Ecol. Effects.

PP#3F1416. Endothall on rice. Evaluation of analytical method and residue data. JAN 22 1974

Coordination Branch
and Toxicology Branch, RD

The Pennwalt Corporation proposes a 0.05 ppm negligible residue tolerance for residues of endothall in or on rice grain resulting from application of the mono (N, N-dimethylalkylamine) salt. Endothall is the common name for 7-oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid and is to be used as an aquatic herbicide. We note that no tolerance is proposed for rice straw.

Tolerance at 0.1 ppm are established for residues of endothall in or on cottonseed and potatoes (Section 180.293). Interim tolerances at 0.2 ppm are established for sugar beets and potable water (food additive tolerance).

Conclusions

1. We tentatively conclude that endothall per se is the residue of concern in rice. The tracer study referred to in Section E, Exhibit 21, p.3, dealing with the catabolism of endothall in the rice plant would be helpful in affirming this conclusion; the petitioner should be so informed.

2. The analytical method is adequate for the determination of endothall per se. Should the rice metabblism study reveal the presence of toxic residues other than endothall, a validated analytical method capable of determining total toxic residues will be required.

3a. The residue data for "rice grain" appear to support the 0.05 ppm tolerance level for the r.a.c. rough rice. The exact nature of the samples analyzed should be specified (e.g., rough rice, brown rice, polished rice). Because the samples were stored prior to analyses for periods ranging from about 8½ months to 3½ years, storage stability data (including storage conditions) are required before a final conclusion can be made regarding residues in the r.a.c. Additional residue data will be required if residue stability over long intervals can not be demonstrated or should the rice metabolism study indicate the presence of toxico degradation products.

3b. No data are such submitted for milling fractions. We can draw no conclusion as to residue levels in these fractions (hulls, bran, etc.) until the questions regarding residues in rice are resolved. If finite residues are present, residue data for the processing fractions (and food additive tolerances, if appropriate) will be required.

3c. In the absence of residue data for rice straw, no conclusion regarding an appropriate tolerance level can be made. Such data are required, together with an appropriate tolerance proposal.

4. Because of the questions regarding residue levels in rough rice, its fractions and straw, we are unable to classify this use with respect to Section 180.6(a).

Recommendations

We recommend against the proposed tolerance because of the deficiencies cited in Conclusions 1-4.

These deficiencies must be resolved before this proposal can be given further consideration.

Detailed Considerations

Formulation

This use entails application of a 5% endothall acid equivalent (as the mono (N,N-dimethylalkylamine salt) formulation (trade name HYDROTHOL® 191). The inert ingredients are exempt from the requirements of a tolerance under Section 180.1001.

The technical material is reported to be approximately 91% acid monohydrate and [redacted] as impurities.

Proposed Use

A single annual treatment (California only) at rates of 2-3 lbs endothall acid equivalent/A is to be made (either with ground or aerial equipment) 25 to 60 days after sowing rice, when submerged aquatic weeds are present. The rate applied is dependent on water depth. Treatment is prohibited before rice emerges above water surface and after heading begins. Water is not to be released from flooded fields or used for domestic purposes or watering livestock within ten days of treatment, after which time residues will have dissipated to levels below the 0.2 ppm interim tolerance established for water (see Residue Data).

General cautionary statements-evidently related to the use of this formulation in lakes and ponds-include prohibitions against use where fish are important resources and against food or feed use of fish taken from treated water within 3 days of treatment.

Product Identity information has been removed

Nature of the Residue

The degradation of endothall in plants, animals, soil, water and by aquatic microorganisms has been discussed in previous reviews, most completely in PP#1F1105 (see memo, 11/4/71, A. Smith). No additional data are submitted in this petition.

Studies conducted with the tolerant plants, red beets, sugar beets and spinach, as well as susceptible aquatic weeds, cotton, potatoes, and water using ^{14}C ring-labled endothall have shown that endothall is absorbed, translocated and rapidly degraded. The majority of the activity becomes incorporated into natural plant components. Endothall per se is considered to be the residue of concern in these plants and water. Degradation most likely involves a pathway involving splitting of the oxabicyclo ring, as indicated by the nature of the ^{14}C products resulting from assimilation of the labeled compound and evolution of $^{14}CO_2$.

