2-19-76

EEE BRANCH REVIEW

DATE: IN ______ OUT ______ IN 12/8/75 OUT 2/19/76 IN ______ OUT ______

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 4581-EOU

PETITION OR EXP. PERMIT NO. 3F1416

DATE DIV. RECEIVED 11/17/75

DATE OF SUBMISSION 11/12/75

DATE SUBMISSION ACCEPTED 3C1D Yes 2b

TYPE PRODUCT(S): I, D, (H), F, N, R, S

PRODUCT MGR. NO. 24 Jacoby

PRODUCT NAME(S) Hydrothol 191 Rice Herbicide

COMPANY NAME Pennwalt

SUBMISSION PURPOSE Tolerance petition and new registration for rice

CHEMICAL & FORMULATION endothall (7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid) 5%, and N,N-dimethylalkylamines (from coconut oil) 6.2%

1.0 Introduction

1.1 Endothall has been registered under various names for many uses, mostly aquatic. Among them are Aquathol, Accelerate, Q-Diel, Endothal, Des-I-Cate.

1.2 See previous reviews for

1.3 This is for use on rice.

1.4 The proposed tolerance is 0.05 ppm on rice grain (as endothall).

2.0 Directions for use

Apply 2-3 lbs. endothall a.e./acre 25 to 60 days after sowing and after rice emerges from surface of water but before heading. Apply by air or ground no more than once yearly.

2.1 Precautions

Do not release water from flooded fields within 10 days of application. Do not use fish from treated water within 3 days of application. Fish will be killed by dosages above 0.3 ppm. Do not use where fish are important resources. Avoid contact with or drift to desirable plants or crops to avoid injury.

Dispose of away from water supplies by burial or incinerator in approved places.

3.0 Discussion of data

3.1 The following data appropriate to environmental chemistry considerations were submitted by reference.

The section entitled "Information Regarding PR Notice 70-15 and Potential Hazard to Applicators, Wildlife, and the Environment" submitted with the Substantive Amendment to Petition Nos. 1F1105 (2H5016) of June 1975.

2. Residues in water, fish, and other water organisms and animals (Section D of this petition, pages D-13 to D-53 and D-67 to D-76).

3. Biomagnification (Section D of Petition No. 2H5016, April 1972).

4. Metabolism (Section D of this petition, pages D-77 to D-91).

5. Duration of Biological Activity (Section H of this petition, pages H-7 to H-15).

Information regarding dissipation, movement, metabolism, etc. in terrestial soil can be found in Petition No. 1F1105, December 1970, Section D, pages D-1 to D-18.

3.2 From the above list and from the lists of exhibits of data concerning endothall found in EPA files and supplied previously by Pennwalt the following studies have been found relevant to this review:

3.2.1 On basic soil metabolism:

3.2.1.1 From PP 1F1105 submitted 3/29/71 (but dated 12/1/70)

4 Progress Report on the Soil Behavior of Endothal - Oregon State University - 1963

10 Breakdown of Endothal in Soil - Horowitz, M., Weed Research - June 2, 1966

3.2.2 On soil persistence:

From PP 1F1105 3/29/71

2 Studies on Endothal Movement and Stability in the Soil - Oregon State University

3 Movement and Persistence of Endothal as Influenced by Soil Texture, Temperature, and Moisture Levels - Comes, R. D., et al, Journal of the A.S.S.B.T. - 1961

3.2.3 On leaching:

From PP 1F1105 3/29/71

2 Studies on Endothal Movement and Stability in the Soil - Oregon State University

3 Movement and Persistence of Endothal as Influenced by Soil Texture, Temperature, and Moisture Levels - Comes, R. D., et al, Journal of the A.S.S.B.T. - 1961

3.2.4 On hydrolysis:

3.2.4.1 From PP 1F1105 3/29/71

2 Studies on Endothal Movement and Stability in the Soil - Oregon State University

5 Preliminary Investigations of the Behavior of Endothal in Water - Oregon State University

3.2.4.2 From PP 1F1165 7/9/75

73 Disappearance Tables for Endothall in Water from Section D, Water Petition Nos. 1F1105 and 2H5016

78 Disappearance Tables for Endothall in Water - Partial Treatments from Section D of Water Petition Nos. 1F1105 and 2H5016

