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EFGWB Out:

JAN 29 1993

To: Walter Waldrop, PM #71
Special Review and Reregistration Division (H7508C)

From: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File # : 083601

Common Name : Triphenyltin Hydroxide (TPTH)

Product Name : n.a.

Company Name : Hoechst Celanese Corporation

Purpose : Review photodegradation in water and photodegradation on soil studies.

Type Product: fungicide Action Code: 627 EFGWB #(s): 92-0156, 0368 Review Time: 7 days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1			162-4			164-4			166-1		
161-2	420495-02	Y	163-1			164-5			166-2		
161-3	421198-01	Y	163-2			165-1			166-3		
161-4			163-3			165-2			167-1		
162-1			164-1			165-3			167-2		
162-2			164-2			165-4			201-1		
162-3			164-3			165-5			202-1		

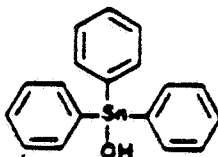
Y= Acceptable (Study satisfied the Guideline)/Concur
P= Partial (Study partially satisfied the Guideline; additional information is still needed)
S= Supplemental (Study provided useful information, but Guideline was not satisfied)
N= Unacceptable (Study was rejected)/Non-Concur

1. CHEMICAL:

chemical name: Triphenyltin Hydroxide

common name: TPTH

structure:



physical/chemical properties:

molecular formula- $C_{18}H_{16}OSn$
molecular weight- 367 g/Mol
physical state- crystalline
melting point- 118-120°C
aqueous solubility- 4.3 mg/l at 22°C and pH 5

2. TEST MATERIAL:

^{14}C -phenyl-labeled TPTH, specific activity 20.75 mCi/g.

3. STUDY/ACTION TYPE:

Review of a Photodegradation in Water study and a Photodegradation on Soil study.

4. STUDY IDENTIFICATION:

Burkle, W.L. 1991. Hoe 029664- ^{14}C (Fentin Hydroxide, TPTH) Photodegradation on Soil Surface. Unpublished study performed by Hoechst Aktiengesellschaft, FRG and submitted by Hoechst Celanese Corporation, Somerville, NJ. Received by EPA on December 6, 1991. MRID: 421198-01.

Burkle, W.L. and H.J. Jordan, 1991. Hoe 029664- ^{14}C (Fentin Hydroxide, TPTH) Direct Photolysis in Aqueous Solution. Unpublished study performed by Hoechst Aktiengesellschaft, FRG and submitted by Hoechst Celanese Corporation, Somerville, NJ. Received by EPA on December 10, 1991. MRID: 420495-02.

5. REVIEWED BY:

Dana Spatz
Chemist, ECRS #2
EFGWB/EFED/OPP


Date: JAN 26 1993

6. APPROVED BY:

Emil Regelman
Supervisory Chemist, ECRS #2
EFGWB/EFED/OPP


Date: 1/29/93

7. CONCLUSIONS:

PHOTODEGRADATION IN WATER

This study is acceptable and fulfills the Photodegradation in Water data requirement. TPTH was relatively stable to photodegradation in pH 7 sterile aqueous buffer when irradiated by a filtered xenon artificial light source.

The degradation half-lives of 111 days and 93 days for the irradiated samples and 155 days for the dark control indicate that photolysis plays a minor role in the degradation of TPTH. The primary degradate formed in the irradiated samples was monophenyltin (up to 17% of applied). Diphenyltin (2-3%), benzene (5-6%) and CO₂ (1-2%) were also identified.

PHOTODEGRADATION ON SOIL

This study is acceptable and fulfills the Photodegradation on Soil data requirement. TPTH did not photodegrade on soil irradiated by a filtered xenon artificial light source.

TPTH was metabolized via successive tin phenyl cleavage resulting in diphenyltin, monophenyltin, and benzene. The degradation pattern of the irradiated samples was very similar to that of the dark control and the half-lives (t_{1/2}= approximately 30 days for both the irradiated samples and dark control) were essentially equal. This indicates that soil photolysis did not play a role in the degradation of TPTH.

