PP# 1612

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PP# 5F1612/FAP# 5H5084. Benomyl in or on rice.
Evaluation of analytical methods and residue data.

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E. I. du Pont de Nemours and Company proposed that tolerances be established for combined residues of the fungicide benomyl [methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate] and its metabolites containing the benzimidazole moiety (calculated as benomyl) as follows:

Pesticide Tolerances (PP# 5F1612)

5 ppm in or on rice

15 ppm in or on rice straw

Food Additive Tolerance (FAP# 5H5084)

20 ppm in or on rice hulls when present therein as a result of preharvest application of the fungicide to the raw agricultural commodity rice.

Tolerances for residues of benomyl and its metabolites containing the benzimidazole moiety are established [40 CFR 180.294] on a variety of commodities, including meat, milk, poultry and eggs, at levels ranging from 0.1-50 ppm. There are also food additive tolerances established at 50 ppm for residues in raisins and concentrated tomato products [40 CFR 123.30] and dried citrus pulp; at 70 ppm for residues in dried apple pomace; and, at 125 ppm for residues in dried grape pomace and raisin waste [40 CFR 561.50].

No other benomyl petitions are pending.

Conclusions

1a. The nature of the residue in plants and animals is adequately understood. The residues of concern are benomyl *per se* and its metabolites containing the benzimidazole moiety.

1b. No residues of STB or BUB will result from the cooking of treated rice.

2. Adequate analytical methods (fluorometric and liquid chromatographic) are available for enforcement purposes.

3. The proposed tolerance levels of 5 ppm for rice, 15 ppm for rice straw, and 20 ppm for rice hulls are adequate to cover anticipated residues arising from the proposed use. No food additive tolerances are needed for the milling fractions, bran and polishings.

4. The established meat, milk, poultry, and egg tolerances are adequate to cover both the existing and proposed feed uses. The proposed feed uses fall into Sec. 180.6(a)(2).

5a. A label restriction to the effect, "water drained from treated areas must not be used to irrigate other crops" is needed.

5b. EEE requests a revision of the label restriction re crayfish to read as follows: "Do not use in areas where catfish and crayfish farming are practiced."

5c. EEE has stated that soil persistence data indicate that rotational crop data are needed. Such data, when received, may demonstrate the need for label restrictions on rotational crops.

Recommendations

We recommend against the proposed tolerances for the reasons cited in conclusions 5a, 5b, and 5c.

Proposed Use

Du Pont "Benlate" Benomyl Fungicide is recommended for use on rice for the control of rice blast (*Piricularia oryzae*), stem rot (*Sclerotium oryzae*), and panicle blight (*Cercospora* spp).

Apply 1 to 2 lbs. (i.e., 0.5-1 lb. ai) per acre in sufficient water to obtain thorough coverage of the plants. For aerial application, use 3 to 10 gals. per acre. Make the first application at booting; make a second application at heading. Under severe disease conditions, use the higher rate.

Limitations: Do not apply within 21 days of harvest. Do not apply to stubble rice. Do not harvest crayfish after application. Do not use alkaline pesticides such as basic copper sulfate, Bordeaux mixture, or lime sulfur, as a tank mixture with "Benlate."

We note that EEE (R. E. Mey, Jr. and E. B. Brittin, 5/22/75) has indicated that the restriction, "do not harvest crayfish after application" is not acceptable. EEE states that a label restriction such as "Do not use in areas where catfish and crayfish farming are practiced" is needed.

A label restriction to the effect, "Water drained from treated areas must not be used to irrigate other crops" is also needed.

Additionally, label restrictions on rotational crops may be required; EEE has indicated that data have not been submitted yet to allow them to assess the hazards of residues in rotational crops.

Manufacture and Formulation

The manufacturing process for benomyl was submitted in conjunction with PP# 4F1466 (Amendment of 7/9/74), but has not heretofore been incorporated in a review.

Benomyl is manufactured [redacted]

Technical benomyl consists of minimum of 95% methyl-1 (butylcarbamoyl)-2-benzimidazolecarbamate. The manufacturing impurities consist of [redacted] We do not anticipate a residue problem from these impurities with the possible exception of [redacted]

Benomyl is marketed as a 50% wettable powder, trade name Benlate, containing 53% technical benomyl as active ingredient. The inert ingredients are [redacted]; all are exempt from tolerances under Section 180.1001.