The metabolism of endothall by aquatic microorganisms has recently been reported by Sikka and Saxema (J. Agr. Food Chem. 21, 402; 1973). After short-term incubation of Arthrobacter with ^{14}C ring-labled endothall, the label was incorporated into cellular amino acids, proteins, nucleic acids, lipids, other natural components, and also released as carbon dioxide.

These studies allow the tentative conclusion that endothall per se is the residue of concern in rice. However, the unsubmitted study regarding the catabolism of endothall in the rice plant using radiotracer techniques (referred to in Section B, Exhibit 21, p.3) would be helpful in affirming this conclusion; the petitioner should be so informed.

Residue Methods

The method applicable to rice grain and straw is essentially the same as that used successfully in the second trial on potatoes (see memo, 4/2/73, PP#1F1057, K. Zee). The chopped sample is blended with acidified acetone. After filtration, the extract is cleaned up by treatment with activited charcoal. The acetone is removed and the aqueous solution subjected to additional clean-up by use of a cation exchange resin column. The endothall in the eluate is then adsorbed on activated charcoal and recovered by boiling with acetic acid. Treatment of the residue with 2-chloroethylamine hydrochloride results in formation of the N-chloroethylimide derivative of endothall. The imide is partitioned into chloroform and after further clean-up with activated charcoal and attaclay is determined by a GLC technique employing either a nitrogen-specific microcoulometric or a Coulson conductivity detection system.

Recoveries on rice grain at fortification levels of 0.05-2.0 ppm ranged from 74-94% (82% av). No validation data are submitted for rice straw; however, in view of the method's wide product applicability, no problems are anticipated. Control values are all reported as less than 0.05 ppm; representative chromatograms indicate their actual magnitude to be ca. 0.03 ppm.

Based on our review of the chromatograms, we judge the method to be capable of a practical sensitivity of ca. 0.1 ppm. Endothall residues can be detected at lower levels, but can not be accurately quantitated.

We conclude that the method is adequate for determination of endothall per se. A method trial was not requested because of the method's similarity to that successfully tested on potatoes at the 0.1 and 0.2 ppm levels.

Should the rice metabolism study (see Nature of the Residue) show the presence of toxic residues other than endothall per se, we will need a validated analytical method or methods capable of determining total residues.

Residue Data

The data reflect 7 studies conducted in 5 California locations. Rice grain samples treated according to the proposed use at rates of 2-6 lbs (up to 2X maximum recommended) endothall acid equivalent/A and harvested at intervals of 105-135 days showed no detectable endothall residues (less than 0.05 ppm). These data are questionable, however, since the samples were stored prior to analysis for periods ranging from 8½ months (2 studies) to 3½ years. The average time of sample storage is nearly 2 years. Storage s stability data (including storage conditions) are required before a final judgment regarding residue levels can be made. Additional residue data will be necessary if residue stability over long storage intervals can not be demonstrated.

Tentatively, we conclude that the proposed tolerance is adequate to cover residues of endothall per se in rice grain resulting from the proposed use. Should the rice metabolism study indicate the presence of toxic degradation products, additional residue data will be required.

There are no residue data pertinent to rice processing fractions. We are withholding comment on residues in the fractions (hulls, bran, etc.) until the questions regarding storage stability and degradation are resolved. The exact nature of the samples analyzed should also be specified (e.g., rough rice, brown rice, polished, etc.).

No data for rice straw are presented. Such, data, reflecting treatment in accord with the proposed use, are required, together with an appropriate tolerance proposal.

Two decline studies regarding endothall residues in rice paddy water are presented. Residue levels declined from ca. 0.5 ppm 2 days after applie cation of 2 lbs endothall acid equivalent/A to a maximum of 0.06 ppm 10 days after treatment. Thus, the 0.2 ppm interim tolerance for water will not be exceeded under the ten-day water use restriction (see Proposed Use). There will also be no problem with residues of dimethylcocoamine, since data in PP#1F1105 show detectable residues (<0.05 ppm) in water at the proposed 10 day water use restriction interval.

Since this use is restricted to California, residue data for crayfish and catfish are not a consideration.

Meat, Milk, Poultry and Eggs

Rice grain, hulls, bran, polishings and rice straw are livestock feed items. Because of the previously discussed questions involving residue levels in rough rice, fractions and straw, we are unable to classify this use with respect to Section 180.6(a). At such time as residue levels in all feed items are determined, the goat and poultry feeding studies discussed in previous reviews should be adequate to categorize this use.

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