8. RECOMMENDATIONS:

The Photodegradation in Water (161-2) and Photodegradation on Soil (161-3) data requirements have been satisfied.

The remaining data requirements to be fulfilled are:

164-1	Soil Field Dissipation
165-4	Accumulation in Fish
201-1	Droplet Size Spectrum
202-1	Field Drift Evaluation

9. BACKGROUND:

Triphenyltin Hydroxide is a nonsystemic, protectant, foliar fungicide registered for use on pecans, carrots, potatoes and sugar beets. Of the total usage, 85% is applied to pecans. TPTH is a Restricted Use Pesticide. The TPTH Registration Standard was issued in September 1984. On December 17, 1984 TPTH was placed into Special Review with the issuance of a PD 1. The trigger for initiation of a Special Review was data indicating that TPTH produces teratogenic effects in laboratory animals.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached DER's.

11. COMPLETION OF ONE-LINER:

One-liner has been amended.

12. CBI APPENDIX:

Not applicable.

DATA EVALUATION RECORD

STUDY 1

CHEM 083601

Triphenyltin Hydroxide

§161-3

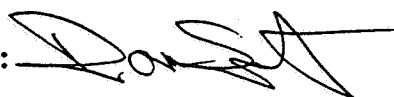
STUDY ID 42119801

Burkle, W.L. 1991. Hoe 029664-¹⁴C (Fentin Hydroxide, TPTH)
Photodegradation on Soil Surface. Unpublished study performed by Hoechst
Aktiengesellschaft, FRG and submitted by Hoechst Celanese Corporation,
Somerville, NJ. Received by EPA on December 6, 1991.

REVIEWED BY: Dana Spatz

TITLE: Chemist

ORG: EFGWB/EFED/OPP

SIGNATURE: 

JAN 26 1993

CONCLUSIONS:

Photodegradation on Soil

1. This study is acceptable and fulfills the Photodegradation on Soil data requirement. The data indicate that TPTH does not photodegrade on soil exposed to a xenon artificial light source at $25 \pm 2^\circ\text{C}$.
2. ¹⁴C-phenyl labeled TPTH applied to stainless steel plates covered with 2 g of biologically active silt loam soil and irradiated (12/12 hours light/dark cycle) with artificial light (filtered xenon) did not photodegrade during the course of the 32 day study. The degradation patterns of the irradiated samples and the dark control as well as their degradation half-lives ($t_{1/2}$ = approximately 30 days for both the irradiated samples and dark control) indicated that soil photolysis did not play a role in the degradation of TPTH.

Although the author reports that microbial degradation led to the formation of diphenyltin (DPT) and monophenyltin (MPT), which were detected in both the exposed and dark samples, the likelihood also exists that the hydrobromic acid extraction caused a dephenylation leading to DPT and MPT. Whether or not the degradation of TPTH was solely microbial or due in part to the extraction procedure, it is clear from the data that photolysis of TPTH in the environment under natural sunlight conditions is not expected to occur.

3. It should be noted that because of the uncertainty about the degree to which the disappearance of TPTH was due to the acid extraction, the half-life values may be somewhat questionable. However, because the degradation patterns of the irradiated samples and the dark control were very similar, any degradation that took place was not due to photolysis.

METHODOLOGY:

A biologically active silt loam soil (15.3% sand, 66.6% silt, 18.1% clay, 1.23% organic matter, pH 5.6, CEC 16.12 meq/100 g) was used. The soil was first sieved (2 mm) and about 70 g were added to 100 ml of water. The resulting slurry was poured over 20 weighed 4 x 4 cm stainless steel plates which were placed in a tub. After evaporation of most of the water at room temperature, the weight of moist soil was 1.5 - 2.5 g/plate. 6 plates each were assembled to get three sets of individual samples: irradiated set 1, irradiated set 2 and dark control.

^{14}C -phenyl labeled TPTH (radiochemical purity 99.6%, specific activity 20.75 mCi/g) was dissolved in acetone to prepare the stock solution. An aliquot containing approximately 5 mg of test substance was removed and concentrated to dryness in a nitrogen stream. The residue was redissolved in 5 ml of ethanol to prepare the solution for application. 127.3 ug of TPTH was applied to a soil sample. Based on the area of the soil plate, the application rate was 0.796 kg ai/ha. The soil plates were kept moist by repeated addition of drops of water.

