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PP#file 1452

PP#4F1452. Benomyl on Tomatoes. Evaluation of the analytical method and residue data.

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Coordination Branch
and Toxicology Branch, RD

E.I. DuPont de Nemours and Company proposes a tolerance of 5 ppm to be established for residues of the fungicide benomyl, methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate, and its metabolites containing the benzimidazole moiety in or on tomatoes.

Permanent tolerances have been established (40 CFR Section 180.294) ranging from 0.1 ppm in milk, meat, fat, meat byproducts and eggs to 15 ppm in a variety of commodities. Food additive tolerances have been established for a number of food and feed items in the range of 50 to 125 ppm (21 CFR Section 121.343, 121.1254).

Benomyl tolerance petitions currently pending are PP#4F1421 on beans and bean vine forage, PP#4F1427 on pineapple, PP#4F1466 on soybeans, and PP#4E 1479 on blueberries.

Conclusions

1. The degradation of benomyl in plants and animals is understood. The terminal residues on tomatoes are comprised of benomyl per se, methyl-2-benzimidazolecarbamate (MBC), and 2-aminobenzimidazole (2AB).

2. An adequate analytical method is available for determining the terminal residues of benomyl and for enforcing the proposed tolerance on tomatoes. The method will not distinguish between the three species but will determine the total residues as 2AB.

3(a) The proposed tolerance is adequate to cover residues resulting from the proposed use of benomyl on field and greenhouse tomatoes.

(b) We will need residue data for the concentrated tomato processed items, such as, ketchup and/or tomato paste, in order to determine whether or not a concentration of benomyl residues takes place.

4. The proposed use of benomyl on tomatoes falls into Category 2 of Section 180.6(a), when tomato culls are used as a livestock feed item. The established tolerance of 0.1 ppm in milk, meat, fat, meat by-products of livestock is adequate to cover any residues from this use. There is no poultry feed item involved in this proposal, therefore, it is Category 3 situation with respect to poultry and eggs.

5. The manufacturing process for benomyl should be submitted.

Recommendations

We recommend against the establishment of the proposed tolerance for the reasons given in conclusions 3(b) and 5, and we defer to EEB regarding the question of soil persistence from the proposed use.

Detailed Considerations

Formulation

Benomyl is available as a technical material consisting of at least 95% methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate. We do not have the benomyl manufacturing process in our files. It should be submitted. The impurities consist of [redacted] We do not anticipate a residue problem from these impurities. [redacted]

"Benlate" benomyl fungicide, a 50% active wettable powder, is to be used for the proposed control of *Botrytis* gray mold, *Cladosporium* leaf mold, *Cercospora* white mold on field and greenhouse tomatoes. The inert ingredients consist of [redacted] are exempt under Section 180.1001.

Proposed Use

"Benlate", 50% active, is applied to the tomato plants when the disease first appears; then repeated at 7-to 14 days intervals as needed. It is applied as a spray with sufficient water to obtain through coverage of the plants. Greenhouse tomatoes will be treated at rates of ¼ lb. to ½ lb. a.i. per 100 gallons of water while field treatments will range from ¼ lb to ½ lb. a.i. per acre. Treatments will be permitted up to the day of harvest.

MANUFACTURING PROCESS INFORMATION AND INERT INGREDIENT INFORMATION ARE NOT INCLUDED

The label directions do not state the maximum number of applications per growing season however, the petitioner explains that while there may be many applications during the bearing life of the plant, there is only a 5 week growth stage from fruit set to harvest. Consequently, they state that 5 applications are the maximum number of treatments a tomato crop will likely receive. We agree with this conclusion.

Nature of the Residue

CB summarized the benomyl metabolism studies on beans, cotton, apples, oranges, and cucumbers in the review by W.J. Boodee (see memo of 2/20/70, PP# 0G0936). These studies indicate that field degradation of benomyl results in residues of methyl-2-benzimidazolecarbamate (MBC) and 2-aminobenzimidazole (2AB). The degradation products eventually breakdown to smaller organic fragments and carbon dioxide. Since the studies of the various r.a.c.'s exhibit a consistent metabolic pathway, we conclude that the residues of benomyl (and its metabolites containing the benzimidazole moiety) on tomatoes will be benomyl per se, MBC and 2AB.

In the joint memo of CB, R.J. Hummel et al (10/25/72), we reviewed data on two additional possible degradation products, 3-butyl-s-triazino [1,2a] benzimidazole-2,4-(1H,3H) dione, (STB), and 2-(3-butylureido) benzimidazole, (BUB). From these data, we concluded that STB and BUB will not be formed in tank mixes (@pH<9), in plants, in post-harvest dips or in soil. We believe these findings also apply to the proposed use of benomyl on tomatoes and conclude that these two degradation products will not form part of the benomyl residues on tomatoes or their processed fractions (see Residue Data).

