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

9/28/82

From Charlotte RCB 9/28/82

SEP 15 1982

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP# 2F2716/FAP# 2H5359. Dyfonate® in or on potatoes. Evaluation of analytical methodology and residue data.

FROM: M. Nelson, Chemist
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THRU: C. Trichilo, Chief
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Hazard Evaluation Division (TS-769)

TO: Wm. Miller, PM 16
Registration Division (TS-767)

Stauffer Chemical Company proposes that 40 CFR 180.221 be amended by revising upward to 0.2 ppm the presently established tolerance of 0.1 ppm for the combined residues of the insecticide 0-ethyl S-phenyl ethylphosphonodithioate [trade name, Dyfonate®; ISO/BSI name fonofos] and its oxygen analogue, 0-ethyl S-phenyl ethylphosphonothioate in or on potatoes.

Additionally, it is proposed that a food additive tolerance be established at 3 ppm for said combined residues in or on potato waste (peels).

Presently established tolerances (40 CFR 180.221) range from 0.1-0.5 ppm on various rac's. There are no established food additive tolerances for fonofos.

The previous petition (PP# 9F0548) re Dyfonate/potatoes is hereby incorporated into this review by reference.

Conclusions

1a. The nature of the residue in plants is adequately understood. Parent plus oxon are the residues of concern.

1b. A large animal (lactating ruminant) metabolism study, presently lacking, is needed. Pending receipt and review of such a study, we can not consider the nature of the residue in animals to be adequately delineated for purposes of this petition.

2a. Adequate analytical methodology is available to enforce the proposed tolerances on potatoes and potato waste (peels).

2b. The potato field trial data was reportedly analyzed by methods WRC-71-26 and RRC-72-35. We request information on those methodologies (extraction and clean-up procedures, determinative conditions, etc.) so we can determine if they are adequate for purposes of providing residue data.

2c. Depending on the outcome of the requested feeding studies (see Conclusions 4a and 4b), enforcement methodology may be needed for meat, milk, poultry, and eggs. (If this is the case, the methodology would need to be validated, and method trial(s) conducted in EPA laboratories.)

3a. Based on the information provided by the petitioner, and contingent upon satisfactory resolution of Conclusion 2b, we conclude that the proposed 3 ppm food additive tolerance for potato waste (peels) is appropriate.

For consistency within the Regulations, we suggest that the tolerance if/when established be expressed in terms of "processed potato waste".

3b. Taking into consideration that up to 3 ppm residue will be permissible in peels and that peeling losses reportedly average 10-15%, we conclude that a 0.2 ppm tolerance level for whole potatoes may not be adequate. We suggest 0.5 ppm as a more appropriate level and request a revised Section F to reflect this. Alternately, the petitioner can provide actual data demonstrating what residue levels in whole potatoes (representative varieties, immature and mature, new and old, etc.) will be when ca 3 ppm residue is present in/on the peels, and propose an appropriate tolerance for whole potatoes based on that.

3c. Depending on the outcome of the requested feeding studies (see Conclusions 4a and 4b), tolerance proposals may be needed for meat, milk, poultry, and eggs.

4a. A new lactating ruminant feeding study, run at higher levels, is needed. We suggest dosing levels of 0, 1.5, 5, and 15 ppm as suitable.

4b. A poultry feeding study, presently lacking (except for quail), is needed. We suggest dosing levels of 0, 0.3, 1.0, and 3.0 ppm. (Other levels might be preferable to the petitioner if there are future plans involving other poultry feed items).

4c. We defer classification of the proposed uses as to 40 CFR 180.6(a) pending receipt and review of the requested feeding studies (see Conclusions 4a and 4b).

5. The Codex sheet is attached. Revising the potato tolerance [0.1 to 0.5 ppm] will create an unavoidable conflict with Canadian limits.

Recommendations

We recommend against the proposed tolerance requests at this time for the reasons stated in Conclusions 1b, 2b, 2c, 3b, 3c, 4a, 4b, and 4c.

PM, note comment under Conclusion 3a.

Detailed Considerations

Manufacture and Formulation

An outline of the manufacturing process and a listing of the impurities in the technical mix (typically 93% pure, at a minimum) are appended to this review as a Confidential Attachment.