A Hanau Suntest photoreactor was used for simulation of sunlight radiation. A Xenon burner was installed at the top of the reactor and surrounded by a filter system. Light below 290 nm was filtered by an interference filter. The lamp and sample chamber were cooled by a blower. The Suntest was kept on a 12/12 hours light/dark cycle by an automatic time switch.

Two sets of soil plates were placed inside the closed steel irradiation chamber which was fitted with an air inlet and outlet. An additional plate contained the thermocouple for recording temperature. The upper side of the chamber was covered with a quartz plate. The bottom was cooled with a cooling cycle to keep the temperature of the samples constant at $25 \pm 2^\circ\text{C}$. The temperature decreased to approximately 20°C during the dark phase on both the irradiated and the dark control samples. A slow stream of moistened air was pulled through the chamber. The air outlet of the sample chamber was connected to a sequence of traps containing a unit with acidified (pH 3, H_2SO_4) water and 0.5 g of suspended XAD-2 resin, a Carbo-Sorb unit, and a cold trap with 25 ml of methanol cooled with dry ice. The first unit absorbed water soluble and non-polar (XAD-2 resin) volatile degradates. The Carbo-sorb trapped $^{14}\text{CO}_2$. The final trap ensured complete absorption of the volatiles. A third set, also equipped with a plate affixed to a thermocouple and absorption traps, was incubated in the dark.

One soil plate in each of the series (set 1, set 2, dark control) was removed at the following times:

0, 1, 3, 8, 16, and 32 days after initiation.

The absorption media were exchanged at the same times and after Day 3 (the cold trap) at additional intermediate intervals. At each sampling, the radioactivity was determined in the soil extracts (acetonitrile/water 4:1, and hydrobromic acid (40%)/water/acetone/methanol 1:4:8:2), extracted soil, carbo-sorb, water after filtering XAD-2 resin, methanol extract of XAD-2 resin, extracted XAD-2 resin, and solution in the cold trap.

The moist soil was scraped from the steel plate into a centrifugation tube. The plate was rinsed with the first extractant, acetonitrile:water (4:1) starting on day 3. The soils of days 0 and 1 were twice extracted with the second extractant 25 and 5 ml hydrobromic acid (40%)/water/acetone/methanol. The soils removed at the later dates were extracted once with the first extractant (25 ml) and afterwards with the second one (25 ml), followed by a third extraction step with the second extractant (5 ml) in order to increase the extraction yield by dissolution of the soil degradates di- and monophenyltin. The radioactivity of ^{14}C -containing samples was determined by LSC. The extracted compounds were investigated by TLC. The volatile products were analyzed by HPLC.

REPORTED RESULTS

The reported half-lives (32.6, 27.9 and 30.6 days for irradiated set 1, irradiated set 2, and dark control, respectively), and the fact that the composition of the radioactivity fractions in the dark control was similar to that of the irradiated samples demonstrate that photolysis on soil is a minor degradation process compared with soil metabolism. TPTH was metabolized via successive tin phenyl cleavage resulting in diphenyltin, monophenyltin, and benzene. It must be stated however that in addition to metabolism, the 2nd-tier extraction process involving hydrobromic acid very likely also caused some dephenylation. In addition to the parent TPTH, significant portions of diphenyltin could be detected at the first sampling date. The authors assert that this finding and the varying amounts of DPT were probably caused by the hydrobromic acid.

Total recovery of the applied radioactivity ranged from 84 to 105%. Most of the radioactivity was contained in the soil extract. However, a significant portion consisted of organic volatiles (20%). Most of the volatile radioactivity was trapped in the cold trap. This radioactivity was identified as benzene by HPLC. A significant amount (8%) of radioactivity was also identified as $^{14}\text{CO}_2$.

