

US EPA ARCHIVE DOCUMENT

Propargyl Bromide

PP # 5F0426

Petitions Control Branch and
Division of Toxicological Evaluation

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Division of Food Standards and Additives

AF 15-946

Combined profile reviews of PP #5F0426 and PP #5F0427, "Trizone" on various crops.

The Dow Chemical Company proposes the inorganic bromide tolerances tabulated below for residues resulting from soil fumigations with "Trizone," a mixture containing 61% methyl bromide, 30% chloropicrin, and 9% propargyl bromide (6.8% 3-bromopropyne and 2.2% related brominated C₃-hydrocarbons).

| <u>Crop</u> | <u>Inorganic Bromide Tolerances (ppm)</u> | |
|--------------|-------------------------------------------|----------------------------|
| | <u>from propargyl bromide</u> | <u>from methyl bromide</u> |
| broccoli | 5 | 15 |
| cauliflower | 5 | 15 |
| peppers | 5 | 15 |
| pineapples | 5 | 15 |
| strawberries | 5 | 15 |
| tomatoes | 15 | 25 |
| eggplant | 15 | 25 |
| | 20 | 40 |

PP #5F0426 pertains to 3-bromopropyne and PP #5F0427 to methyl bromide, each in combination with the other as components of the Trizone mixture. The same data are given in both petitions and we have accordingly combined the profile reviews.

The petitioner has not proposed combined numerical tolerances, but proposes instead to amend Sec. 120.3 (erroneously given as Sec. 130.3) to provide that where a mixture of propargyl and methyl bromides is used, the overall quantity of inorganic bromide to be tolerated shall be the sum of the individual tolerances, in the same agricultural commodity, for propargyl and methyl bromides. Since there is no practical way to distinguish the individual residues of the two bromide fumigants, it would seem advisable to combine the individual tolerances directly in one regulation. Whether this should be done in this manner or as proposed by the petitioner can be decided after the final review.

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The petitioner has stated claims that the mixture is a more effective fumigant than either methyl bromide or propargyl bromide alone and that the proportions used are critical. The amount of chloropicrin present is much lower than the maximum shown in the USDA Summary of Registered Agricultural Pesticide Chemical Uses for chloropicrin alone when used as a pre plant soil fumigant.

Although chemical abstracts uses "3-bromopropyne" for this compound, "propargyl bromide" is favored by industry and appears on a number of labels registered with the USDA. Either name is acceptable but 3-bromopropyne is preferred.

Conclusions

Adequate data are available to:

1. evaluate the residue methods. No try-out is required.
2. determine the possibility of residues of the fumigants per se on the crops. A preliminary evaluation indicates no 3-bromopropyne residues by a method sensitive to about 0.01 ppm.
3. estimate the maximum likely inorganic bromide residues in all the above crops.
4. estimate potential residues of inorganic bromide in meat and milk from the feeding of pineapple bran.

Recommendation

If toxicological considerations permit, we recommend that these two petitions be filed.

A preliminary review of the data indicates that 15 ppm from 3-bromopropyne and 25 ppm from methyl bromide would be more appropriate tolerances for muskmelons than those now proposed.

Detailed Considerations

Proposed Usage

Preplant applications are to be made at rates of 160-200 lbs Trizena/A by injecting to a depth of 4-6 inches into the soil with a special chisel-type applicator. Treated areas are to be covered with polyethylene film and exposed to the fumigant for at least 48 hours (longer depending on temperature). The original directions called for aerating 2-3 weeks for transplants, and 3-4 days for seeds.

JH

At a conference held September 22, 1964, we pointed out that the supporting data did not reflect the shorter aeration period for seeding and that the USDA Summary required at least 7 days aeration for chloropicrin (alone). In new labelling submitted September 25, 1964, a uniform 2-3 weeks preplant interval is proposed for these crops.

Residue Methods

The petitioner has developed a gas chromatographic method for determining residues of 3-bromopropyne. The crop is macerated with water and extracted with benzene. An aliquot of the extract is injected without cleanup into a gas chromatograph equipped with an electron capture detector. The validation data on this procedure are adequate for final review. The petitioner claims a sensitivity of 0.1 ppm but we estimate tentatively that the sensitivity is actually about 0.01 ppm.

The original petitions contained no methods for residues of the fumigants methyl bromide and chloropicrin per se. We raised the question of chloropicrin residues at the September 22, 1964, conference and the petitioner sent us a method for chloropicrin. The procedure involves macerating the sample, acidifying, heating in a closed system and trapping chloropicrin in absorber tubes containing isopropyl alcohol and sodium peroxide. Refluxing the alcoholic solution converts chloropicrin to nitrite which is determined colorimetrically after a Bratton-Marshall reaction. The validation data presented on this method are adequate for final review.

