



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Memorandum

Subject: Triphenyl Tin Hydroxide; Response to Registration Standard; M&T Residue Analytical Method (TA-49); Residue data for Pecans and Peanuts; Accession Nos. 266045 and 266046; RCB Nos. 1702.

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M&T Chemicals Inc. has submitted a residue analytical method (TA-49) along with residue data for phenyltin species ($\phi_a\text{SnX}_4\text{-a}$) in pecans and peanuts; this information was provided in response to the Triphenyltin Hydroxide (TPTH) Registration Standard (issued 9-30-86). A similar submission for $\phi_a\text{SnX}_4\text{-a}$ in sugarbeets, soybeans, peanut hulls, carrots, and potatoes was recently reviewed by S. Hummel (see, TPTH S.F., memo dated 9-4-87).

Tolerances are established (40 CFR 180.236) for triphenyltin hydroxide, per se, in or on peanut hulls at 0.4 ppm; carrots and sugarbeet roots at 0.1 ppm; pecans, peanuts, and potatoes at 0.05 ppm; and kidney and liver of cattle, goats, hogs, horses, and sheep at 0.05 ppm. Tolerances are pending for residues of TPTH on rice (PP#0F2340), soybeans (PP#3F2833/FAP#3H5384), and eggs, milk, meat, fat, and meat by-products of cattle, goats, hogs, horses, and sheep (PP#0F2340).

The TPTH Reg. Standard identifies 4 formulations which are registered for use on food and feed crops; they are: (1) a 47.5% wettable powder, (2) a 40% flowable liquid, (3) a 19.7% flowable liquid, and (4) a flowable mixtures containing 40.9% sulfur and 5.1% TPTH.

DIRECTIONS FOR USE

No label or EPA Reg. No. was provided for the product used in conjunction with this submission. The information presented below was taken from the TPTH Reg. Standard.

Pecans: TPTH may be applied in the form of a wettable powder containing 47.5% ai. Application is made as a delayed dormant spray when leaves are unfloding or as a foliar spray when small nuts are forming. Aerial application may be made at the rate of 0.36-0.71 lbs. a.i./A. Ground application may be made at a rate of 1.5-4.5 ozs. /100 gal with full coverage spray. The maximum number of applications is not specified. Use restrictions include: repeat application as often as every two weeks, but no applications should be made after the shucks begin to open; Do not graze dairy or meat animals in treated areas.

Peanuts: TPTH may be applied in the form of a wettable powder containing 47.5% ai. Application is made as a water spray with the first application made 6 weeks after planting or as signs of leaf spot appear. 2.4 to 3.8 ozs. ai/A are applied (in 10-100 gallons of water per acre using ground equipment or 3 to 10 gallons per acre using aircraft). Repeat application at 10 to 14 day intervals; the maximum number of applications is not specified. Use restrictions include: do not allow hogs to feed on peanuts in treated fields; do not use vines as feed; and do not use in combination with emulsifiable concentrate or oil spray formulations.

PLANT AND ANIMAL METABOLISM

Tolerances were initially established for the parent compound only; however, upon review of additional information provided in connection with PP#0F2340 (E. Leovey, RCB, memo of 9-17-80) and PP#3F2823/ FAP#3H5384 (K. Arne, RCB memo of 7-14-83 and J. Doherty, TOX, memo of 10-28-83), the Agency now considers the residues of concern in plants and animals to be intact TPTH, and its di- and monophenyltin hydroxides (or oxides). This conclusion is expressed in the TPTH Registration Standard as follows:

" In addition to the parent compound the metabolites di- and monophenyltin hydroxides (oxides) should now be included in all residue tolerances (see J. Doherty, TOX Branch memo on PP#3F2823/FAP#3H5384 dated October 28, 1983). The existing tolerances are expressed in terms of parent compound, TPTH alone."

