EEE BRANCH REVIEW

DATE: IN ______ OUT ______ FISH & WILDLIFE

IN 7/19/77 OUT 9/8/77 ENVIRONMENTAL CHEMISTRY

IN ______ OUT ______ EFFICACY

FILE OR REG. NO. 1016-69 & 78

PETITION OR EXP. PERMIT NO. ______

DATE DIV. RECEIVED ______

DATE OF SUBMISSION ______

DATE SUBMISSION ACCEPTED 3CID-2B-Yes

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

PRODUCT MGR. NO. Sanders (12)

PRODUCT NAME(S) Temik, Aldicarb

COMPANY NAME Union Carbide

SUBMISSION PURPOSE New Use on Tobacco

CHEMICAL & FORMULATION Aldicarb ([2-methyl-2(methylthio) propionaldehyde O-(methylcarbamoy) oxime]) (Temik)

1.0 **Introduction**

1.1 Temik, Aldicarb

1.2 Percent Active: 10 and 15 granular products

1.3 Both Products Registered

10% a.i. #1016 - 69
15% a.i. #1016 - 78

1.4 Acc #091372. Vol. 2 of 6, 4 of 6, and 5 of 6.
Acc #09624. July 1977 Compilation book of above vols.

1.5 See Other reviews:

PP #6F1829 8/23/76
1016 EUP 11/04/75

1.6 The registrant is proposing a new use: Registration of Temik 10 and 15% granular aldicarb for use on tobacco.

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DIRECTION for use

Crop	Pests Controlled	Dosage TEMIK 10G (Based on 48 inch Row Spacing) Pounds per acre	Ounces per 1000 feet of row	Time of Application	Recommended Application
Tobacco (flue-cured only)	Nematodes	30	44	At time of bed preparation not to exceed two weeks before transplanting.	Apply granules in a 12"-24" ba[r] over the bed, incorporate 4"-6[''] into the soil and place transp[lants] into treated area, OR apply gr[anules] as an over-all broadcast, inco[rporate] 4"-6" into the soil followed b[y] pulling soil from middle to fo[rm] beds. Place transplants into area.

Carton: Back Panel

2.1 <u>Disposal</u>

Keep out of any body of water. Do not contaminate water when cleaning of equipment or disposing of wastes.

3.0 <u>Discussion of Data</u>

3.1 <u>Physics - chemical degradation</u>

3.1.1 Hydrolysis - data submitted or referenced.

3.1.2 Photodegradation - data not submitted or referenced.

3.2 <u>Metabolism</u>

Aerobic soil - data submitted or referenced.

An Aerobic soil - data not submitted.

3.2.2 Effect of pesticides on microbes - data submitted or referenced.

3.2.3 Effect of microbes on pesticides - data not submitted or referenced.

3.2.4

3.3 <u>Mobility</u>

3.3.1 Leaching - data submitted or referenced.

3.3.2 Volatility - data submitted or referenced.

3.4 <u>Field Dissipation</u>

3.4.1 Soil - data submitted or referenced.

3.5 <u>Accumulation</u>

3.5.1 Rotational crop - data not submitted.

3.5.2 Fish accumulation - data submitted or referenced.

3.6 For evaluation of data submitted, see review 1016-6978 [6F1829] orgages 9/7/77.

4.0 General Conclusions

From the data that was presented, a partial assessment of hazards to the environment can be established, a full assessment (scientifically confident) cannot be made without physico-chemical (photolysis), and metabolism (pesticide effects on microbes) for this use. We will present what can be derived from the data presented.

4.1 Hydrolysis and temik will hydrolyze at 80° and 100°C, with a t1/2 at pH 6 and 8 of 19.0 hours, 49 minutes, 115 minutes, and 7 minutes, respectively. T-sulfoxide and sulfone under the same parameters had t1/2's of 80 minutes, 3.1 minutes, 20 minutes, 0.5 minutes, 120 minutes, 1.5 minutes, and <0.5 minutes, respectively. This study would not support any proposed use because temperatures of 80 and 100°C are not indicative of conditions normally found in the field where temik is applied. Not enough data (3 points needed) to extrapolate to lower temperature values. The study was not a material balance study (full extent of rate and decline of parent) and formation of degradate cannot be made. Not done in the dark (it has not been established that temik does not photolyze).