Some of the inorganic bromide residues were determined by Dow's X-ray fluorescence method. The sensitivity of this method, as reported by the petitioner, is only 5 ppm. Since the numerical level of the combined proposed tolerances is at least 4 times the sensitivity level, the data obtained by this method are considered acceptable.

There are other data, for these crops, obtained by the method of Shrader et al., Ind. and Eng. Chem. 14, 1 (1942). This is similar to our enforcement method for present bromide tolerances and is adequate for obtaining residue data. No method try-out is necessary.

Residue Data

Organic Residues

3-Bromopropyne residue assays were run on each crop. The treatments reflected the proposed use, except in the case of pineapples which were treated with pure 3-bromopropyne instead of the mixture. A few samples of peppers, eggplant, muskmelons, and strawberries appear to have residues ranging from 0.01-0.05 ppm, by a method sensitive to about 0.01 ppm. The petitioner claims that these results are due to contamination. A preliminary evaluation indicates that the claim may be justified, and that probably there are no residues of 3-bromopropyne in these crops.

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As originally presented, the petitioner relied on the findings of the 1950 hearings to support the presumed absence of methyl bromide and chloropicrin residues. We considered this adequate for the more volatile methyl bromide, but we were reluctant to rely solely upon the findings of the hearings in regard to chloropicrin. At our request at the September 22, 1964, conference, the petitioner sent us residue data on crops grown in soils which had been fumigated with chloropicrin. These data include residue studies on white potatoes, sweet potatoes, and strawberries. The doses involved exceed the chloropicrin portion of the proposed Trizene applications. While only one of these three crops, strawberries, is involved in the pending petition, we would expect potatoes to have a greater tendency to acquire chloropicrin residues than the crops in the petition. Therefore, we consider these studies adequate to determine the possibility of chloropicrin residues resulting from the proposed use.

Inorganic Bromide Residues

Crops were grown in soil treated with 3-bromopropyne and Trizene. The residues due to methyl bromide were calculated by difference.

Bromelli and Cauliflower

Only one study is available for each of these crops. However, the combined data constitute a reasonable basis for estimating residues and we conclude that the data on these two crops are adequate for final review.

Muskmelons

We consider the data for this crop in three studies conducted in Michigan and New York adequate for final review. From the high residues reported (combined max. 35 ppm, avg. 24 ppm) it would appear that the petitioner underestimated the tolerances needed for this crop. Fifteen and 25 ppm would be more appropriate than the levels of five and 15 ppm actually proposed.

Peppers

Three studies are reported for New York and Michigan and overall we consider the pepper data adequate for final review.

Pineapples

Two of the three Hawaiian studies with Trizene reflect preplant intervals of more than two weeks. The long growing season for this fruit makes this deficiency a minor^{one} in addition, the data are supported by three studies involving Brozone (69% methyl bromide, 1.4% chloropicrin, and 30% petroleum hydrocarbons) and two studies involving 3-bromopropyne alone.

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Another study with ethylene dibromide is not pertinent to the proposed use. We consider these data adequate for final evaluation.

Strawberries

Seven studies in Maryland, New York, and California are of limited value because of preplant intervals exceeding 14 days. Four other studies in Michigan and New York with the support of the first group are adequate for final review.

Tomatoes

Four studies in Michigan and New York provide adequate data for final review.

Explant

Only two studies in Michigan and New York are available. Since this is a minor crop, we consider these data to be adequate. The combined individual tolerances proposed for explant is the only instance where the 50 ppm inorganic bromide tolerance on the same crops for residues resulting from soil fumigation with Nemagon would be exceeded.

Residues in Meat and Milk

The feeding of pineapple bran to cattle could cause inorganic bromide residues in meat and milk. However, the combined individual tolerances proposed for pineapple would yield residues in bran no greater than those from pineapple grown in Nemagon-treated soil. This question was discussed in detail in the (FSA (J. Alpert) memo of 2/18/63 in PP #294).

Other Considerations

The use of tomatoes grown in Trisone-treated soil may result in higher than tolerance level residues in concentrated tomato products. These residues would be within the 250 ppm inorganic bromide tolerance established by FAF 782 for residues resulting from Nemagon. We defer to PCB on the need for a food additive regulation to cover similar residues from Trisone.

In view of the volatility of these fumigants and the solubility of inorganic bromide compounds, we would not expect residues to build up in the soil. There are some limited data on soil residues from ethylene dibromide in PP #34 which may be pertinent to our final evaluation.

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