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SURMES				ban 4E with met	hvicara	thron and/or	•
CHEMIC	AL & FURM	ULATION to	xaphene for rpyrifos (0,	testing on cott 0 -Diethyl 0-(3, Phosphorothics	on. 5,6-Tri	chtoro-2-pyr	ridyi)

- 1.0 Introduction
- 1.1 Other names for chlorpyrifos are Lorsban, Dursban, Dowco 179, ENT 27311.
- 1.2 Percent active: 40.07 chlorpyrifos and 22.8 aromatic petroleum derivative solvent.
- 1.3 Product currently registered (#464-448) for use on Cotton (except in Arizona and California) and Peaches.
- 1.4 Chorpyrifos has been reviewed many times before, listed below are the most recent reviews.

6720-EAA 9782-LU	8/3/76 6/11/76
9198-GT	6/10/76
299-172	5/3/76
464-448, 449, 523	5/2/76
5G-1595	3/13/76
464-LRT	8/13/75
464-368	8/13/75
6F-1673	10/6/75

- 1.5 This is the first time a tank-mix combination has been submitted for Lorsban 4E.
- 1.6 A total of 2100 gal. (8400 a.i. = \sim 4 lbs. a.i./gal). are to be shipped for testing on 1200 acres in six states (Alabama, Arkansas, Georgia, Mississippi, South Carolina, and Texas).
- 1.7 The applicant proposes the use of Lorsban 4E as a tank mix with methyl parathion and/or toxaphene for evaluation on cotton.
- 2.0 Directions for Use.

Mix the specified dosage in sufficient water to ensure thorough coverage of plants and apply using aerial or power operated ground equipment. For aerial application, use at least one (1) gallon of water/A. Treat when the field counts indicate damaging insect populations are developing or present. Application should be made at the rate of (1) pint/A (0.5 lb. of chlorpyrifos/A) in combination with (1) lb. of methy/parathion/A, or 2 lb. of toxaphene/A, or (1) lb. of methyl parathion plus (1) lb. of toxaphene/A. Re-treat as necessary to maintain control. Do not apply within 14 days before harvest.

2.1 Disposal

Keep out of lakes, streams, ponds, tidal marshes and estuaries. Do not apply where run off is likely to occur. Do not apply when weather conditions favor drift from treated areas. Do not contaminate water by cleaning of equipment or disposal of wastes. Keep away from domestic water supplies.

Do not reuse empty container for any purpose. Promptly crush or perforate and bury with wastes in a location away from water supplies. Follow official local pesticide container desposal regulations where applicable.

Material not used for test purposes specified under the experimental program will be used and/or disposed of in accordance with the EPA regestered label, which will be affixed to each container of product used in the test program.

3.0 Discussion of Data.

No new environmental chemistry data submitted. Review of 2/5/76, (Gandhi-Ney) removed the crop rotation restriction on Lorsban. Lorsban is temporarily dependent (hydrolysis), not mobile, organic matter dependent on adsorption, little microbial decomposition, and photodegrades in the presence of water.

4.0 Conclusions.

Chlorpyrifos has been used on a variety of products (turf, fruit, and field crops). Rates of 0.25 lbs. a.i./A to 4.0 lbs. a.i./A were used. The EUP calls for 0.5 lb. a.i./A on a field crop (cotton) use, as compared to 0.25 lb. a.i./A on one other field crop (sorghum). If extrapolation may be needed in the future, regression analysis (with the value for confidence interval) would be useful for any positive correlation between the two rates.

Mention was also given in the review on Sorghum to the "active" aromatic petroleum derivative solvents. It was accepted due to "the pesticide or product relating to an evaluation of the effects on man or the environment, if fundamentally different from the properties considered by the Agency in the establishment of data requirements of the Registration guidelines...therefore the data are not germane to determine...the effect on man or the environment." We would expect that this action would still be in effect for this EUP.

For this EUP only hydrolysis and aerobic soil metabolism studies are required. We have enough data in our file to concur with this use under the EUP.