3.2.5 On degradation in water with suspended solids:

3.2.5.1 From PP 1F1105 3/29/71

(See 3.2.4.1, No. 5)

3.2.5.2 From PP 1F1105 7/9/75

63 Publication, "Persistence of Endothall in Aquatic Environment as Determined by Gas-Liquid Chromatography" by Sikka

64 Pages 10, 11, 12, 13, 14, 17, 41 of Annual Report of July 1973 to July 1974, "Aquatic Plant Control Using Herbicides in a Large Potable Water Supply Reservoir" by Schreck, Department of Fisheries & Wildlife Sciences, VPI

73 Disappearance Tables for Endothall in Water from Section D, Water Petition Nos. 1F1105 and 2H5016

78 Disappearance Tables for Endothall in Water - Partial Treatments from Section D of Water Petition Nos. 1F1105 and 2H5016

79 Residue Data from Endothall Aquatic Treatments from Section D of Water Petition No. 2H5016

3.2.5.3 From 7F0570 3/23/67

22 Endothal Derivatives as Aquatic Herbicides in Fishery Habitats. Charles R. Walker, U.S. Department of the Interior - 7/63 (disodium endothall - di di(N,N-dimethyl-cocoamine)salt of endothall)

3.2.5.4 From PP 2H5016 5/1/72

37 Extracts from Fate of Herbicides in the Aquatic Environment by H. C. Sikka, Annual Report October 1, 1970 - September 30, 1971 submitted to office of the Chief of Engineers, Department of the Army, Washington, D.C. (also data on adsorption)

3.2.6 On degradation in bottom sediment:

(See 3.2.5.4 above, No. 37)

3.2.7 Fish and aquatic organism residue studies including model ecosystems and field studies.

3.2.7.1 From PP 1F1105 3/29/71

9 The Uptake and Incorporation into Normal Constituents of C^{14} of Radioendothal by Fish - Oregon State University - June 20, 1960

3.2.7.2 From PP 1F1105 7/9/75

67 Publication, "Uptake, Distribution, and Metabolism of Endothall in Fish" by Sikka

68 Unpublished Report, "A Special Study on the Uptake, Distribution, and Metabolism of Endothall in Catfish", Pennwalt Analytical Section

80 Results of Residue Determinations - Salt Water Organisms - Oysters, Clams, and Flounder from Section D of Water Petition No. 2H5016

81 A Special Study with ^{14}C Labelled and Non-Labelled Endothall in Water, Fish, and Crayfish from Section

82 Goldfish Feeding Study from Section D of Water Petition No. 2H5016

88 Chromatograms - Fish (check, fortified, treated)

3.2.7.3 From PP 7F0570 3/23/67

22 Endothal Derivatives as Aquatic Herbicides in Fishery Habitats, Charles R. Walker, U.S. Department of the Interior - 7/63 (disodium endothall - di di(N,N-dimethylcocoamine) salt of endothall)

23 Endothal - Summary of Metabolic Studies with Disodium Endothall on Different Organisms, Marvin L. Montgomery and Virgil H. Freed, Department of Agricultural Chemistry, Oregon State University - 11/12/64

26 The Uptake and Incorporation into Normal Constituents of C^{14} of Radioendothal by Fish, Agricultural Chemistry Dept., Oregon State University - 6/20/60 (disodium endothall)

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3.2.8 On Crop Uptake

From PP 1F1105 3/29/71

6 The Absorption and Metabolism of Endothal when Used as a Post-Emergence Treatment for Beets - A Progress Report - Oregon State University - February 13, 1961

7 The Absorption and Translocation of C^{14} Labelled Endothal in Red Beets and Spinach - Oregon State University

8 The Distribution of C^{14} Radioendothal in Anacharis - Oregon State University - June 22, 1960

14 Translocation of Assimilates and Phosphate in Detached Bean Leaves - Leonard, O. A. and R. K. Glenn - Plant Physiology - 1968

