Environmental Chemistry Evaluation of 1,2-dimethyl-3,5-diphenyl pyrazolium methyl sulfate. (Avenge. CL 84777)

PP# 4G1453

Submitted by American Cyanamid 1/15/74

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I. Introduction

1. Applicant proposes new chemical as a herbicide for wild oats in barley with the following temporary tolerances:

barley straw 0.5 ppm
barley grain 0.05 ppm (negligible residue)
and meat fat and meat by-products of cattle, goats, hogs, horses and sheep at 0.02 ppm (negligible residue)

2. Other names for this chemical are AC 84777 and CL 84777. Product name is Avenge 2A-S, which contains 2 lbs active ingredient per gallon.

3. Note recommendation for tank-mix with MCPA.

II. Directions for Use:

Apply 0.63 to 1.0 pounds active ingredient per acre, depending on degree of wild oat infestation. Under adverse conditions such as cold weather, drought or low soil fertility, apply at maximum rate 1 lb active/A. Applications should be made when majority of wild oat plants are in 3-5 leaf stage (approximately 9 days after emergence). Do not apply Avenge if rain is predicted within 6 hours. Apply Avenge 2A-S in 5-10 gallons water by ground equipment or 3-5 gallon by aerial application. Avenge may be used as tank mix with MCPA. Do not allow livestock to graze on fields sprayed with Avenge until after harvest.

Note maximum number of applications not specified on label.

III. Discussion of data.

1. Soil Metabolism of Avenge Section D2IV C-375 ✓

Parent compound labeled in N-methyl carbon with ^{14}C. After ion exchange to remove radiolabeled anion, it was mixed with equimolar amount of deuterated (meta-phenyl position) parent. Four planters 3" wide and 4-1/2" tall with Wisconsin soil (sand-silt-clay 24-56-20) treated with parent compound mixture at 2 lbs per acre in top 1" soil. Treated soil was mixed thoroughly after drying and replaced in planter, which received water equivalent to 1" rain per week. Planters retained in greenhouse. At 3 and 10 weeks soil from planter sectioned into top 2" and bottom 2". Each section extracted twice with methanol (5 ml/g)

and 3x with 2% 12N HCl in methanol by shaking. Extracted soil radioassayed by combusting. Weeds growing in ten week sample analyzed for ^{14}C in upper and lower plant portions.

Results: At 3 weeks 83% of ^{14}C was extractable from top 2" with 18% of ^{14}C bound there and 1.5% of applied ^{14}C found in lower 2". At 10 weeks 76% of total ^{14}C extractable with 15% bound and 3% of applied ^{14}C found in lower 2". ^{14}C residues in adventitious weeds in 10 week sample were less than 0.1% of total applied. TLC analysis showed that all ^{14}C was present as parent compound and parent cation associated with other anions.

Conclusions:

a. Applicant concludes that parent compound remains inert in the soil, probably because the parent cation is ion exchanged to clay particles in soil. Applicant states that better extraction methods have been developed but does not describe them.

Applicant concludes that parent compound does not leach; reviewer feels leaching study is necessary, preferably using soil containing photodegraded parent. Biodegradation apparently does not occur.

b. Very persistent.

c. Somewhat like paraquat.

2. " Soil Metabolism and Photodecomposition " Section D2 IV-A

In this exhibit, applicant attempts to correlate soil persistence and photodegradation. Since field residue studies and laboratory persistence studies demonstrate such dissimilar halflife of parent Avenge and since leaching, volatility, and biodegradation do not account for such loss, applicant conjectures that photodegradation accounts for field residue losses. Some photolysis studies now in progress show that parent compound degrades in aqueous solution to 19 fragments, 6 of which make up significant portion of total residue. Identification is underway.

In this exhibit, also, it is stated that greenhouse tracer studies and outdoor confinement-cylinder studies have progressed through 6 month stage. Data presented only on greenhouse work through 10 weeks, and no data on outdoor confinement cylinder studies.

Recommendations:

1. All data from the greenhouse and outdoor confinement-cylinder studies must be submitted prior to registration.

2. The photodegradation studies are needed prior to registration.

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3. A description of the better extraction methods for extracting parent compound from soil.