- 5.0 Recommendations
- 5.1 We concur with the proposed use under the EUP.
- 5.2 All data under Section 3 of the Regulations will be needed prior to registration. These data, for example, are:
- 5.2.1 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. 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.
- 5.2.2 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 radioisotopic or comparable 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. 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

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as wavelengths, concentration, photosensitizers, and solvents other than water. Supplemental rate and photo-product 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, wavelenght, 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.

Aerobic soil metabolism. Rate, type, and degree of metabolism of 5.2.3 the pesticide residues are to be determined in a sandy loam, loam, silt loam, or other textured soil appropriate to the intended application sites. Radio-labeling in one or more positions in the pesticide molecule is required to assure adequate coverage of chemical transformations. Where radio-labeling will be of little benefit, comparable detection techniques are required. Residues comprising more than ten percent of initial application or 0.01 ppm should be identified. A material balance, including nonextractable residues, must be provided. The experimental dose rate must approximate field application rate. Treated soil must be maintained at temperatures of 18 to 30°C at or below 75% of 0.33 bar moisture content. Collect data until a ninety percent loss of the pesticide occurs and until patterns of formation and decline of metabolic products are established. Preferred sampling times are at pre-treatment, 0, 1, 2, and 7 days, 2 and 3 weeks, and 1, 2, 3, 4. 6. 9 and 12 months. The study need not be conducted for more than one year for terrestrial crop and non-crop uses, and terrestrial/ aquatic uses.

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

Anaerobic soil metabolism. This study is required for field and vegetable crop uses to determine differences in rate and patterns of metabolism between aerobic and anaerobic 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 anaerobicity by either waterlogging or purging with inert gases. Preferred sampling intervals are thirty and sixty days after anaerobicity has been established.

- Effects of microbes on pesticides. Impact of microbes on pesticide transformation is measured by comparisons of metabolic processes under sterile and non-sterile 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.
- Effects of pesticides on microbes. Data on effects of pesticides 5.2.6 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 equatic 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 Mostoc, and nitrifiers such as Nitrosomonas and similar degradation, include at least one each of soft 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.

5.2.7 <u>Leaching</u>

Leaching through soil is dependent upon pesticide formulation. physical and chemical properties of pesticide and soil and environmental conditions. Add pesticide to soil(s) corresponding to the highest

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recommended rate for a single application and study leaching using radioisotopic or comparable techniques to provide a quantitative estimate of mobility in soil. Each study will include soils as sand (agricultural), sandy loam, silt loam, clay or clay loam having a pH range of 4 to 8 with at least one soil having an organic matter content less than one percent. Use a minimum of four soils to study pesticide leaching and elute each immediately with the equivalent of twenty acre-inches water. Use one of the above soils to study leaching of pesticide residues wherein the pesticide is aged in soil under aerobic conditions for thirty days prior to eluting with the equivalent of one-half acre-inches water per day for forty-five days. Two basic techniques for measuring leaching are soil column and soil thin-layer chromato-graphy (soil TLC).

5.2.8 Field Dissipation.

(1) General. A field dissipation study under actual use conditions is required. Decline curve under field conditions define the duration of potential hazard. Continue analyses until a ninety percent loss of the pesticide occurs or until patterns of formation and decline of degradation products are established, or to the maximum time specified below.

Sampling times include pre-application, day of application, and shortly post-application for each single or multiple application. Succeeding samples are dependent upon degradation and metabolism characteristics and potential for reentry. Identification of residues comprising more than ten percent of initial application or 0.01 ppm is needed for the registrant to construct decline curves of residues in foliage, litter, soil and water.

Terrestrial. Terrestrial field dissipation tests are specified below. If multiple applications are anticipated then this use pattern must be reflected in the study.

- (A) Field and vegetable crop uses. Take soil samples in increments to a depth of 12 inches from sites in four agricultural use areas for a maximum test duration of eighteen months.
- 5.2.9 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 pk, temperature, and oxygen content.