ANALYTICAL METHODOLOGY

This submission contains the following reports:

1. "Validation of a Method for the Separation and Determination of Phenyltin Species ($\phi_a\text{SnX}_4\text{-a}$) in Pecans by Liquid Chromatograph/Atomic Absorption Spectroscopy Plus Crop Residue Analyses" by A. Marino, 9-29-86.
2. "Validation of a Method for the Separation and Determination of Phenyltin Species ($\phi_a\text{SnX}_4\text{-a}$) in Peanuts by Liquid Chromatograph/Atomic Absorption Spectroscopy Plus Crop Residue Analyses" by A. Marino, 9-26-86.

The data for both reports were generated using M&T Method No. TA-49. M&T Method TA-49 is essentially identical to M&T Methods TA-43, TA-45, TA-46, TA-47, and TA-48 ; these methods differ only in their initial extraction, which is optimized for a specific sample type. M&T Methods TA-43, 45, 46, 47, and 48 were recently reviewed by RCB (S. Hummel, TPTH S.F., memo of 9-4-86), therefore only a brief overview of M&T Method TA-49 will be provided in this review, as follows:

M&T Method TA-49 is applicable for assaying triphenyltin hydroxide, its degradation products (tetraphenyltin, diphenyltin oxide and phenyl stannic acid), and inorganic tin (as tetra-butyltin). 100 grams of chopped nuts are extracted with a solution of methanol/water/tartaric acid. The solubilized tin compounds are partitioned into hexane (containing the chelating agent tropolone), then converted to their corresponding tetraorganotin species by reacting with BuMgCl . Triphenyltin hydroxide ($\phi_3\text{SnOH}$) converts to triphenylbutyltin ($\phi_3\text{SnBu}$), diphenyltin oxide ($\phi_2\text{SnO}$) converts to diphenyldibutyltin ($\phi_2\text{SnBu}_2$), phenyl stannic acid (ϕSnOOH) converts to phenyltributyltin (ϕSnBu_3), and inorganic tin (Sn) if present is converted to tetra-butyltin (Bu_4Sn). Tetraphenyltin ($\phi_4\text{Sn}$) if present will remain as tetraphenyltin since it is already in the tetraorgano form. After conversion, the organotins are separated by reverse phase HPLC (C-8) and their respected fractions (1.5 mL) are collected and assayed for elemental tin by atomic absorption-graphite-furance spectroscopy. The methods reported limit of sensitivity is 0.05 ppm for each compound with recoveries from fortified control samples reported as follows:

% RECOVERED FROM FORTIFIED PECAN CONTROL SAMPLES

| Added Conc. (ppm) | $\phi_4\text{Sn}$ | $\phi_3\text{SnOH}$ | $\phi_2\text{SnO}$ | $\phi_1\text{SnOOH}$ | Bu_4Sn |
|----------------------|-------------------|---------------------|--------------------|----------------------|------------------------|
| 3.0 | 99 | 103 | 83 | 85 | 99 |
| 1.0 | 88 | 125 | 117 | 103 | 99 |
| 0.1 | 95 | 88 | 117 | 105 | 109 |
| 0.05 | 86 | 78 | 77 | 94 | 94 |
| control | ND ^a | ND | ND | ND | ND |
| control | ND | ND | ND | ND | ND |

a ND (< 0.05 ppm)

% RECOVERED FROM FORTIFIED PEANUT CONTROL SAMPLES

| Added Conc. (ppm) | $\phi_4\text{Sn}$ | $\phi_3\text{SnOH}$ | $\phi_2\text{SnO}$ | $\phi_1\text{SnOOH}$ | Bu_4Sn |
|----------------------|-------------------|---------------------|--------------------|----------------------|------------------------|
| 3.0 | 98 | 104 | 99 | 96 | 90 |
| 1.0 | 84 | 104 | 99 | 102 | 77 |
| 0.1 | 83 | 95 | 109 | 108 | 73 |
| 0.05 | 73 | 83 | 74 | 99 | 71 |
| control | ND ^a | ND | ND | ND | ND |
| control | ND | ND | ND | ND | ND |

a ND (< 0.05 ppm)

Peanuts: 5 Field trials were conducted in GA (2), AL (1), VA (1), and Unknown (1). These 3 states accounted for >67% of the 1983 peanut production in the United States (Agricultural Statistics, 1984). The names of field investigators, location of the treatment sites within the state, weather conditions during the trial, number of acres treated, date crop was planted/harvested, crop stage at treatment, method of treatment, storage conditions of the harvested crop, and portion of harvested crop assayed were not provided.