15 Physiological Changes in Fruit Trees During Chemical Defoliation - Rakitin, Yu.V. and A. Imamaliev - K. A. Timiryazev Institute of Plant Physiology, Academy of Sciences, USSR, Moscow - 1958

3.2.9 Effects on microorganisms

From PP 1F1105 3/29/71

1 Microbiological Examination of Endothall (letter, T. Lewandowski to Paul Munter, August 20, 1953)

13 Studies on the Effects of Herbicides on Soil Nitrification - Debona, A. C. and L. J. Audus - Weed Research - 1970

3.2.10 Effects on Endothall by microorganisms

3.2.10.1 From PP 1F1105 3/29/71

2 Studies on Endothal Movement and Stability in the Soil - Oregon State University

11 Microbial Effect on Endothal - Oregon State University (Letter, F. H. F. Au to O. Keckemet - October 15, 1962)

12 Studies on Soil Bacteria (Arthrobacter globiformis) Capable of Decomposing the Herbicide Endothal - Jensen, H. L., ACTA Agr. Scand. 1965

3.2.10.2 From PP 1F1105 7/9/75

66 Publication, "Metabolism of Endothall by Aquatic Micro-Organisms" by Sikka

6

3.2.10.3 From PP 2H5016 7/1/72

(See 3.2.5.4, No. 37)

3.2.10.4 From 3F1416 2/1/75

2 Sikka, H. C. and J. Saxena. Metabolism of Endothall by Aquatic Microorganisms. J. Agr. Food Chem. 21:402-406 (1973) (See also 3.2.10.2-66)

3.2.11 Metabolism

3.2.11.1 From PP 1F1105 3/29/71

6 The Absorption and Metabolism of Endothal when Used as a Post-Emergence Treatment for Beets - A Progress Report - Oregon State University - February 13, 1961

8 The Distribution of C^{14} Radioendothal in Anarcharis - Oregon State University - June 22, 1960

9 The Uptake and Incorporation into Normal Constituents of C^{14} of Radioendothal by Fish - Oregon State University - June 20, 1960

16 Respiration Studies on Cotton using Endothall C-14 - Gulf South Research Institute - September 24, 1968

3.2.11.2 From 7F0570 3/23/67

23 Endothal - Summary of Metabolic Studies with Disodium Endothall on Different Organisms, Marvin L. Montgomery and Virgil H. Freed, Dept. of Agricultural Chemistry, Oregon State University - 11/12/64

3.2.11.3 From PP 2H5016 5/1/72

(See 3.2.5.4, No. 37)

Note: The reports referenced to 1F1105 December, 1970 (See 3.1) do not correspond to those found physically therein (as referenced in 3.2.1.1.ff). Since those found are more appropriate than those referenced we conclude that an error in reference has been made which needs to be corrected. Our evaluation is based on the data in our files as indicated below.

3.3 The following have been reviewed recently, are pertinent for this use and were judged adequate:

7

3.3.1 Residue data on Irrigated Upland Crops

3. Residues to be Expected in Crops from Irrigation with Treated Rice Field Flood Water

3.3.2 Residue Accumulation in Fish

11 Letter to E. Bowles from J. F. Williams, February 8, 1974

12 Results of Residue Determination in Water and Fish

3.3.3 See review for 4G1449 on 3/14/75 for details

3.4 Condition of the data packages and internal methods of reference.

Due to the large number of separate submissions for endothall containing products, the volume of data submitted pertinent to this review is massive. Many of the studies are redundant, however. In addition, the numbering of the exhibits for the company's internal use is such that some non-related studies may have identical reference numbers. Exhibit "X_n" from one PP 1F1105 this may not contain the same information as "X_n" of another PP 1F1105.application submitted 2 or 3 years later. Therefore, ~~to reduce confusion,~~ our references in this review will be to the index numbers of the referenced study found earlier herein. Thus, "Progress Report on the Soil Behavior of Endothal - Oregon State University - 1963" will hence be referred to as study 3.2.3.1-4, when discussed with other leaching data or 3.2.1.1-4 when soil metabolism is discussed (c.f.).