4. It must be noted that radiotracer work was conducted on soil incorporated Avenge, where label specifies surface broadcast spray application.

3. Field Soil Persistence Interim Report Section D1-5 Report C-418

Analytical Method M-471 GLC Determination of Avenge (CL-84777) Residues in Soil.

Soil samples were extracted from soil-sea sand mixture in chromatographic column using 2x 4% HCl in methanol, partitioned against benzene (discarded) and partitioned into methylene chloride. Clean up on alumina chromatographic column using 10% methanol in methylene chloride, evaporate to dryness and made to volume for GLC in acetone. GLC using nitrogen specific detector. Recovery samples fortified 30 minutes prior to extraction. No recovery data on fortified aged soil samples; this will be necessary prior to registration. Recovery averages are 95% at 0.1 ppm, 89% at 0.5 ppm and 82% at 1 ppm, when extracted 30 minutes after fortification and without allow enough time for ion exchange binding (as in aged samples).

Results:

Five tests in four states at rates between 0.5 and 2.0 lb active/A. Interim report covers 3 months post-treatment and fields will be resampled at 6 and 12 months. While applicant concludes that residues had decreased 50% or more at all locations at the 3 month interval, the conclusion that degradation is the cause of the decrease is not substantiated. Other factors may cause the lack of accountability, and especially increased soil binding over longer time periods. The analytical method is adequately validated by recovery data at 0 days of aging, but recovery data demonstrating the extractability of residues from aged soil is needed to validate results at the 3 month sampling interval. Reviewer feels that residues become more and more bound over time and less and less extractable. Such event would appear superficially as a decrease in soil residues. In addition to the possibilities of soil binding, the effects of photodegradation as a cause have not been fully investigated. In another study, applicant states that parent compound is rapidly photolyzed in aqueous solution in sunlight to 19 highly polar fragments. These fragments have not been identified as yet, nor has the analytical method for soil residues been validated against photolysis products. Applicant contends in the other study that photolytic degradation is the probable cause of the decline in soil residues in the environment. No data is presented.

Conclusions:

While applicant concludes that apparent residues of parent Avenge have decreased 50% in 3 months, reviewer concludes that the lack of supportive information precludes the determination of the halflife in the field.

Recommendations:

1. The recovery study must include data on the recovery of residues from aged treated soil.

2. Data from the 6 and 12 month post-treatment sampling intervals are needed.

3. Information on photolytic products in soil and the extractability of same using the soil residue method should be submitted.

4. Identification of the crop listed as "S.F." in Experiment 60918-73-15d-R.

4. Photodegradation of Avenge

In section D2 IV-A, applicant states that parent compound is photodegraded in aqueous solution by sunlight to 19 highly polar fragments, six of which constitute a sizeable portion of the total residue. These photoproducts have not been identified, although investigation is proceeding. No details or other information on photodecomposition is submitted. Such data must be submitted prior to registration.

Conclusion:

Photodegradation study must be submitted.

5. Effects of Avenge on Microorganism Activities in Soil. Section D2-V

Avenge was added to Nixon sandy loan (pH 5.9) at 1 and 10 lbs per acre (0.5 and 5.0 ppm). Normal activities of soil microorganisms monitored.

Results:

No adverse effect at either treatment rate on the following activities: carbon dioxide evolution, carbon cycling, oxygen consumption, nitrification, sulfur oxidation, dehydrogenase activity.

6. Rotational Crop Uptake Study

While this study was discussed at June 7, 1973 meeting between American Cyanamid and RD personnel, it has not been submitted. This data is necessary prior to registration. Since we have no information as to possible uptake of soil residues kg rotation crops, the label must bear the crop rotation restriction, "Do not replant Avenge treated areas to any crop not specified on this label for 18 months after last treatment".

A root crop must be included in the rotational crop uptake study.