Application of Supertin 4L (4 lbs. ai./gal) ranged from 0.24 to 0.6 lbs. per acre. 2 applications were made; PHIs ranged from 14 to 22 days. No product label for Supertin 4L was provided; nor was its EPA Registration Number identified. The maximum use per acre per season was not stipulated.

No residues (ND <0.05 ppm) were reported; however, the raw data for several samples (identified below) clearly indicate the presence of residues >0.05 ppm.

| <u>Sample</u> | <u>Residue (s) >0.05 ppm</u> |
|---------------|------------------------------------------|
| 9PN-0302 | $\phi_3\text{SnOH}$, $\phi_2\text{SnO}$ |
| 10PN-0301 | $\phi_1\text{SnOOH}$ |
| 11PN-0301 | $\phi_3\text{SnOH}$ |

We conclude that the peanut residue data cannot be fully evaluated until additional information is provided. The data indicate that residues above the current tolerance (0.05 ppm) may occur.

Conclusions

1. TPTH tolerances were initially established for the parent compound only. The Agency now considers the residues of concern in plants and animals to be intact TPTH, and its di- and monophenyltin hydroxides (or oxides). This conclusion appears in the TPTH Registration Standard.

2. A current label for Supertin 4L must be provided.

3a. M&T Method TA-49 appears to be adequate for assaying TPTH, its degradation products (tetraphenyltin, diphenyltin oxide and phenyl stannic acid), and inorganic tin (as tetra-butyltin), each at 0.05 ppm. The registrant must submit a "non-confidential" analytical method so that a Method Try Out (MTO) can be performed; ultimately the method must be available for enforcement purposes.

No data were submitted to demonstrate lack of interference from other organotin pesticides; Vendex, hexakis(2-methyl-2-phenylpropyl)distannoxine has a tolerance for pecans at 0.5 ppm.

STORAGE STABILITY DATA

No storage stability data for pecans or peanuts were provided. Information concerning the effects of storage and transportation on potential residues in or on pecans must be provided (see, R. Loranger, Review of Study Protocol, memo of 6-21-85).

RESIDUE DATA

The TPTH Registration Standard states that available residue data on pecans and peanuts do not support existing tolerances. In response to these data gaps, M&T Chemical Inc. provided the Agency with residue data from field trials on pecans and peanuts; these field trials were not adequately documented in the submitted reports. The registrant should refer to RCB's recent review (S. Hummel, TPTH S.F., memo of 9-4-86) of M&T Methods TA-43, TA-45, TA-46, TA-47, and TA-48 for a detailed explanation of the information required to document a residue field trial. A review of the information and residue data provided follows:

Pecans: 4 Field trials were conducted in GA (2), AL (1), and TX (1). These 3 states accounted for >71% of the 1983 pecan production in the United States (Agricultural Statistics, 1984). The names of field investigators, location of the treatment sites within the state, method of application, weather conditions during the trials, number of acres treated, date trees were planted, crop stage at treatment, storage conditions of the harvested crop, and portion of the harvested crop assayed were not provided.

Application of Supertin 4L (4 lbs. ai./gal) ranged from 0.28 to 25.6 lbs. per acre. 2 applications were made; PHIs ranged from 50 to 78 days. No product label for Supertin 4L was provided; nor was its EPA Registration Number identified. The maximum use per acre per season was not stipulated. No residues ND <0.05 ppm were found.

We conclude that the pecan residue data cannot be fully evaluated until additional information is provided.