Nature of the Residue

Plant metabolism studies of benomyl (summarized in our review of PP# 0G0936, W. J. Boodee, 2/19/70) indicate a rapid stepwise degradation to MBC, then to 2-aminobenzimidazole (2-AB), and finally to smaller organic fragments and CO_2. From the consistent metabolic behavior demonstrated by benomyl in various plants (beans, cucumbers, apples, oranges, and cotton), we conclude that a similar degradative route occurs in rice. The residues of concern are benomyl per se, MBC, and 2-AB.

We have previously established (R. J. Hummel et.aal., 10/25/72, PP# 1F1033) that the benomyl conversion products, 3-butyl-s-triazino [1,2a] benzimidazole-2,4-(1H,3H)dione (STB) and 2-(3-butylureido) benzimidazole (BUB)--compounds formed under laboratory conditions when benomyl is either heated (50°C, 6 hours) or used in an alkaline medium (pH >9)--will not be formed in tank mixes at pH <9, in or on plants, in postharvest dips and sprays, and soil.

Benomyl metabolism in animals has been discussed in previous petitions (see memos of W. J. Boodee, PP# 0G0936, 2/19/70 and PP# 1F1010, 3/29/71). In addition to the metabolites found in plants, the 4-hydroxy and 5-hydroxy isomers of MBC are also components of the terminal residue in animals.

We conclude that the nature of the residue in plants and animals is adequately understood.

No data were submitted with this petition showing how the cooking process affects benomyl residues. Such data were submitted with PP# 4F1421 for beans, however, and were discussed in our reviews (R. J. Hummel) of 4/19/74 and 7/30/74. Therein it was shown that when beans fortified with 2 ppm benomyl were boiled, only residues of MBC were detected in the cooking water and in the cooked beans. However, when water was fortified with benomyl and boiled, 2% conversion to STB occurred.

Using the rationale that benomyl is known to be rapidly metabolized in plants (complete conversion in beans within 5 days; see aforecited 2/19/70 review) to MBC and further to 2-AB (neither of which can be converted to STB or BUB; see aforecited 7/30/74 review), it was concluded that following the prescribed PHI (28 days) no residues of benomyl per se would remain in/on beans and thus no possible conversion to STB or BUB upon cooking could result.

Using a similar rationale for rice, and noting that a minimum 21-day PHI is entailed, we translate the above cooking study data for beans to rice and conclude by analogy that no residues of STB of BUB will result from the cooking of treated rice.

Analytical Methods

Residue data were obtained by two methods: the liquid chromatographic method of Kirkland, et. al. (J. Ag. Food Chem. 21, 368 (1973)) and the fluorometric method of Pease and Holt (JAOAC 54, 1399 (1971)).

The LC method was described in detail in connection with PP# 4F1466 (see review of R. Beyak, 6/20/74). Residues of benomyl and MBC are measured as MBC and any 2-AB present in the residue is simultaneously determined as a separate LC peak; the sum of these three components constitutes the total benomyl residue.

The fluorometric method was described in detail in connection with PP# 2F1240 (see review of D. V. Reed, 5/23/72). The method measures residues of benomyl consisting of benomyl, MBC, and 2-AB as 2-AB, and the results are reported in terms of benomyl.

Both these basic methods have previously undergone successful MTO's (fluorometric in re PP# 0F0906, see B. Puma memo of 11/3/71; LC in re PP# 2F1192, see B. Puma memo of 3/22/72). Both methods have previously been adjudged adequate for enforcement purposes (see R. Beyak review, 6/20/74, PP# 4F1466).

Validation data were submitted for benomyl residues in rough rice, straw, rice hulls, bran, and polished rice. Fortification levels of benomyl ranged from 0.05-5 ppm and recovery values were adequate in each substrate tested. The sensitivity of the LC and fluorometric methods were judged to be ca. 0.15 ppm based on blank values. Representative chromatograms were provided.