4.2 Metabolism (soil, aerobic): Temik will metabolize in clay, fine sand, clay loam, and much type soils with different pH values (6.0-8.0), moisture (3-100%), and organic matter (1-78%) to t1/2 values from <1 wk. to >56 days. Ten degradates were found with temik sulfoxide and sulfone being predominant. The compound exhibits volatility and binding in the soil. Organic matter plays a significant role in the fate of temik in the soil. A total of three aerobic soil metabolism studies were submitted and these three combined give us an acceptable soil (aerobic) metabolism study. We have a good description of temik and its characteristics in soil. This combined acceptable study will support proposed uses in terrestrial, and terrestrial/aquatic (forest) type applications. There is no acceptable aerobic aquatic study and this will not substitute for uses requiring this data (Aquatic and Aquatic impact uses).

4.3 Metabolism (Microbial): Temik does not exhibit microbiocidal effects to the microorganisms tested. This study would not support any proposed use where required (some terrestrial, aquatic, terrestrial/aquatic [forest] and some aquatic impact uses). "Eye ball" methods are not scientifically sound in enumerating bacterial numbers. Plant pathogens and/or fecal pollution indicators which are not indicative of commensal soil populations are unacceptable.

4.4 Mobility (leaching):

The ability of temik and its degradates to leach, depends on the soil type, particularly the organic matter. In muck soil the sulfoxide degradate leached through 7" of soil; loamy type soil parent, sulfoxide, and other leached; in clay type soil the same three leached. The sulfone metabolite did not leach and either is bound or volatilized. Since the leaching studies show temik and its degradates do leach, we can say that the point is proven. Not all soil characteristics such as pH, CEC, bulk density and percent sand, silt, clay; and an aged study were not submitted (not needed, degradates do leach), we can say that in lieu of these deficiencies, the studies can be used to support proposed uses, for terrestrial applications. Since the parent compound and its degradate leach (in sandy type soils) a caution should be taken to the contamination of ground water tables and the food web.

4.5 Mobility (volatility):

Temik does volatilyze and its rate is dependent upon moisute level of the soil and temperature. The type of soil will play a role on the rate of volatility. These studies were not done under actual use conditions. If toxicology branch requires reentry data for temik, these studies would not support reentry data, for the aforementioned reasons.

4.6 Field Dissipation (soil):

In the sandy loam soils tested temik had an extrapolated t1/2 of ~1 week. Temik sulfoxide and sulfone had extrapolated t1/2's of ~2 weeks. These studies give us a rough idea of field dissipation; however, no areas of high organic matter and four agricultural use areas were evaluated, which in soil metabolism showed extremely long half-lives in some cases. Not all characterization of the soils were given including percent sand, silt, clay, organic matter, CEC, and bulk density. These studies would not support any proposed uses for this compound.

4.7 Accumulation (Fish):

Temik at 3.0 ppm is lethal to bream,, large mouth bass, bull frogs and cricket frogs. Temik is lethal to fish up to 10 days after treatment. The study would not support any proposed use because only one exposure system (static) was used. Determinations of residues in whole body, edible tissue and viscera or carcass were not analyzed. Catfish were not used in the static system, radioisotopic techniques, and characteristics of the water were not used for methodology or reported. Preapplication samples were found to contain residues; the validity of the study would be questionable. Temik appears to influence the pH of the water (registrant claims no effect) and pH of water after day 7 was not given. Due to the lethality, rates in water or aging in water may have to be changed to show accumulation.