COMMENTS

1. Immediately before and after the irradiation experiment, the total light intensity at the sample position was determined with a uranyl sulfate/oxalic acid actinometer. Based on the results of these measurements (data not provided) and the intensity distribution of the used light, the mean photon flux was calculated. Total light intensity was approximately that of sunlight in June at 52° N latitude at sea level (central Europe).
2. In addition to TLC, HPLC separation of the soil extracted degradates was attempted, but failed due to inconsistent elution times of the parent and total retardation of monophenyltin (or co-elution of monophenyltin and diphenyltin). The study author stated that confirmatory identification was not necessary however, because TPTH has shown very similar behavior in different degradation/metabolism studies.

This rationale may not be valid because the other degradation/metabolism studies referred to were presumably conducted in the dark. Photolysis can give very different degradation products. However, based on the results of the irradiated samples and dark control in this study, it is highly unlikely that photodegradation of TPTH is a significant route of degradation.
3. An absorption spectrum of TPTH was not provided.
4. Figures 16-19 show that when hydrobromic acid was used in the extraction procedure, there was an increase in DPT and MBT, compared with the acetonitrile extraction. It cannot be determined how much of this increase was due to the acid extraction converting TPTH to DPT and MBT, and how much was due to the fact that acetonitrile was unable to completely extract these degradates.
5. The extent to which the acid extraction added to the total radioactivity recovered at each sampling interval was not provided.

TPTH

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_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 2

CHEM 083601

Triphenyltin Hydroxide

§161-2

STUDY ID 420495-02

Burkle, W.L. and H.J. Jordan, 1991. Hoe 029664-¹⁴C (Fentin Hydroxide, TPTH) Direct Photolysis in Aqueous Solution. Unpublished study performed by Hoechst Aktiengesellschaft, FRG and submitted by Hoechst Celanese Corporation, Somerville, NJ. Received by EPA on December 10, 1991.

REVIEWED BY: Dana Spatz

TITLE: Chemist

ORG: EFGWB/EFED/OPP

SIGNATURE:



JAN 26 1993

CONCLUSIONS:

Photodegradation in Water

1. This study is acceptable and fulfills the Photodegradation in Water data requirement. TPTH was relatively stable to photodegradation in pH 7 sterile aqueous buffer when irradiated by a filtered xenon lamp.
2. ¹⁴C-phenyl labeled TPTH in sterile aqueous buffer (2 mg/L, pH 7) was irradiated with artificial light (filtered xenon) for up to 197 hours (equivalent to 26 days and 35 days constant sunlight for apparatus II and apparatus III, respectively). The degradation half-lives of 111 days and 93 days (12 hrs. light/12 hrs. dark) for the irradiated samples and 155 days for the dark control indicate that photolysis plays a minor role in the degradation of TPTH. The primary degradate formed in the irradiated samples was monophenyltin (up to 17% of applied). Diphenyltin (2-3%), benzene (5-6%) and CO₂ (1-2%) were also identified.

METHODOLOGY:

¹⁴C-phenyl labeled TPTH (radiochemical purity 98.1%, specific activity 20.75 mCi/g) was dissolved in acetone to prepare the stock solution. An aliquot containing approximately 4 mg of test substance was removed and concentrated to dryness in a nitrogen stream. The residue was redissolved in 5 ml of ethanol to prepare the solution for application. 100 ul of this solution was added to each of the glass vessels containing 40 ml buffer solution (pH 7). Three sample series, each with 7 individual samples, were prepared in this way (SUNTEST II, SUNTEST III, DARK CONTROL). Based on radioactivity measurements, 3,708,900 dpm or 79.0 ug active ingredient were applied per 40 ml sample. This is equivalent to 2.00 mg TPTH/L.

A Hanau Suntest photoreactor was used for simulation of sunlight radiation. A Xenon burner was installed at the top of the reactor and surrounded by a filter system. Light below 290 nm was filtered by an interference filter. The lamp and sample chamber were cooled by a blower.

The intensity of the radiated light was measured actinometrically at the start and end of the irradiation series. Based on the results of these intensity measurements, the mean values for both irradiation lamps were obtained. The relative intensities of the lamps were then calculated. The relative intensity is the ratio of the photons impinging upon the surface of the sample solutions during a certain time of the study to the mean number of sunlight photons reaching the same area of the earth's surface during the same time at 52° latitude north at sea level in June.