Technical fonofos formulations with registered uses on potaotes are: Dyfonate 4-E (EPA Reg. No. 476-2056), Dyfonate 4-EC (EPA Reg. No. 476-2134), and Dyfonate 4-ED (EPA Reg. No. 476-2190), all of which are emulsifiable liquids containing 4 lbs ai/gal; and, Dyfonate 10-G (EPA Reg. No. 476-1995), a granular product containing 10% ai w/w.

All the inerts in these 4 formulations are cleared for use under Section 180.1001.

Proposed Uses

The uses proposed are those presently registered for potatoes for each formulation, plus an additional at-planting in-furrow usage of the 10-G formulation for ID, OR, and WA only for use with sprinkler irrigated potatoes.

Summary. 10-G: 20-40 lbs (2-4 lbs ai)/A broadcast, prior to planting, and incorporated; or 20 lbs (2 lbs ai)/A banded, at planting, below seed pieces, Pacific NW only; or 20 lbs (2 lbs ai)/A in-furrow, at planting, with seed pieces, ID, OR, and WA only, sprinkler irrigated potatoes only. 4-E, 4-EC, or 4-ED: 2 or 4 qts (2-4 lbs ai)/A broadcast, prior to planting, and incorporated; in Northern, Western, and Pacific NW regions only, may be tank-mixed with Eptam 7-E; or 2 qts (2 lbs ai)/A banded, preplant, soil injection with fluid fertilizer.

Nature of the Residue

The metabolism of fonofos in potato plants has been studied; see, J. McBain et al., "Metabolic Degradation of O-Ethyl S-Phenyl Ethylphosphonodithioate (Dyfonate) in Potato Plants", J. Agr. Food Chem. 18:6, 1139-1144 (1970).

Menzie, in Metabolism of Pesticides: An Update (1974) summarized McBain's study as follows:

> "Potato plants were grown in soil treated with dyfonate. In addition to unchanged dyfonate, seven metabolites were identified: oxon, EOP, EOP-CH_3, ETP-CH_3 and some unknowns. The water-soluble metabolites included EOP, ETP, $MPSO_2$ and several unknowns of which 49% gave rise to EOP when subjected to acid hydrolysis. Two unknown materials were cleaved by B-glucosidase or glusulase but less by B-glucuronidase. This suggested that the two metabolites existed in the plant largely as glycoside and sulfate conjugates (McBain et al., 1970)."

A metabolic schema for Dyfonate (from Menzie) is attached to this review. We consider the parent compound and its oxon metabolite to be the residue of concern in plants. (Note: Dyfonate is non- to slightly systemic).

The only animal metabolism data that appears to be available is on mice (see Menzie, Update II (1980)) and rats (see PP# 7F0548), and we have previously concluded (eg, see J. Wolff review of 11/30/70, PP# 0F0960) that dyfonate metabolism therein is similar to that in plants, proceeding primarily via hydrolysis and oxidation.

Since this present petition proposes a food additive tolerance of 3 ppm for potato waste (peels), which the petitioner indicates is fed to livestock (blended in equal parts with silage and/or grain), it now becomes relevant to request a large animal (lactating ruminant) metabolism study.

Pending receipt and review of such a study, we can not consider the nature of the residue in animals to be adequately delineated for purposes of this petition.

Analytical Methodology

The analytical method submitted with this petition is "Determination of Residues of Dyfonate and Dyfonate Oxygen Analog", WRC-70-39, 6/25/70.

This method, which supersedes WRC-69-12, is intended for the determination of said residues on a variety of crops, including potatoes.

Summary. Dyfonate and Dyfonate oxygen analogue are separated from the crop by extraction with benzene; oils, when present (not relevant for potatoes), are separated from the extracted residues by liquid-liquid partitioning (using different partitioning liquids for Dyfonate and Dyfonate oxygen analogue); interfering extractives, if present, are removed by separate clean-up of the parent and oxon on silicic acid columns of different acidities (pH's 4 and 7); and, the residues are determined by GLC on a DC-200 column with a rubidium sulfate flame detector. [Note: the silicic acid clean-up may not be required for some crops, such as potatoes.]

The detection limits for the method are reportedly 0.05 ppm for Dyfonate and 0.03 ppm for the oxygen analogue. This is borne out by the chromatograms submitted.

The principles of this method are similar to those of the enforcement method in PAM II. A successful method trial of that basic procedure was run on asparagus and peanuts in conjunction with PP# 7F0548.

A confirmatory procedure based on TLC analysis is also available in PAM II, if needed.