4.8 Ancillary Studies:

Temik is metabolized in plants to primarily the sulfoxide metabolite (and unknown #1). A total of 8-10 metabolites were found in plants and 11 in the soil. Activity was uniformily spread throughout the plant. In the greenhouse temik is soil dependent for mobility and is readily mobile in sand (coarse). Temik sulfoxide was the major metabolite and found in the 6-8" layer of the column. Temik after ~1 year in the soil is not lethal to insects. A large amount of activity is lost and is probably due to volatilization. Laying hens were found to have nitrile sulfoxide, oxime sulfone, oxime nitrile, and 13 unknowns in their fecas when fed temik and temik sulfone. These studies are ancillary. The studies can be used to support any proposed use that is applicable.

4.9.1 Ancillary Study:

Special review - Substitute chemical program.

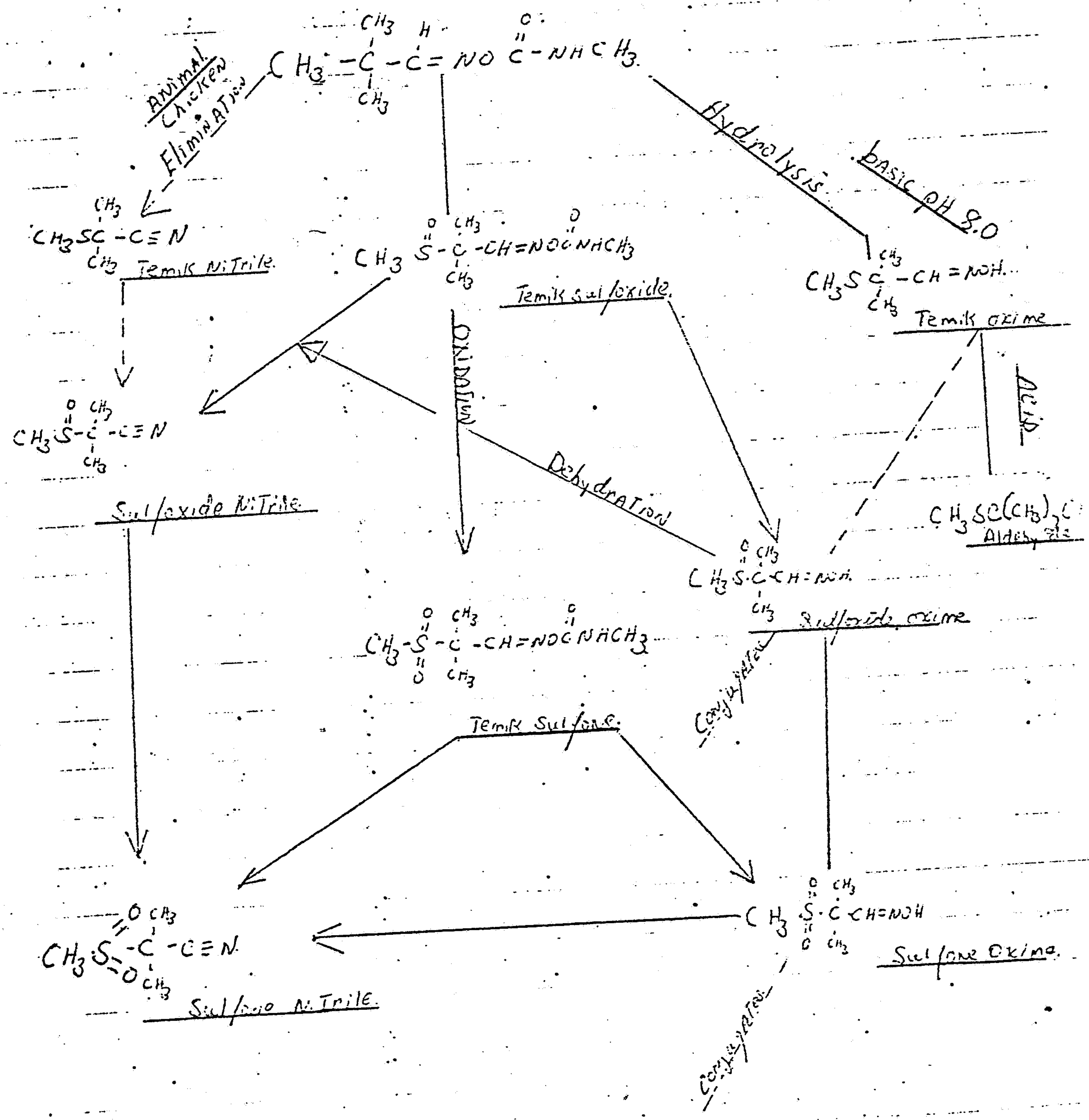
All the studies submitted are data that has been previously reviewed, except a study on hydrolysis and oxidation which stated temik under alkali conditions is hydrolyzed to oxime, then further by acid to aldehyde. Aldicarb is stated to be oxidized to aldicarb sulfoxide and then to aldicarb sulfone. This is an ancillary data package.study. It could be useful in some aspects (plant metabolism studies) to give support to appropriate uses.