3.5 Soil Metabolism Studies

A radiolabel study using $^{14}CO_2$ evolution was described in 3.2.1.1-4. Experimental details were lacking. Results were reported in CPM. On 33% of the applied dose was recovered as $^{14}CO_2$ in 17 days. Based on rates of evolution, the greatest amount of decomposition appeared to have occurred in the first week. It was also concluded that the remainder of the radioactivity remained in the soil as breakdown products which became "normal metabolic products such as fatty acids." These conclusions are not supportable by the data. The soil was only described as a loam from E. Oregon.

Using the same soil and varying temperatures, it was found that rates of CO_2 evolution were reduced at 5°C. Low moisture content (less than 16% moisture) resulted in reduced CPM. These data seem to indicate that microbial activity is at least partially responsible for endothal breakdown.

Further studies examined a variety of soils (nonewwell defined according to usual requirements) for endothal loss ($^{14}CO_2$ evolution). Some differences were noted among them and adsorption was implied as a controlling factor. The rates of $^{14}CO_2$ evolution and % adsorption tended to be inversely correlated for the various soils. Microbial populations in each soil were not taken into account. However, another study did not corroborate the effect of adsorption of decomposition.

These were preliminary studies. The test protocols were not well described. Controls did not appear adequate. It is difficult to accept the conclusions based on this limited data. The trend of this work did seem to indicate that microbial activity and/or soil adsorption might affect decomposition of endothal.

Another study investigated a formulation of endothal containing an antioxident and a bactericide. At 6 lbs./acre, evolution of $^{14}CO_2$ indicated that at 10 days only 29% of the applied material was evolved compared with a control. It was concluded that the additives reduced decomposition by the numbers seem comparable to those found in the first study (33% loss in 15 days). A parallel bioassay was run which seemed to indicate that the additivies did increase endothal persistence.

Other studies reported in this same exhibit (3.2.1.1-4) include a metabolism study in which an active soil (for endothall decomposition) was extracted with an aqueous medium to remove microorganisms, following by incubation of endothal in the solution. No endothal degradation in the aqueous medium was observed. Degradation in solution with suspended sediment showed no degradation in 24 hours but extensive loss thereafter (48 hours). Metabolites (not identified) appear to have been degraded also. The intermediate products are thus not stable.

A separate set of studies using Israeli soils 3.2.1.1-10 also indicated microbiological breakdown as a probable mode of loss. Bioassays were used and sampling was such that rate of loss can not be estimated. A second study investigated repeat applications of 2-6 kg/ha. Bioassay data showed reduced persistence for the second application (1.5 months after the first). The "enrichment" is further evidence for microbial effects on decomposition of endothall.

Conclusions: Though none of the studies alone would be considered adequate, the overall trend is such that microbial degradation may be considered a major mode of loss for endothal in soil. The question of effects of adsorption is not as strongly addressed. We cannot concur, based on these data, that soil adsorption is a major factor in endothal loss. No anaerobic studies, per se, were done. The reduced rates of loss in aqueous soil solution imply some possible effect, but oxygen tensionwas not measured. (Note: Summaries of these studies appear in report 3.2.7.3-23 along with others. No new data seems to occur in this summary.)

3.6 Soil persistence. See 3.5 for other studies. Part of one study (3.2.2-3) deals with persistence of endothal using bioassay as a determinant. Treatment rate is 6 lbs./acre on clay loam, sandy loam and sandy clay loam soils. The report consists of a summary with no tabular or graphic data. The summary reported a difference in response with different soils. The lighter soils permitted flax germination after 14 days while the clay loam required 28 days. "Inactivation" of endothal was "complete" at 42 days. Temperature effects were noted with "inactivation" being 12 times more rapid between 15° and 20° when measured after 1 week.

