MEMORANDUM

SUBJECT: PP#8E3608: Clomazone in Succulent Peas (MRID 404920-00 and 404920-01; RCB#3350).

FROM: Alfred Smith, Chemist
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THRU: Charles L. Trichilo, Chief
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TO: Hoyt Jamerson
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and

Toxicology Branch
Hazard Evaluation Division (TS-769C)

The Interregional Research Project No. 4 (IR-4) and the Agricultural Experiment Stations of Georgia, Illinois, Idaho, Oklahoma, Oregon, and Washington, propose a tolerance for residues of the herbicide chemical clomazone (Dimethazone), 2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone, in or on succulent peas at 0.1 ppm.

The FMC Corporation has submitted a letter (1/15/88, E. M. Cuirle) which authorizes the use of FMC data in support of this tolerance proposal.

A permanent tolerance of 0.05 ppm has been established for clomazone in soybeans ($180.425).

Conclusions

1. If it is the intent of the petitioner and efficacy considerations permitting, section B should be revised to explicitly include tank-mix uses.
1a. Section B should be revised to state that the 0.5 lb a.i./A rate applies to all soil types. Alternatively, additional residue data at the higher rate (1.0 lb act/A) should be submitted.

2. The nature of the residue is adequately understood. The tolerance is appropriately expressed in terms of the parent compound clomazone.

3. An adequate analytical method is available for enforcement.

4. Residues in succulent peas, canned peas, or pea cannery waste are not likely to exceed the proposed tolerance for peas (0.1 ppm). No detectable residues (<0.03 ppm) were noted in peas from the proposed or exaggerated (2X) rates. Therefore, the proposed tolerance of 0.1 ppm is excessive. A level of 0.05 ppm is adequate and should be proposed.

4a. The use of trifluralin in tank-mix combination with clomazone would not affect the clomazone residue level.

5. No residues are likely to occur in eggs, milk, meat, fat, or meat byproduct of livestock [§180.6(a)(3)].

6. There are no Codex proposal or Canadian or Mexican Limits for clomazone in succulent peas.

Recommendation

RCB recommends against the proposed tolerance. A favorable recommendation is contingent upon resolution of the deficiencies noted in Conclusions 1, 1a and 4.

Detailed Considerations

Manufacturing Process

The manufacturing process and technical clomazone have been fully discussed in reviews of PP#4G2987 (memo of L. S. Propst, 4/17/84) and PP#4F3128. The manufacturing impurities are not expected to produce a residue problem.

Formulation

Clomazone is formulated as Command® 4EC Herbicide, an emulsifiable concentrate containing 47% active ingredient (4 lbs a.i./gallon), for use on soils planted to succulent peas.
Proposed Use

**Succulent Peas:** broadcast 1 pint (0.5 lb a.i.) of Command 4EC per acre and incorporate before planting. Do not allow livestock to graze on treated pea vines, and treated vines or vine trash are not to be fed to livestock.

**Tank-Mixture**

A tank mix use with Command and Treflan is indicated:

Section C, "Minor Use Pesticide Clearance Request Form," Item 9, Proposed Labelling. The dosage rate is expressed as 0.5 lb a.i./A (with or without combination with Treflan, 0.5 lb trifluralin). This tank mix use is also indicated in the IR-4 Research Protocol, PR. No. 3296, p.4 of 172. If it is the intent of the petitioner and efficacy considerations permitting, the tank mix combination should be explicitly stated in the proposed use section.

Treflan contains the herbicide chemical trifluralin, (alpha, alpha, alpha-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine). Trifluralin has an established tolerance of 0.5 ppm in peas. This tolerance is to cover residues resulting from preplant soil incorporated applications of 0.75–1.0 lb a.i./A.

**Soil Types**

Section A (pg. 7 of 28), Table I (Command Herbicide Applied Alone) indicates that the application rate varies with the soil texture (coarse soils, 0.75–1.0 lb a.i./A; medium soils, 0.75–1.0 lb a.i./A; fine soils, 1.0 lb a.i./A). However, only a single rate (0.5 lb a.i./A) is proposed for peas. Section B should be revised to state that the 0.5 lb a.i./A applies to all soil types. Alternatively, additional residue data at the higher rates should be submitted.

**Nature of the Residue**

The metabolism of clomazone in plants (soybeans, alfalfa) has been extensively discussed in reviews of PP#4G2987 and PP#4F3128. Studies with radiolabelled clomazone (C\(^{14}\)-methylene label; C\(^{14}\)-carbonyl label; C\(^{14}\)-phenyl ring label) show that residues of clomazone are absorbed from soil or foliar treatments, metabolized, and translocated.

Metabolic residues in alfalfa plants and soybean plants and soybean seeds consist of free and conjugated components. In plants the parent compound decreases with time, and the metabolic components (free and conjugated) increase with time as expected.
The residue components in plants consist of the parent compound (trace, less than 1%), 5-keto clomazone, 5-hydroxy clomazone, 3',5'-and 6'-hydroxy clomazone, hydroxymethyl clomazone, and the cleavage product o-chlorobenzyl alcohol (OCBA). (See chart for chemical structures.) The component OCBA comprises 48–54% of the plant residue. The components 5'-hydroxy clomazone and hydroxymethyl clomazone are reported together and comprise 19–20% of the residue. The 3'-and 6'-hydroxy clomazones each represent about 10% of the residue. The remaining components represent less than 10% each. The components of the residues for alfalfa and soybeans are qualitatively similar, but vary quantitatively.