4.9.2 From literature sources of information, we found that a majority of tobacco is grown in the Carolinas, Georgia, Kentucky, and Tennessee. Most is grown on sandy type soils, and requires well-drained soil for production. We also note that tobacco is not normally rotated. We feel the rotational crop uptake concern is minimal and would not require a crop uptake study. We do, however, think that ground water contamination may occur since aldicarb and its degradate do leach in sandy soils.

METABOLISM CHARTS

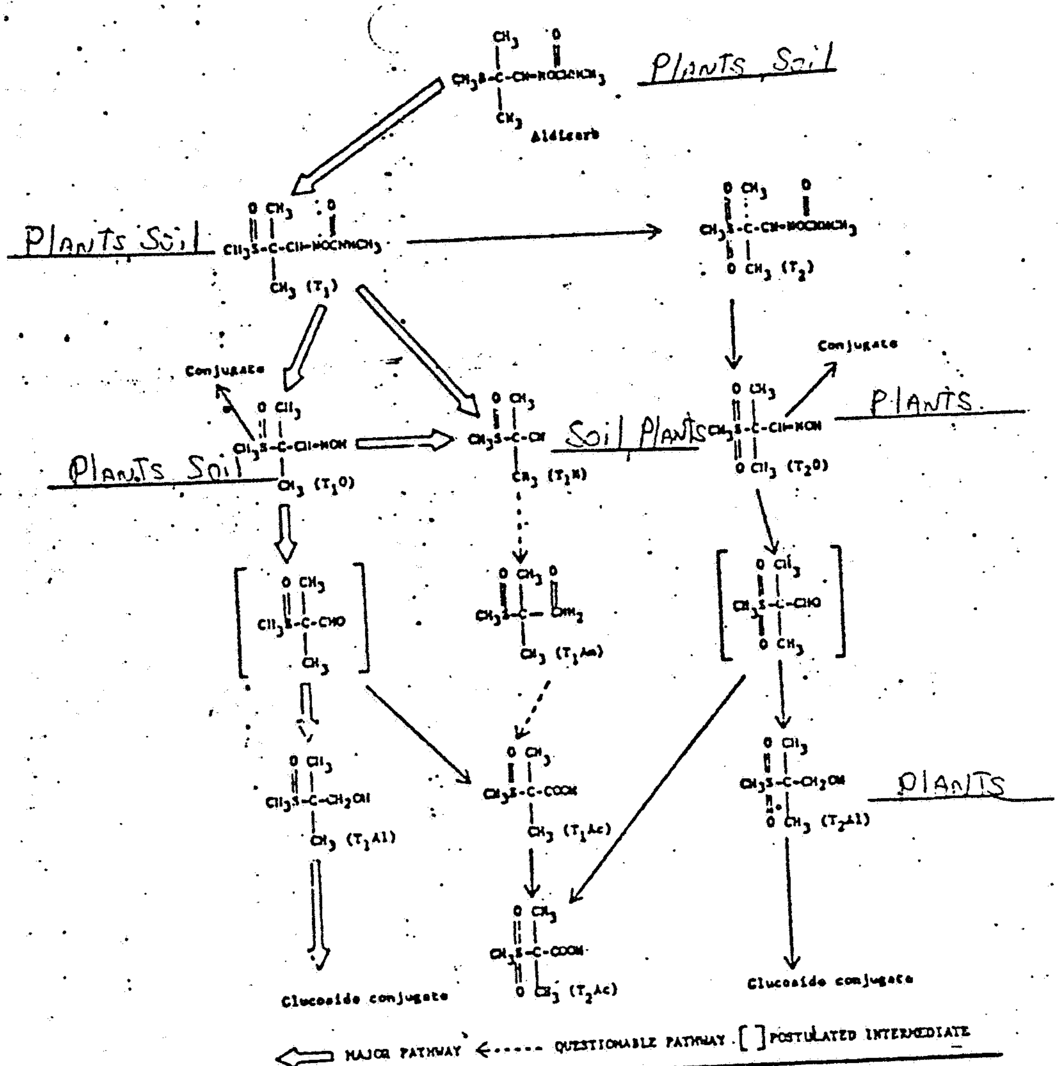
Metabolism Charts

TEMIK



UNKNOWNS NOT included.

———— – – – – Probable



Compound	Abbreviation
2-Methyl-2(methylsulfinyl)propionaldehyde O-(methylcarbamoyl)oxime (Aldicarb sulfoxide)	T_1
2-Methyl-2-(methylsulfonyl)propionaldehyde O-(methylcarbamoyl)oxime (Aldicarb sulfone)	T_2
2-Methyl-2-(methylsulfinyl)propionaldehyde oxime (Oxime sulfoxide)	T_1O
2-Methyl-2-(methylsulfonyl)propionaldehyde oxime (Oxime sulfone)	T_2O
2-Methyl-2-(methylsulfinyl)propionitrile	T_1N
2-Methyl-2-(methylsulfinyl)propionamide	T_1Am
2-Methyl-2-(methylsulfinyl)propanol	T_1Al
2-Methyl-2-(methylsulfonyl)propanol	T_2Al
2-Methyl-2-(methylsulfinyl)propionic acid	T_1Ac
2-Methyl-2-(methylsulfonyl)propionic acid	T_2Ac

Source: Bartley et al., op. cit. (1970).

5.0 **Recommendations**

5.1 We cannot concur with the proposed added use on tobacco.

5.2 The following studies were not submitted nor referenced and are required (data gaps):

(1) Photo degradation in soil
(2) Photo degradation in water
(3) Aged leaching study:
  (a) since other leaching studies show temik and its degradates to leach, we do not need an aged leaching study.
(4) An aerobic soil metabolism.
(5) Rotational Crop Data 9/29/77

5.2.1 Degradation studies are used to determine rates of loss and identification of pesticide residues which may adversely affect non-target organisms. Pesticide and their degradates may be available to non-target organisms as residues in fish and may contaminate the food web. Hydrolysis and photolysis are two routes of physico-chemical degradation that may effect non-target organisms or be available for uptake in the food web.

Microbial degradation with its biochemical transformations may be of greater importance than physico-chemical transformation. Microbes are among the most important group of organisms involved in the biochemical transformation of pesticides in soil and sediment. Microbe interactions may affect the availability of pesticides to non-target organisms and accumulations in the food web.

5.3 The following studies are not acceptable; their deficiencies are noted.

5.3.1 Hydrolysis. PP 3F1414 book 1, Section D. June, 1973, found in Compilation book for Environmental Chemistry, July, 1977.

(1) Information is needed concerning the lighting conditions in this study; since pesticides are usually suseptable to both hydrolysis and photolysis.

(2) The temperature evaluated of 80° and 100°C, are not conducive with temperatures found in the environmental conditions of pesticide application to the environment.