Another study (3.2.2-2) employs a flax bioassay (root length) to estimate effects on soil stability. The data are not presented in sufficient detail to be useful. They proport to show a half-life of 4 weeks, but only two time intervals (2 and 4 weeks) were employed.

Conclusions: These data tell us very little with respect to the expected persistence of endothal or its metabolites in soil. The assay systems were inadequate. The metabolism and persistence studies fail to give data which would permit a description of the time course or mechanisms of endothal degradation.

3.7 Leaching

Using the same assay system as the studies on soil persistence (flax root elongation) data was obtained on endothall movement in soil (3.2.3-2). Using a rate of 24 lb./A and 1" or 4" rain, but only 1-2" for the 1" rainfall. There was not much difference whether the rainfall was applied immediately or 2-4 weeks after treatment. Additional studies at 4 lbs./A and 1-4 inch rain showed that rainfall of 2-4 inches caused similar effects and that rate of application did not matter much. Movement in sand was greater than in clay.

Endothal acid was compared with disodium endothal. At 1 lb./A and 1" rain the acid showed similar leaching to that of 1 lb./A of the disodium salt. Clay and sand penetration were nearly identical. A 4" rain with 5 lb./A of the acid formulation showed close correlation for the leaching in sand with 24 lb./A of the disodium salt but the clay retarded endothal acid more than the sodium salt.

Another set of studies (3.2.3-3) combined a soil column and bioassay procedure. Eight inch columns were treated with the equivalent of 4 lb./A endothall and 2 surface inches of water were applied. Sections were removed 1 day after leaching and subirrigated to permit germination of flax seeds. Green weight of flax seeds 30 days after planting was used as parameter of phytotoxic effect.

Not all data was tabulated. Reduction in weight was reported, but the depth in the soil column to which endothal leached was not mentioned in some cases (sprinkler irrigation). Where tabular data was available, endothall was found to inhibit flax planted in the 0 and 1/2 - 1-1/2 inch sprinkler irrigated columns and in 0, 1-2 - 1-1/2 and 1-1/2 - 3 inch columns subirrigated. Soil type had some effect with lighter soils pemmitting endothall to move away from the surface (as evidenced by lower % inhibition at the surface) as compared with a clay loam.

Finally a graphical presentation of data on 8 inch columns revealed that inhibition greater than 40 percent was observed at 4-6 and 6-8 inches for all 3 soils (sandy loam, clay loam and sandy clay loam) as well as for the sandy clay loam at 3-4 inches. These data did not permit a determination of amounts of endothal moved, amounts in leachate, per cent of applied found at each layer, etc.

These studies give no indication of the rate at which endothal moves through soils. They do suggest a very leachable material, but the degree of leachability is not resolved by the above studies.

3.8 Hydrolysis

Four hydrolysis studies have been submitted. ONe (3.2.4-2) was a bioassay study of endothal effect on flax seedling root length after 10 days at varying pH. There was no difference among pH 4, 5, 7, 8.5 or 10 at 2 ppm while 10% greater activity remained at pH 7-8.5 for the 0.5 ppm treatment.

A much more informative study (3.2.4-5) involved use of ^{14}C-labeled endothal (4.5 ppm) in aqueous solution, in solution plus soil and with the addition of a carbon source (sucrose). The solution in wa water alone showed little breakdown in 8 days. Slightly more rapid loss was noted when soil was present. With soil, water and sucrose the rate for the first 7 days was much more rapid than the other two with an anomalous slowdown between 7 and 8 days. Additional data reiterated the effects of soil and carbon substrate on endothal loss implying a microbial mode of loss from water.

Plastic pools filled with water, plants and fish served as simulated ponds from determination of loss of endothal from water (3.2.4-73). Half-lives were from 10-15 days with sharp drops at these times. Residues were analyzed by G.C. Various formulations were employed. At least one was Hydrothal 191, which is under consideration herein. Similar results were observed in the field using lakes and ponds. Twenty day half-lives were occasionally found but 10-15 days was more common. (3.2.4-73 and 3.2.4-78).