Two animal metabolites, methyl-4-hydroxy-2-benzimidazolecarbamate and methyl-5-hydroxy-2-benzimidazolecarbamate, have been identified (in addition to those found in plants) in rat and cow feeding studies and may form part of the benomyl residues (see memos of W.J. Boodee, PP#0G0936, 2/20/70 and PP#1F1010, 3/29/71).

We conclude that the nature of the benomyl residues in plants and animals has been adequately characterized.

Analytical Method

Benomyl residue data were determined by the fluorometric method of Pease and Holt (JAOAC, 54, 1399; 1971). The method was discussed in detail by D.V. Reed (see memo of 5/23/72, PP#2F1240) and is being used for enforcement purposes for a number of benomyl tolerances.

The method will determine benomyl, MBC, and 2AB as the 2AB species, however, the results are reported in terms of the parent compound, benomyl. The method sensitivity and the maximum level of apparent residues in tomato control samples is 0.6 ppm on a 25 gm sample (proposed tolerance is 5 ppm).

Recoveries of benomyl on tomatoes at 0.2 to 8.0 ppm fortification levels average 94.8% with a range of 72-132% (n=10). Recovery data for the benomyl metabolites are not reported in the present petition; however, satisfactory recoveries of 2AB were reported in the reviews of PP# 0F1000 (stone fruits), PP#1F1045 (cucumber, le melons and squash), and PP# 0F0906 (bananas).

We conclude that the fluorometric method is adequate to enforce the proposed tolerance of benomyl residues on tomatoes.

Residue Data

Residue data for benomyl and its metabolites containing the benzimidazolecarbamate moiety on tomatoes are submitted from field and greenhouse studies. The studies were conducted from 1968-72 and located in the six states of Arkansas, California, Florida, Indiana, Ohio and Texas. In field studies, the maximum residues at " 0 " days from the proposed use ranged from 2.4 ppm after 3 applications to 4.8 ppm after 4 applications at 2X the maximum proposed rate. The benomyl residues decreased to 1.4 ppm and 2.8 ppm for the 1X and 2X rates, respectively, at 4 days after the last treatment.

The maximum residue level for greenhouse applications is 2.6 ppm after 5 treatments at (2X) the proposed rate and sampled on the day of the last treatment. Benomyl residues of 0.19 ppm resulted from 8 treatments at the proposed rate and sampled seven days after the last treatment.

Residue data are not given for the processed products of tomatoes. The production of tomato juice and canned tomatoes do not require a concentration of tomato solids, therefore, we would not expect benomyl residues to concentrate in these fractions. On the other hand, the production of ketchup and tomato paste require a solids concentration of three to four times that found in tomatoes. Consequently, we will require benomyl residue data on one of the last two processed items, preferably, the tomato paste.

Since the tomato fractions are acidic in nature, we would not expect the formation of the benomyl degradation products, STB and BUB, in the processed fractions and will not require the corresponding residue data. For the conditions of STB and BUB formation, see the CB joint memo of 10/25/72.

Radio-labeled benomyl at 2 ppm was added to beans in a processing study and cooked for 30 min. in water. The applied radioactivity was completely recovered and the data show a quantitative conversion of benomyl to MBC, (see memo of R.J. Hummel, PP#4F1421, 4/19/74). Therefore, we would expect that the benomyl residues in processed tomato items be converted to MBC.

We conclude that the residues of benomyl and its metabolites containing the benzimidazolecarbamate moiety will not exceed 5 ppm on tomatoes from the proposed use on field and greenhouse tomatoes. However, we will require additional residue data for the concentrated tomato processed fractions, preferably tomato paste, to determine whether or not the residues of benomyl will concentrate in the process.

Meat, Milk, Poultry and Eggs

No new feeding study are submitted with the present petition. There are established tolerances for benomyl and its metabolites containing the benzimidazolecarbamate moiety in meat, milk, poultry and eggs at 0.1 ppm. The tolerances were based upon feeding levels of 50 ppm and 25 ppm in the diets of livestock and poultry, respectively, (see memos of W.J. Boodee, PP#1F1010, 3/29/71 and R.J. Hummel, PP#2F1218, 4/12/73). These feeding studies were used to support tolerances of 125 ppm and 70 ppm for dried grape and apple pomace, respectively, (PP#2F1218, PP#1F1033) as well as other feed items with lower tolerances. Therefore, we do not expect a feeding problem resulting from the use of benomyl on tomatoes should culled tomatoes containing residues at the proposed tolerance of 5 ppm be used as a feed item. In the event a transfer of residues in milk, meat, and meat by-products of livestock does occur, the presently established tolerances will be adequate to cover them.

We conclude that the proposed use of benomyl on tomatoes will result in a category 2 situation of section 180.6(a) with regard to the use of culled tomatoes as a feed item for livestock. There are no poultry feed items involved in the proposed use of benomyl on tomatoes; thus, we judge this use to be a category 3 situation of section 180.6(a) with respect to poultry and eggs.

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