(3) A material balance study was not submitted. Both degradates formed and pictures of chromatograms were not submitted.

(4) Methodology of the in juice analytical procedure U. C. 21149-III-SBF could not be found in the review package.

(5) This study will have to be repeated. Accepted protocol may be found in section 5.5(1). The thin juice analytical procedure UC 21149-III-SBF methodology will have to be submitted.

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5.3.2 Microbial Metabolism. ACC #091372 Vol. 2 of 6 Tab #13.

(1) Animal or plant pathogens and indications of fecal pollution are unsuitable for microbiocidal or static determination. They are not commensal organisms found in soil.

(2) ~~Usual~~ Visual enumeration techniques of bacterial growth is unacceptable.

(3) This study will have to be repeated, acceptable protocol can be found in sect. 5.5 (3, 4).

5.3.3 Accumulation (Fish)

(1) A flow through system was not evaluated.

(2) Radioisotopic techniques not used.

(3) Catfish not used in the static system.

(4) Soil not aged properly (2-4 weeks - aerobic conditions) prior to initiation of exposure in the static system.

(5) Determinations of residue in whole body, edible tissue, and viscera or carcass were not analyzed.

(6) Characteristics of the water were not given.

(a) O_2 content.

(b) Temperature

(7) This study will have to be repeated. Acceptable protocol may be found in section 5.5(7).

5.3.4 The following studies combined are an acceptable soil metabolism (aerobic study).

(1) Acc #091372, Vol. 2 of 6, Tab #7, pg. 2

(2) Compilation ES data book, July 77, II-1.

(3) Acc #091372, Vol. 2 of 6, Tab #2, pg. 907.

5.3.5 The following studies combined are an acceptable soil leaching study.

(1) Acc #091372, Vol. 2 of 6, Tab #9, pg. 4

(2) Acc # 091372, Vol. 2 of 6, Tab #15.

5.3.6 The following studies are scientifically acceptable, but have deficiencies.

5.3.7 Volatility

Acc # 091372, Vol. 2 of 6, Tab #9, pg. 4

(1) Not evaluated under actual use conditions.

Acc # 091372, Vol. 2 of 6, Tab #9,

(1) Same as above.

Acc # 091372, Vol. 2 of 6, Tab #9, pg. 7

(1) Same as above.

5.4.3 In volatility studies 50% in study (1) is unaccounted for. A claim is made that they are "nontoxic" omimeaP and nitrile compounds. Was this analyzed? What are normal outdoor conditions used for the second study (sect. 7.6.1 - 7.6.3).

5.5 The following descriptions are examples of acceptable protocol for either data gaps and/or data with deficiencies.

1. Hydrolysis. Pesticides may enter natural waters via direct application, mobility from treated areas, industrial discharge, and as a result of disposal and cleanup of containers and equipment. Hydrolysis data are required for all pesticides. Studies are to be conducted in darkness using radioisotopic or other comparable detection techniques at different pH values (acidic, neutral, and basic) at two concentrations and two temperatures. Aliquots in duplicate should be taken at four sampling time intervals, with at least one observation made after one-half of the pesticide is hydrolyzed, or thirty days, whichever is shorter. A material balance (accountability at the completion of an experiment of the pesticide introduced into a defined system including both identified and unidentified products), half-life estimate, and identification of degradation products for the pesticide must be provided (10% or greater). Studies utilizing distilled water provide an upper limit estimate for persistence of pesticides in the aquatic environment. Hydrolysis in natural waters may be carried out to supplement studies in distilled water. Concentrations should approximate use rate and 10 X use rate.