Though the laboratory studies were generally inadequate, the numerous field studies were sufficient to show that endothall does not persist in the aqudous phase of the aquatic environment.

3.9 Degradation in water having suspended solids:

Several studies on rates of loss in natural lake and pond water have been made. Two were mentioned above (3.8). Additional studies of this type dealing only with natural lake and pond treatment were included in the same submission 3.2.5.2-64 and -79.

An interesting study using two types of assay (bioassay and colorimetric) was presented in 3.2.5.3-22. Using plastic enclosures in a farm pond to contain aquatic flora and bottom fauna the study followed the time course of endothal loss over 24 days. The rate of loss was concentration dependent, being more rapid at 0.1 - 0.3 ppm and slower above those rates. Plateaus were seen at the highest rates between 10 and 20 days after which loss resumed. Analysis of residues suggested initial rapid absorption by plants followed by release after plant decomposition began. This release could account for the plateau though the authors did not so speculate. Since the chemical analysis was for the amine portion of the cocoamine endothall formulation it is very likely that natural products were assayed as well as the pesticide. Except for the lowest rate, half-lives for the pesticide were 7 days to 10 days.

? ||
Probably invalidates the studies. H. Applestein 4/81

Two studies are more pertinent to the problem of the presence of sediment in flood rice fields. Both examined degradates in hydrosoil. In one (3.2.5.2-63) both GC and radiochemical means of analysis were used. In a pond the loss from water as measured by GC showed the same plateau as above where, after 50% loss, a nearly level curve occurred between 4 and 24 days followed by a rapid decline to zero from 24 to 28 days. Hydrosoil levels seemed to increase slowly during the "plateau" period then decline more rapidly than they previously had increased. The decline came at the same time as the recurrence of rapid loss from water. Complete loss from hydrosoil took 2 weeks longer than the corresponding loss from water. Results using aquarium were similar with the uptake by sediments more obvious. The radiolabel study revealed that residual ^{14}C in sterile pond water was parent endothall. About 7% of initial endothall was lost from water in 1 day, but the decrease was balanced by an increase in ^{14}C in the hydrosoil.

Another ^{14}C study involved only hydrosoil (3.2.5.4-37). Evolution of $^{14}CO_2$ was used as a determinant of endothal loss. The amount of ^{14}C residue in the soil after 2 weeks was also determined. Identity was determined by chromatography. In one week 10% was evolved as CO_2 but the rate declined so that 30% was evolved after 2 weeks. About 20-30% was "adsorbed" on the soil and could not be recovered by ethanol extraction, but most of it was released by 2N HCl in ethanol. The chromatography revealed ^{14}C residues (other than CO_2) were endothall.

These studies indicate that endothal is lost from pond water rapidly (1-2 week half life) initially. There may be a temporary decrease in rate of loss due to rerelease of endothall by decomposing target plants, but the rapid loss is likely to resume until no detectable residues occur in about 1 month. Hydrosoil does adsorb endothall, but decomposition does seem to take place so that loss from both water and hydrosoil is seen to resume after about 3 weeks. Autoclaved pond water and hydrosoil treated with endothall, do not lose residual ^{14}C, but exchange the residue between the two phases. This reinforces the apparent microbial nature of endothall loss.

3.10 Adsorption:

Only one study specifically addresses the problem of adsorption in hydrosoil. Endothall was added at 2 and 4 ppm to two soils (unidentified). After 1 and 4 days the adsorption was determined. Maximum adsorption occurred at 1 day and was concentration dependent. One soil adsorbed 90% while the other adsorbed 30% of the applied endothal. Which soils was which was not determinable due to the summary nature of the report (3.2.5.4-37).

The study reinforces data presented earlier which shows that sediment adsorption is important to endothall loss from natural water. The study does cast doubt that all types of sediment conditions have been tested, since the two soils varied so completely in adsorption characteristics.

3.11 Degradation in bottom sediments

(see discussions for 3.9 and 3.10)

3.12 Fish and aquatic organism studies:

The largest number of pertinent studies deal with fish and/or other aquatic organism residues. Some have been reviewed previously [see PP 3F1416 (2/1/75)] and many are redundant. Therefore only the significant findings will be discussed herein. See 3.2.7 for a listing of studies.