Irradiation Apparatus	Mean Relative Intensity*
Suntest II	3.21
Suntest III	4.28

*Hours of irradiation/hours natural sunlight

All buffer solutions and equipment were sterilized prior to beginning the study. During the study, 40 ml of the buffer, to which the test substance had been added, were irradiated in six connected cylindrical glass vessels (replicates Suntest II and Suntest III). These sample vessels were closed with quartz tops. They were placed inside a steel container with a cooling cycle to keep the temperature constant at $25 \pm 1^\circ\text{C}$. An additional vessel contained the thermocouple for recording temperature. A slow stream of air was pulled through the sample vessels. The air outlet of the sample system was connected to a sequence of traps containing a unit with acidified (pH 3, H_2SO_4) water and 0.5 g of suspended XAD-2 resin, a Carbo-Sorb unit, and a cold trap with 20 ml of methanol cooled with dry ice. The first unit absorbed water soluble and non-polar (XAD-2 resin) volatile degradates. The Carbo-sorb trapped $^{14}\text{CO}_2$. The final trap ensured complete absorption of the volatiles.

A third set of sample vessels, also equipped with a thermocouple and absorption traps, was incubated in the dark.

One sample vessel from both of the irradiated series (Suntest II and Suntest III) was removed at the following times:

0, 6, 24, 48, 100, 150, and 197 hours after initiation.

A dark control sample vessel was removed at the following times:

0, 6, 24, 48, 118, 168, and 215 hours.

The absorption media were exchanged at the same times. At each sampling, the radioactivity was determined in the buffer solution, carbo-sorb, water after filtering XAD-2 resin, methanol extract of XAD-2 resin, ethyl acetate extract of XAD-2 resin, extracted XAD-2 resin, and solution in the cold trap.

The radioactivity of ^{14}C -containing samples was determined by LSC. The buffer solutions were also investigated by TLC.

REPORTED RESULTS

The half-lives (111, 93, and 155 days for irradiated set II, irradiated set III, and dark control, respectively), demonstrate that photolysis in water is relatively slow. TPTH was degraded in the irradiated samples via successive tin phenyl cleavage resulting in diphenyltin, monophenyltin, and benzene. The same degradates were found in the dark control, although the monophenyltin levels were much lower in the control samples.

After 197 hours of irradiation, 1-2% of the applied radioactivity was detected as $^{14}\text{CO}_2$. 5-6% of the applied was an apolar volatile degradate, the properties of which indicated benzene. 2-3% of the applied was degraded to diphenyltin and up to 17% to monophenyltin. TPTH comprised 67-72% after 197 hours of irradiation. Degradation in the dark control was negligible after 215 hours (TPTH comprised 94% of the applied radioactivity).

Total recovery of the applied radioactivity ranged from 93 to 103% with one sampling point (150 hrs, Suntest II) at 82%. Most of the radioactivity was contained in the buffer solution with less than 10% of the applied found in the volatile traps.

COMMENTS

1. Immediately before and after the irradiation experiment, the total light intensity at the sample position was determined with a uranyl sulfate/oxalic acid actinometer. Based on the results of these measurements and the intensity distribution of the used light, the photon fluxes were calculated and compared with that of sunlight in June at 52° N latitude at sea level (central Europe) for half-life calculation purposes.
2. Between the 48- and 100-hour samplings, both light sources failed for 18 hours due to a loss of current. Sampling was therefore prolonged for this time interval in all three series. The absolute irradiation times however, did not change. Only the times of the dark control were prolonged for 18 hours from sampling after 100 hours onwards.

3. An absorption spectrum of TPTH in pH 7 buffer solution was provided. There was little to no absorbance at wavelengths above 290 nm.
4. Volatiles were characterized, but not identified.
5. The sample data collected at 150 hours in the irradiation series Suntest II and 197 hours in Suntest III were excluded from the half-life calculations by the author for "evidently" being outliers. However, no statistical data were provided to justify the exclusion. The respective half-lives using all data points are 89 days and 123 days.

TPTH

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