Method WRC-72-3, 3A is discussed in the 9/28/73 review of F. Gee, PP# 3F1379, in re meat, milk, bird (quail) and egg residue determinations.

The principle of the method is reportedly similar to that of the crop enforcement method, with some exceptions (eg, use of different extracting solvent). We note, however, that difficulties were encountered with liver, which reportedly degraded both Dyfonate and its oxon.

We withhold judgment as to whether workable enforcement methods for meat, milk, poultry, or eggs will be needed (in which case, method trials would also be needed) in conjunction with this petition. The determining factor will be whether the feeding studies (see Residues in Meat, Milk, Poultry, and Eggs Section) that need to be run indicate detectable residues, and therefore the need for tolerances for meat, milk, poultry, or eggs and enforcement methodology.

As for the crop methodology, the petitioner has validated method WRC-70-39 on a variety of crops, including potatoes. At fortification levels of 0.05 ppm for Dyfonate and 0.03 ppm for its oxon, recoveries of 72-80 and 80-117%, respectively, were reported in potatoes. Control values in potatoes (whole, peel, pulp) were reported as being <0.05 ppm for Dyfonate and <0.05 ppm for the oxon in all cases.

It would thus appear that adequate methodology is available for enforcement purposes on potatoes.

However, we note that the residue data was apparently not obtained by the analytical method (WRC-70-39) that was submitted, and which we have discussed.

The analytical residue reports the petitioner has submitted indicate methods WRC-71-26 and RRC-72-35 were utilized in analyzing potatoes.

Accompanying validation data for those methods indicate that at fortification levels of 0.03-0.05 ppm of Dyfonate or its oxon, recoveries of 70-120% were reported in potatoes (whole, peel, pulp). Control values were <0.05 ppm for Dyfonate and <0.05 ppm for the oxon in all cases.

But, while we can deduce GLC was used for the determinative step in these methodologies, we do not know the extraction and clean-up steps that were employed prior to GLC analysis. This information is requested so that we can determine if these procedures were adequate for purposes of gathering the residue data of this petition.

Residue Data

A number of residue studies from ID and OR for crop year 1980 have been submitted. These reflect all the various methods of application proposed (broadcast, banded, etc.) and both types (G and EC) of Dyfonate formulations. The use rate ranged 1/2X-2X that proposed for the specific application mode, and PHI's were 76-162 days.

Samples of whole potato tubers, as well as peel and pulp, were subjected to analysis for residues of Dyfonate and Dyfonate oxon.

Residues of Dyfonate oxon were non-detectable (reported as <0.03 or <0.05 ppm) in all ≤1X rate treated samples (whole, peel, or pulp), and were only detected in 2X rate samples in two isolated instances in the peel (at 0.05-0.06 ppm; NDR in any pulp or whole tuber samples).

Residues of Dyfonate per se were non-detectable in all pulp samples and ranged from <0.05-0.15 ppm in whole tuber samples (1/2X-2X rates), with all but two values being <0.10 ppm. (In the two exceptions, 0.15 ppm Dyfonate was reported in whole potatoes receiving 3/4X rate; in one of those cases, however, a duplicate analysis was run and only 0.06 ppm was reported from that.)

Residues of Dyfonate per se ranged from <0.05-0.53 ppm in potato peels from 1X-2X treated potatoes. However, the petitioner states that "the separate peel and whole tuber analyses demonstrate that residues are concentrated on the peel. Although not included with this submission, random samples of peelings taken from potato processing operations in the Pacific Northwest have shown residues as high as 1.8 ppm." Hence, presumably, the request for a 3 ppm food additive tolerance on potato waste (peel).

Information is provided in Potatoes: Production, Storing, Processing (2d ed.) by O. Smith (1977), p. 706, that potato "peeling losses range from 10 to 15%." (Peel loss in processing is dependent upon several factors, including size and shape of potato, depth of eyes, length of storage of the tubers, and type of peeling process (steam, lye, abrasion, etc.) employed.)

Bearing this in mind, we consider that a reasonable doubt thus exists that the 0.2 ppm tolerance proposal for whole potatoes will be adequate in conjunction with the 3 ppm food additive tolerance on potato waste (peels) that the petitioner is also proposing, since this assumes only ca 7% peel loss. In a 15% peel loss situation, assuming 3 ppm residue in/on the peel, a 0.5 ppm tolerance for whole potatoes would be most appropriate.