The results of these studies showed that, in short term experiments, endothall did not accumulate in various types of fish. Only two studies were longer than 5 days. In each case where fresh water fish were exposed the concentration in water was not kept constant.

The one long term exposure involved flounder which did not accumulate endothall residues (3.2.7.2-80). Oysters, clams and crayfish do not accumulate greater than 1X endothall at any time during the tests.

Though none of the studies would be deemed adequate taken alone, combined with each other and our knowledge of endothall persistence in water and hydrosoil the data indicate very limited opportunity for endothal accumulation in aquatic animals.

3.1.3 Crop uptake:

When used pre- or post-emergence with sugar beets, no endothal residue is found in the treated crop, but radioactive residues are taken up from the soil. It was concluded that sugar beets totally metabolize endothal (3.2.8-6). Endothal is also taken up in spinach (3.2.8-7). Much of the labeled material in soil is not endothal extractable after a few days. This second study indicates that uptake may not be of endothall but the label may be due to CO_2 fixation. The conclusion was that ^{14}C labeled materials were natural products.

The data prsented suggest no likely problem to rotational sugar beets, but residues in spinach might be a problem if endothal is present in soil after a rice use. The latter is not likely if the aquatic dissipation data is accurate.

3.1.4 Effects on microorganisms

Studies on effects on microbes include a summary of a contamination report (3.2.9-1) implying no effect on the microbes present and a study on soil nitrification (3.2.9-13).

The nitrification study was the common soil perfusion type. Endothal stimulated ammonia oxidation whereas all other pesticides tested inhibited the process. Endothal had no effect on numbers.

These studies by themselves are insufficient to show the overall effects of endothall on microbes. However, the data below on microbial degradation combined with the nitrification study seem to indicate that endothall is relatively innocuous.

3.1.5 Microbial Degradations:

One study titled "Microbial Effect on Endothal" (3.2.10.1-11) is properly a study of effects of endothal on microbes. Though only a summary, the data showed little or no effect of endothal alone on gram positive bacteria and on fungi (Rhizopus and Aspergillus). Gram negatives and a Micrococcus sp. were somewhat inhibited.

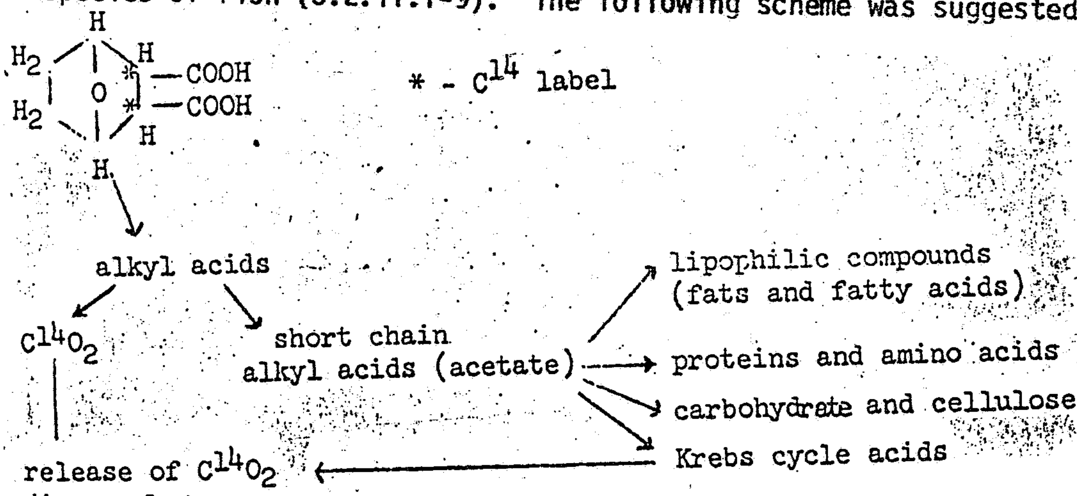
A more useful study by Jensen (3.2.10.1-12) showed that strains of the common Arthrobacter globiformis can be isolated which readily utilize endothal as a carbon substrate.