The soybean seed showed more extensive metabolism. The identified residue components consisted of cleavage products: OCBA; hydroxy-o-chlorobenzyl alcohols (mixture of possibly three isomers); o-chlorobenzoic acids (mixture). About 65–70% of the mature seed residues represent polar components or activity bound to plant solids.

The nature of clomazone residues in plants is adequately understood.

There are no metabolism studies for peas. However, soybeans and peas are sufficiently similar so that the results of the soybean metabolism study can be extrapolated to include peas. Therefore, RCB concludes that the parent compound clomazone is the significant component of the residue in plants. The tolerance for peas is appropriately expressed in terms of the parent compound clomazone.

**Analytical Method**

The method used for residue analysis is "Command Herbicide General Crop/Soil Residue Method" (Test Method No. ACG 124). A crop sample is extracted by refluxing with dilute hydrochloric acid. The mixture is cooled, filtered, and an aliquot is taken for further extraction.

The clomazone residue is extracted from the aliquot by partitioning with hexane. The hexane phase is washed with a bicarbonate solution and concentrated to a suitable volume.

The concentrate is cleaned up on a Florisil column, and the clomazone residue is elute with an ethyl acetate/hexane solvent. The eluate is concentrated to a suitable volume, and the residue is determined by gas chromatography using a nitrogen-phosphorus detector. The method is validated for the parent compound clomazone.
A second determinative system is available which uses a combination of gas chromatography and mass spectrometry. The system may be used as a confirmatory procedure.

The minimum detectable limit for crops is reported to be 0.03 ppm.

A variety of crops including peas and green beans were fortified with clomazone at levels of 0.03-0.10 ppm. Recoveries were 64-130% (average, 94%).

The method has been successfully tested by EPA on soybeans at levels of 0.05 ppm and 0.1 ppm (memo of PP#4F3128, 4/25/85, D. Wright, ACS, COB).

An adequate analytical method is available for enforcement.

**Storage Stability Study**

A study was submitted in PP#4F3128 (memo of 9/24/84, J. Worthington) in which soybeans were fortified with clomazone at 0.2 ppm and held in frozen storage for periods of 0-6 months. Analyses of samples showed no detectable decline over six months.

**Residue Data**

Sample of peas were obtained from crops grown in Illinois, Minnesota, Wisconsin, Idaho, Delaware, Oregon, California, Washington, and New York. The crops were planted in soils treated as proposed and at rates of 1X (0.5 lb a.i./A) and 2X proposed rate. Data for the 2X rate were submitted only for pea samples grown in Minnesota. Some crops were grown in soils which had been treated with a tank mix combination of 0.5 lb clomazone plus 0.5 lb trifluralin (Treflan).

No detectable residues (<0.03 ppm) of clomazone were noted in samples (peas plus pods) at harvest (intervals of 52-85 days after treatment) from any treatment.

Samples of peas which had been treated as above (0.5-1.0 lb clomazone/A, or tank mix of 0.5 lb clomazone plus 0.5 lb trifluralin) were processed to canned peas, and the cannery waste and canned peas were analyzed for clomazone. No detectable residues (<0.05 ppm) were noted in the canned peas or cannery waste.

Residues of clomazone in or on succulent peas, canned peas, or pea cannery waste are not likely to exceed the proposed tolerance for peas (0.1 ppm). The proposed tolerance level of 0.1 ppm is excessive. A level of 0.05 ppm is appropriate and should be proposed.
Trifluralin (Treflan) has registered preplant application rates of 0.75-1.0 lb act/A on peas. The indicated rate of 0.5 lb trifluralin per acre in tank mix with clomazone is not likely to exceed the established 0.05 ppm tolerance ($180.207$).

**Meat, Milk, Poultry and Eggs**

Peas, pea vines, and hay may occasionally be used as feed items in the diet of livestock. However, the label restrictions on grazing treated vines and the feeding of treated vines or vine trash, as well as the absence of detectable residues (<0.03 ppm) in the peas, preclude the ingestion of clomazone residues by livestock. As a result, no residues are likely to occur in eggs, milk, meat, fat, or meat byproducts of livestock [$180.6(a)(3)$] from the proposed use.

RCB:TS-769:A.Smith:vg:CM#2:Rm804:X77484:3/14/88  
cc: Reading File, Alfred Smith, EAB, EEB, D. Marlow,  
PP#8E3608, PMSD/ISB  
2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone, Clomazone

5-Keto Clomazone

5-Hydroxy Clomazone

Hydroxymethyl Clomazone

(3',5',6') Hydroxy Clomazone

0-Chlorobenzyl Alcohol (OCBA)

Chemical structures of Clomazone Metabolites in Plants