2. Photolysis. Sunlight may destroy or chemically alter pesticides in soil, water, and air. Photodegradation studies in water are required for terrestrial, aquatic, terrestrial/aquatic, and aquatic impact uses (except for greenhouse and domestic outdoor uses), and uses where pesticides are discharged into wastewater treatment systems. Studies in soil are required for crop uses and terrestrial/aquatic uses. Studies in vapor phase

are required as part of the assessment of reentry hazard. Conduct photodegradation studies using radio isotopic or comarable detection techniques at one concentration (approximately use rate) under natural or simulated [greater than 280 nm wavelength] sunlight. Such studies must provide a material balance, half-life estimate, and the identification of photoproducts, 10% or greater. Rate studies are conducted in distilled or deionized water at pH of maximum stability, and sampling should continue up to twenty percent degradation with sampling for identification of photoproducts to half-life, or thirty days, whichever comes first. Yield of photoproducts may be increased by changing such conditions as wavelengths, concentration, photosensitizers, and solvents other than water. supplemental rate and photoproduct studies may be carried out in natural water for aquatic uses. Studies performed on the soil used in the soil metabolism studies are preferred but other soil textures will be acceptable. The intensity of incident sunlight and time of exposure must be reported if sunlight is used as a source. Information on artificial light sources should contain type of source, intensity, wavelength, and time of exposure.

Photodegradation data must be supported by incident light intensity and percent transmission. Values for intensity in candles per unit area or lambert units are required for artificial light sources. Latitude, time of year, atmospheric cover, and other major variables which affect incident light are to be reported when natural sunlight is used.

Characteristics of water must be reported including pH, temperature, and oxygen content.

3. Effects of microbes on pesticides. Impact of microbes on pesticide transformation is measured by comparisons of metabolic processes under sterile and nonsterile conditions during a thirty day period. Preferred sampling intervals are 1, 3,

7, 14, 20, and 30 days, but other intervals may be appropriate. Acceptable soil sterilization methods are heat or high energy ionizing radiation. Attempts should be made to identify organisms responsible for degradation. For organisms which are difficult to identify, family names will be sufficient. Isolates that cannot be identified to family level must have descriptive characteristics which can be substituted for generic classification. Alternatively, studies utilizing pure or defined and characterized mixed cultures of bacteria, algae, and/or fungi are adequate.

4. Effects of pesticides on microbes. Data on effects of pesticides on microbes are obtained from studies of effects on microbial functions or microbial populations. Studies of effects on microbial functions constitute a more direct approach, and are preferred to studies of effects on populations. Some effects cannot be measured directly and population studies may be the only recourse. When the functional approach is chosen, data on the effects on nitrogen fixation, nitrification and degradation of cellulose, starch, and protein are required for terrestrial and aquatic uses, and for terrestrial/aquatic uses, an additional pectin degradation study is required. A leaf litter degradation study may be substituted for the cellulose, starch, protein, and pectin degradation studies. When the population approach is chosen, effects on pure or mixed culture populations of representative microorganisms from soil or water or obtained from culture collections should be recorded for terrestrial/aquatic or aquatic uses. Appropriate organisms include free-living nitrogen-fixing bacteria and blue-green algae such as *Azotobacter*, *Clostridium*, and *Nostoc*, and nitrifiers such as *Nitrosomonas* and *Nitrobacter*. For cellulose, starch, pectin, protein, and similar degradation, include at least one each of soil bacteria, actinomycetes, and molds such as *Bacillus*, *Pseudomonas*, *Arthrobacter*, *Cellulomonas*, *Cytophaga*, *Streptomyces*, *Penicillium*, *Flavobacterium*, *Trichoderma*, *Aspergillus*, *Chaetomium*, and *Fusarium*. Animal or plant pathogens and indicators of fecal pollution are unsuitable.

5. Anerobic soil metabolism.. This study is required for field and vegetable crop uses to determine differences in rate and patterns of metabolism between aerobic and anerobic soil conditions. Terrestrial anaerobic soil studies should use the same soil as used in aerobic studies. Obtain an aliquot at the thirty day interval from the aerobic soil study, and establish anerobicity by either water-logging or purging with intert gases. Prefe-red sampling intervals are thirty and sixty days after anaerobicity has been established.