5.2.9.1 Rotational Crops

Studies are required to establish if pesticide residue uptake occurs in rotational crops, emergency replanting, or in situations where crops receive water from treated areas. The applicant must identify crops that can be rotated in the proposed use areas. Treat a sandy loam soil with radiolabeled pesticide at a rate equivalent to that expected under actual use conditions. Following treatment, age the pesticide aerobically for a time approximating the anticipated cultural practice; for example, one year for crops rotated the following year, 120 days for crops rotated immediately after harvest, and 30 days for assessing circumstances of crop failure. Plant a root crop, small grain and leafy vegetable crop at the above times and periodically analyze to maturity. When residues are found, a field study using formulated products shall be undertaken to determine when residues would not occur in subsequent crops under actual use conditions. A crop residue study under actual use conditions is required for those practices where a subsequent crop is treated with the same active ingredient as the initial crop. This study is not required for a cover crop if typically plowed under and not grazed. A crop residue study under actual field use conditions is required where water from treated areas, including holding ponds or effluent and other discharges, is typically used to irrigate crops.

- Combination and Tank Mixes. A laboratory or field study comparing dissipation in soil between a mixture and that of individually applied active ingredients is required. Pesticides are applied individually and as a mixture at the recommended rates to light and heavy textured soils. In the field, sample to a depth of 6 inches; and in the laboratory, sample to the bottom of the container until a residue decline curve is established, or for a maximum test duration of 6 months.
- P.M. Note: If Tox. Branch considers this a cholinesterase inhibitor and so specifies then the following data shall also be needed for their reentry assessment:



Data from the following environmental chemistry studies must be submitted in support of the proposed safe reentry interval.

- (1) Soil metabolism. See 5.2.3 above for data requirements.
- (11) Soil dissipation. See 5.2.8 above for data requirements.
- (iii) Dislodgable residues. Chemical analysis for reentry data must include the levels of dislodgable residues for active substances applied to the crop and their major breakdown products. A dislodgable residue is one which is easily removed from the plant surface by a simple wash and is thereby distinguished from residues released from within the leaf or its surface waxes by more drastic means such as organic solvent extraction or homogenization. The latter are normally not available under conditions of worker exposure. Data from two collecting sites that differ in climatic, crop cultural and edaphic conditions must be selected because data collected in one geographical area may not be relevant to another with different environmental conditions. With proper planning these sites may be the same sites chosen for other environmental chemistry data studies and for collecting tolerance residue data. Before applying the pesticide, the investigator should obtain the spray history of the plot to insure that preexisting residues will not affect the experimental results. The actual application operation must be carefully supervised to insure that quantities delivered are consistent with the proposed or actual label recommendation. Furthermore, the application should be made in the growing season and at the frequency dictated by pest management practices. Sample at zero time, 12 hours, 1 day, 2, 5, 7, 14, 21 and 30 days. A decline curve of the residues, including any plateau which may occur with time must be determined. The final result of the analysis should be a measure of residue potential expressed in mg or ug of the pesticide and its toxic degradation products per sq cm of foliar leaf surface. Samples must be collected from soil in the plot and developed in the same manner, since recent evidence indicates that dust may be a significant dermal and respiratory route of exposure for field workers. Meteorological data in the area containing the plot should be recorded daily between application of the pesticide and completion of the study. If the growth characteristics of the treated crop produce unique micro-environmental conditions, eg, shaded foliage, arboring, samples collected at the plot site must reflect these conditions.

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- (iv) Volatility. Volatility studies under actual use conditions are required for reentry. Monitor air samples for residues at treated sites and at the same time intervals as specified in the Dislodgable residue study above.
- (v) Photodegradation. Vapor phase photolysis studies are required as part of the assessment of reentry hazard.

Ronald E. Ney, Jr.

March 14, 1977

Robert F. Carsel

March 14, 1977

Environmental Chemistry Section

Efficacy and Ecolgoical Effects Branch