No validation data were submitted for the metabolites, MBC and 2-AB. However, such data are available for other R.A.C.'s either in previous petition files (e.g., PP#'s 0F0906, 0F1000, 1F1010, 1F1045, and 1F1145) or with the published LC method.

We conclude that adequate analytical methods are available for enforcement purposes.

Residue Data

Residue data for rough rice and/or straw were submitted from 22 field studies conducted in TX, LA, and AR during the crop years 1969, 1970, 1972-74. Studies reflected 2-3 applications of "Benlate" at 0.25-2 lbs. ai in 10-16 gals. of water per acre by ground or aerial application; PHI's ranged from 7-45 days, and included decline series. Included among the data were results from milling studies for rice fractions (polished rice, bran, and hulls). [Proposed use pattern: 2 applications of 0.5-1 lb. ai/A, 21-day minimum PHI.]

The submitted data for rice grain are adequate to demonstrate that anticipated residues should not exceed the proposed tolerance level of 5 ppm. In fact, the majority of residue values are far below the proposed tolerance level.

The submitted data for rice straw indicate a wide variance in residue levels, ranging from < 0.05 ppm (two 0.5 lb. ai/A applications, 33-day PHI) to 13 ppm (two 0.6 lb. ai/A applications, 23-day PHI). With few exceptions the residue data are well within the proposed tolerance level. After consideration of all the available residue data for straw at hand, we conclude that residues therein are not reasonably expected to exceed the proposed tolerance level of 15 ppm under the proposed conditions of use.

The submitted data for rice milling fractions indicate a food additive tolerance is needed for rice hulls. However, since these milling studies (with rice field-treated at 0.5 lb. ai/A, 31-45 day PHI's) utilized rough rice containing no detectable residues (< 0.05 ppm), these data are of extremely limited usefulness in determining the level at which such a food additive tolerance should be set.

To supplement these data, the petitioner submitted an additional study in which untreated rough rice was fortified with benomyl at 1 or 4 ppm and milled. The weight distribution of the milled fractions was found to be 70% polished rice, 11% bran, and 19% hulls. Analysis of the fortified rough rice and the milled fractions showed that the majority (> 90%) of the benomyl residue present was situated in the hulls, with a small amount in the bran. The concentration factor in the hulls was found to be 3-4X (theoretical = 5X); a food additive tolerance of 20 ppm (based on a 4X concentration factor) is proposed.

Since the data indicate a small percentage of the residue is in the bran fraction, and since there are indications of modest residue losses during milling, use of a 4X concentration factor (vis-a-vis 5X) for rice hulls in this instance does not seem out-of-line. We conclude that the proposed 20 ppm food additive tolerance for rice hulls is adequate.

Residues in the other milling fractions (bran and polishings) are not expected to exceed those in the R.A.C. per se, therefore no food additive tolerances for them are needed.

Residues in Meat, Milk, Poultry, and Eggs

No feeding study data are presented in this petition. Such data h have been previously submitted for cattle (PP # 1F1010) and poultry (PP # 2F1218/FAP#)2H5004) and discussed in our reviews dated 3/29/71 (M. J. Boodee) and 4/12/73 (R. J. Hummel), respectively. Feeding levels were 0, 2, 10, and 50 ppm for cattle and 0, 5, and 25 ppm for poultry. Based on these data, tolerances were subsequently established at 0.2 ppm in poultry liver and 0.1 ppm in eggs, milk, and the meat, fat, and meat by-products of cattle, goats, hogs, horses, poultry (except liver), and sheep.

These established meat tolerances have previously been considered adequate to support residues in feed items ranging up to 125 ppm (dried grape pomace and raisin waste).

The feed items involved in this present petition are rice straw, hulls, bran, and polishings. When consideration is given to the percentage of the animal diet which these may constitute (per the Harris Guide) and the level of residues which these may contain (per the proposed tolerance levels), we can conclude that the established meat, milk, poultry, and egg tolerances are adequate to cover their feed use (as well as concurrent feed use of other commodities with established benomyl tolerances).

We classify the feed uses of rice straw and milling fractions as category 2 of Sec. 180.6(a).

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cc: TOX, EEE, HFO-130(FDA),CHM(5)
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