6. A field dissipation study under actual use conditions is required. Analyses are continued until a ninety percent loss of the pesticide occurs or until patterns of formation and decline of degradation products are established or to a maximum test duration of eighteen months. Soil samples are taken in increments to a depth of 12 inches from sites in four agricultural use areas. Sampling times include preapplication, day of application, and shortly postapplication. Succeeding samples are dependent upon degradation and metabolism characteristics.

I Identification of residues comprising more than ten percent of initial application or 0.01 ppm is needed to construct decline curves of residues in soil.

Characterization of soils must be reported including texture (percent sand, silt, and clay), percent organic matter, pH, cation exchange capacity, and bulk density.

7. Fish residue accumulation data using radioisotopic or comparable technique are required. Two exposure systems are required: flow through (with constant concentration of aqueous solution of pesticide) and static (with ambient concentration of residues).

Sunfish are preferred in flow-through system and catfish required in the static system. For the static system treat water overlayering a sandy loam soil at the proposed application rate and allow system to "age" for 2 to 4 weeks prior to initiation of fish exposure.

Exposure duration is 30 days with suggested sampling times at 0, 1, 3, 7, 10, 14, 22, and 30 days of exposure; while fish and water samples are taken on 0, 1, 3, 7, 10, and 14 days of withdrawal of exposure. Obtain soil and water samples prior to fish exposure intervals. Determine the amount and identity of the residue in water, soil, whole body fish, edible tissue, and viscera or carcass at each sample interval.

Characteristics of water must be reported including pH, temperature, and oxygen content.

5.6 We defer to Environmental Safety the significance of residues in ground water.

I. The use of Temik in Tobacco fields may result in residues in ground water.

A) Temik (parent), Temik sulfane and Temik sulfoxide will leach in sandy soils.

1. Sandy loam

a. At 16 days after treatment (4 lbs C-Temik 1A or 24 ppm ai/A) resulted in 3.93% of total applied in eluted water (water that passed through a 5" soil column). Of this at 16 days .02% was parent (.0032 ppm), .92% T. sulfoxide (.146 ppm), 0% T. sulfane, and .16% other (.025 ppm).

2) Sand

a. At 23 days after treatment (rlb C Temik /A or 24 ppm ai/A) resulted in 83.97% of total applied in eluted water (water that passed through a 5" soil column).

Of this at 23 days 31.47% (1.03 ppm) was parent, .26% (0.08 ppm) was to sulfoxide, 0% sulfane, and .04% (.0013 ppm) others.

3. T. sulfane at 35 days in sandy loam was detected in trace levels.

B) Temik is stable in pH values of ≥5.0. Temik and Temik sulfane and sulfoxide will degrade in pH's of 6, 7, and 8 at 80°C and 100°C will t's less than 24 hours. We have no data on more ambient aquatic environmental temperatures. We do not have enough data to estimate to these temperatures (although we suspect much longer). We do not have a material balance of degradate formed from either parent or t-sulfane and sulfoxide.

C) Temik is pond water at 30 ppm (introduced into the water by the registrant) was conducted on bream, large mouth bass, bull frogs, and cricket frogs (static system) and no accumulation (bio) could be made at 3.0 ppm because it was lethal to those species for up to 10 days of treatment (1.6 ppm left). We defer the significance of Temik in pond water also.

5.7

We defer to Toxicology Branch regarding the significance of volatile products.

1) Laboratory studies show Temik to volatilize depending on soil type (sandy types), temperature, and moisture level from ≅10% to ≅50%. Another laboratory study showed that volatiles were identified as Temik sulfoxide, Temik sulfane, and unknown #3.

5.8

We defer to Toxicology Branch as to the need for reentry data requirements. If Toxicology Branch determines that reentry data are needed, then Registration Division will require the following:

A) Soil metabolism.

B) Soil dissipation.

C) Dislodgable residues.

D) Volatility.

E) Photodegradation (vapor phase).

PM Note: We know that other uses are pending for Aldicarb (Field/veg. crops/for one) and other data gaps exist for these uses (anaerobic soil metabolism and rotational crop data).

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