7. Fish Accumulation Study Section D4 Report C-409

Avenge was ^{14}C-labeled in 3-position of pyrasolium ring. Bluegill sunfish fingerlings exposed to Avenge at 1.0 ppm and 0.01 ppm. The 0.01 ppm was entirely ^{14}C-Avenge while 1.0 ppm consisted of 3% ^{14}C-Avenge and 97% cold Avenge. Exposure period was 28 days and 25% of water removed daily and replaced with fresh water containing enough Avenge to maintain constant levels of 0.01 ppm and 1.0 ppm. Water samples analyzed but results not reported. Fish sampled 1, 3, 7, 14, 21, and 28 days exposure and same sampling dates during withdrawal. Fish samples were 3 fish with duplicate aliquots of edible portions of each fish. Viscera from these three fish pooled for analysis. At 28 days exposure edible portions and viscera pooled and extracted with polar (methanol) and nonpolar (hexane) solvents to determine relative distribution.

Results:

Edible portions of bluegills did not accumulate Avenge over 28 days exposure. Viscera of bluegill accumulated a maximum of 27x at 0.01 ppm exposure. In addition, most of the visceral residues decreased during withdrawal.

Conclusions

Avenge does not accumulate to any significant extent in bluegill during 28 days aqueous exposure.

Recommendations:

A. Object to the temporary permit

The label requires a crop rotation restriction such as: "Do not replant Avenge-treated areas to any crop not on this label until 18 months after last treatment."

B. The following studies are needed before the environmental chemistry review can be completed for permenant registration.

1. Final reports on the field persistence studies, the radiotracer greenhouse study, and the radiotracer outdoor confinement cylinder study.

2. The rotational crops uptake study (including a root crop).

3. The photodegradation studies.

4. A description of the "better extraction methods" for extracting AC 84777 from soil as mentioned in Section D2-IV-A.

5. Recovery data using Analytical Method M-471 demonstrating the extraction efficacy of the method on "aged" treated soil.

6. Identification of the crop listed as "S.F." in Experiment 60918-73-15d-R (and others).

7. Recovery data using Analytical Method M-471 demonstrating the extractability of known photoproducts from soil (if the photoproducts are found to be formed in soil).

8. Leaching studies on aged treated soil residues.

9. Adsorption coefficient of AC 84777 between silt and water.

have 10. The rate of hydrolysis (at 20° C) of a dilute (2-100 ppm) solution of AC 84777 should be determined at pH 5, 7, and 9. The study should be continued until at least 75% of the chemical is hydrolyzed or 4 weeks, whichever is the lesser. Care should be taken to prevent photodegradation or volatilization losses. The study should clearly demonstrate the nature and percentage of the hydrolysis products formed.

have 11. Clarification as to maximum number of applications of Avenge 2A-S.

have 12. An anaerobic soil study is needed. See enclosure. Pat Critchlow - enclose page V-22 of second Draft Guidelines.

13. A complete list of all degradation products by chemical name and structure is needed. Each product should be defined as to its source (e.g., plant metabolism, photodegradation, etc.). All code names or synonyms should be listed.

14. In addition to the environmental data needed for registration, the following are needed to support the registration of tank mixtures:

a. Laboratory study using cold chemicals applied to two soils as recommended in the proposed use. A light and heavy soil will be adequate.

b. Analysis through two halflives of each pesticide applied as a mixture and separately. The same soil types are to be used for the comparison of the mixture vs individually applied chemicals. Sampling depth should be to bottom of container (pot) or 6 inches.

15. All radiolabeled studies should be supported with samples of the following:

a. Sample calculations,
b. Counting efficiencies,
c. Counting times,
d. Background level,
e. Probable error with scintillation techniques.

16. In the future please submit the environmental chemistry data in an orderly manner. For example, keep related studies following each other and do not intervene with different type studies. A suggested format is as follows:

1. Table of content
2. Summary of environmental chemistry data
3. Listing of degradation products
4. Environmental data
   a. Analytical methods
   b. Soil metabolism and dissipation studies
      1. Aerobic soil studies
      2. Anaerobic soil studies
   c. Bound residue study
   d. Field persistence studies and leaching
   e. Photodegradation
   f. Effects on or by microorganisms
   g. Hydrolysis studies
   h. Crop metabolism studies
   i. Crop rotation studies (residues)
   j. Leaching study
   k. Aged leaching study

l. Runoff study
m. Fish accumulation study
n. Animal feeding and metabolism studies
o. Other studies

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