Accordingly, unless the petitioner can provide actual data demonstrating what residue levels in whole potatoes (representative varieties, immature and mature, new and old, etc.) will be when ca 3 ppm residue will be present in/on the peels to guide us, we have little recourse except to conclude that a higher tolerance (0.5 ppm) needs to be proposed for residues in/on whole potatoes. [Note: this conclusion is derived based on the food additive tolerance level (3 ppm-peels) being proposed (which is, in turn, based on random samplings of peelings taken from potato processing operations; treatment history unknown), rather than on the actual field trial studies (samples of known history) which suggest lower tolerances for both whole potatoes and peels would suffice under proposed use conditions.]

Residues in Meat, Milk, Poultry, and Eggs

Based on information in the Harris Guide, the feed items associated with potatoes are cull or surplus potatoes, dehydrated potatoes, cooked potatoes, potato meal, and potato process residue (peelings, trimmings). Potato vines are not considered a feed item.

Potato waste (peels) is the item of primary concern here because of the 3 ppm food additive tolerance being proposed for it. According to Harris, this feed item may comprise up to 50% of the diet of cattle and swine, 30% of the diet of horses, 20% of the diet of sheep, and 10% of the diet of poultry.

Thus, we are concerned about daily ingestion levels up to 1.5 ppm (3 ppm x 50%) for livestock and 0.3 ppm (3 ppm x 10%) for poultry.

A lactating dairy cattle study was submitted in re PP# 3F1379, and was discussed in the F. Gee review of 9/28/73. NDR (<0.01 ppm, milk; <0.03 ppm, tissues) of either Dyfonate or its oxon were found in any milk or tissue (muscle, liver, kidney, fat) sample following 28 days of feeding 0, 0.1, 0.5, or 1.0 ppm Dyfonate in the daily diet.

An additional lactating ruminant feeding study will be needed to provide information as to whether detectable residues would be present in milk or animal tissues from a higher level (in this instance, 1.5 ppm) of daily ingestion. We suggest feeding levels of 0, 1.5, 5.0, and 15 ppm as being suitable. Should detectable residues be encountered in milk or tissues, appropriate tolerances will need to be proposed and enforcement methodology provided (and a method trial of it run).

We note that a bird (quail) feeding study was also submitted with PP# 3F1379. However, we stated at that itme (F. Gee reviews of 9/28/73 and 12/10/73) that the study could not be used as a substitute for a poultry feeding study and that "if future uses are contemplated for poultry feed items that will have real residues, a poultry feeding study will be needed."

A poultry feeding study has never been submitted for this chemical, and one is needed in re this petition. We suggest feeding levels of at least 0, 0.3, 1.0, and 3 ppm. [Note: the petitioner may wish to substitute different feeding levels for the poultry and/or cattle studies if future tolerances for other feed items are contemplated.]

As with cattle, if detectable residues are encountered in tissues or eggs of poultry, appropriate tolerances will need to be proposed and enforcement methodology provided (and a method trial of it run).

Other Considerations

The Codex sheet is attached to this review. There will be a conflict when the potato tolerance is revised from 0.1 to 0.5 ppm (the level we consider appropriate) since the Canadian limit is 0.1 ppm. However, the petitioner's data indicates the need for a higher tolerance; so we support the upward revision (once related deficiencies are resolved).

Attachments

TS-769:RCB:MNelson:vg:CM#2:Rm810:X77377:9/10/82
cc: RF, Circ., Nelson, Thompson, FDA, TOX, EEB EFB, PP#2F2716/FAP#2H535
RDI: Quick, 9/8/82; Schmitt, 9/8/82

CHEMICAL Dyfonate (fonofos)

PETITION NO 2F2716/2H5359

CCPR NO. none

Codex Status

[✓] No Codex Proposal Step 6 or above

Residue (if Step 9): _____

Crop(s) Limit (mg/kg)

none

Proposed U. S. Tolerances

for 180.221

Residue: Dyfonate and its oxygen analogue

Crop(s)	Tol. (ppm)
potatoes	0.2
potato waste (peels)	3.0 (FA)

CANADIAN LIMIT

Residue: fonofos 1/

Crop	Limit (ppm)
potatoes	0.1 2/

MEXICAN TOLERANCIA

Residue: _____

Crop	Tolerancia (ppm)
none	

Notes: 1/ parent as far as is known

2/ "negligible residue" type limit.