Another study (3.2.10.2-66) further examined bactericidal decomposition of endothall. An arthrobacter sp. was isolated from a lake hydrosoil which could utilize endothall. Radioactive (^{14}C) endothall was used as substrate and ^{14}C appeared in the cell fraction as well as being released as $^{14}CO_2$. The products incorporating ^{14}C included citric acid, glulamic acid, aspartic acid, alanine and probably phosphate esters. In fifteen minutes the glutamate fraction had nearly 2/3 of the label. The study clearly demonstrated that endothall is broken down by the bacterial species and the ring labeled carbons show up as TCA cycle intermediates implying strongly that endothall will be rapidly degraded and resynthesized as natural cell products.

These data and others previously described for soil metabolism show that endothall is likely degraded by a microbial route and that it should have a short persistence. Byproducts of endothall should be innocuous. Those species isolated which effect degradation are ubiquitous soil bacteria.

16. ~~3.1.5~~ Metabolism:

These studies, in animals and plants, support the understanding that endothall is readily degraded by many species. A summary of early work (3.2.11.2-23) showed that some crop plants rapidly converted endothal residues to natural plant products. Similar results were found with two species of fish (3.2.11.1-9). The following scheme was suggested.



We conclude that the various metabolism studies support this scheme under aerobic conditions. Anaerobic studies do not seem to have been made.

4.0 Conclusions

4.1 Individual studies submitted in support of this registration are generally inadequate. However, the few adequate studies indicate that endothall is probably an environmentally innocuous compound.

The inadequate studies are those on soil persistence, leaching and hydrolysis. The data on metabolism in plants and animals, some soil metabolism data and the bacterial degradation studies of Jensen and Sikka and Saxema all show a relatively labile chemical which readily enters the Krebs cycle. Thus, under aerobic conditions, endothall breakdown should be rapid. The individual fish accumulation studies are all too short, but the trend is such that no accumulation seems to occur.

4.2 The major lack is an anaerobic soil metabolism study. The studies which show degradation in hydrosoil along with the field studies on lakes and ponds suggest that under the conditions expected in rice fields, endothall probably will degrade rapidly and not be present for subsequent crops.

The conclusion that endothal will not persist is due to a conversation with Dr. Francis Broadbent, U. Cal, Davis. He indicated that depleted or even anaerobic conditions do exist early in the flooding period of rice culture. Values of 1/4 the saturation value at a given temperature are expected as the minimal concentration under normal conditions, but the values may vary with temperature, depth of water and organic content of soils and surface before flooding. Recovery of oxygen levels occurs within 3-4 days usually, due to algal blooms and photosynthetic oxygen and also elimination of decomposable carbon sources. Thus the period of anaerobic conditions is short and aerobic metabolism is liable to dominate. The only concern would be for the production of some identifiable metabolite of endothall which occurs only anaerobically and which would be of concern if taken up by subsequent crops. Such a hypothetical metabolite would have to be resistant to aerobic degradation and form very quickly from parent endothall. No such metabolite has been reported and the necessary characteristics to cause concern are improbable if the metabolite occurred. Therefore, we conclude that such a hazard is minimal and the lack of an anaerobic metabolism study is unimportant to this use in light of other submitted data.

5.0 Recommendation

5.1 No adverse environmental chemistry comments for this use of endothall at this time.

5.2 An anaerobic metabolism study will be needed to support future uses. Such a study should identify major metabolites or the natural constituents to which endothall may degrade under anaerobic conditions.

5.3 Data on rotation crops will be needed for future registrations as appropriate.

REN 3/1/76

Ronald E. Ney, Jr. 2/19/76

M. Segal

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Environmental Chemistry Section
Efficacy and Ecological Effects Branch

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5.3. Data on rotational crop ~~[illegible]~~ conditions will be needed for future registrations as appropriate.

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2/5/76

[illegible]