<u>Tolerance (ppm)</u>
<i>Pistachio nuts.....</i>	<i>0.1</i>

CANADIAN LIMIT Residue :

<u>Crop(s)</u>	<u>Limit (ppm)</u>
<i>none</i>	<i>(on pistachio nuts)</i>

Feed Additive Tolerances Under 21CFR§561.--- Tolerance (ppm)

MEXICAN TOLERANCIA Residue :

<u>Crop(s)</u>	<u>Tolerancia (ppm)</u>
<i>none</i>	

Food Additive Tolerances Under 21CFR§193.--- Tolerance (ppm)

Notes: