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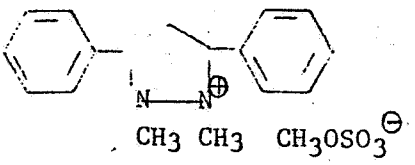
AVENGE® Wild Oat Herbicide:

General Summary of Chemodynamic Properties and Fate in the Environment

General



CH_3 CH_3 $CH_3OSO_3^{\ominus}$

The active ingredient of AVENGE® wild oat herbicide is 1,2-dimethyl-3,5-diphenyl-1H-pyrazolium methyl sulfate) difenzoquat methyl sulfate). It is also known by its code numbers "CL 84,777" and "AC 84,777". All of the biological activity of the compound lies in the cationic portion.

Solubility

The compound is highly water soluble (Exhibit 1), ranging from 26.8% (w/w) at 0°C to 85.6% at 56°C. At room temperature (23°C) the water solubility is 76.5%. In nonpolar organic solvents such as hexane, benzene and dioxane, its solubility is quite low, 0.1% (w/v), but in moderate to high polarity solvents solubility is substantial (e.g. methylene chloride - 36.0%, chloroform - 50%, methanol - 62%).

Partitioning Behavior

Studies of the partitioning behavior of CL 84,777 (Exhibit 2) between water and chloroform have shown that at room temperature and at starting concentrations in the aqueous phase of 8 and 8,000 ppm, the $C_{organic}/C_{aqueous}$ ratios are 0.22 and 0.07, respectively. AVENGE is believed to exist as an undissociated ion pair in the chloroform phase, but as the fully dissociated salt in the aqueous phase. The partitioning of the cation into the organic phase can be greatly enhanced by "salting-out" (i.e., saturation of the aqueous phase with sodium chloride) or by flooding the system with an anion, such as perchlorate; which forms a very strongly associated ion pair; in both cases the $C_{organic}/C_{aqueous}$ exceeds 20 and essentially quantitative extraction of the cation from the aqueous phase can be achieved with two partitioning steps.

The partitioning behavior of AVENGE between n-octanol and water has been studied (Exhibit 2) as an indicator of bioaccumulation potential. The $C_{organic}/C_{aqueous}$ ratio was found to be 0.03 at 8,000 ppm and 0.11 at 8 ppm, suggesting that significant bioaccumulation is highly unlikely. This finding is in complete agreement with the results of bioaccumulation studies in fish (Exhibit 7).

Dissociation Constants

By virtue of its quarternary salt nature, the AVENGE cation is permanently charged and does not become neutral at any pH. Thus the concept of dissociation constants is not applicable. In certain solvents (such as chloroform) and with certain anions (such as perchlorate), ion-pair complexes are formed which are very strongly associated and which are relatively more organophilic than would otherwise be true.

Adsorption to Soil and Leaching Potential

A variety of experiments with soil in the laboratory (Exhibit 19), greenhouse (Exhibits 17, 18) and field (Exhibit 12) has shown that AVENGE is very tightly adsorbed to soils and does not leach to an appreciable extent, either as a fresh or aged deposit.

Hydrolysis

AVENGE at 20 ppm is completely stable to hydrolysis in the dark over a four-month period at pH values of 5, 7 and 9 at room temperature (Exhibit 20). Three and fifty percent solutions of the compound in water are completely stable for 25 days at 56°C (Exhibit 1) if protected from strong light.

Photochemical Studies

Exposure of water solutions or thin films of AVENGE to sunlight or supplementary greenhouse lighting (approximately 12,500 foot-candles from 1000-watt alkali halide lamps) results in extensive degradation of the compound (Exhibit 16). The process in water appears to be autocatalytic (i.e., the degradation rate increases with time of exposure); after an initial lag, the process under the alkali halide lamps proceeds for some time at a rate corresponding to a half-life of about 18 days, after which the rate increases gradually to one corresponding to a half-life of about 11 days. Except for a somewhat longer lag time, the process in distilled water appears to be about the same as in natural pond water. An early experiment (Exhibit 20) suggested cleavage of the pyrazolium ring to produce azomethane and cyclopropenyl fragments but extensive further work (Exhibits 13, 16, 21) has failed to confirm this mechanism. Studies with authentic azomethane (Exhibit 21) have shown that the physical and chemical properties of the compound are such that it could not have been isolated by the procedure described in the first report (Exhibit 20); it is too volatile and too photolytically unstable to survive the experimental conditions.

Further, these studies (Exhibit 21) have shown that even if azomethane were produced, it photodegrades so rapidly in both air and water that it could not constitute a hazard in the environment. In an extensive series of water photolysis experiments (Exhibit 16), no azomethane could be found by sensitive direct GLC procedures at any time interval under any of several exposure conditions. Both N-methyl and ring-labeled tracers degraded at essentially the same rate and yielded essentially identical chromatographic patterns, thus further negating the possibility that any significant amount of azomethane could be formed. The fact that both the N-methyl and ring labels were present in all of the major photodegradation products indicates that little, if any, fragmentation of the parent structure occurs.

The products are more polar, as judged by chromatographic behavior, than the parent. They have been characterized by chemical demethylation and microderivitization tests as hydroxylated derivatives of AVENGE which retain the quaternary salt feature of the parent (See Figure attached).

In the water photolysis experiments, no loss of radioactivity is encountered. However, when exposed as dry thin films (Exhibit 16), very substantial amounts of radioactivity (about 85% in 14 days) are lost. The nonvolatile radioactivity consists of about 1/3 unchanged parent plus the same pattern of spots seen in the water photolysis experiments. Photodegradation studies of AVENGE deposits, both as thin films on glass and as surface deposits on soil (Exhibit 13), have shown that AVENGE is readily demethylated photolytically and that the only volatile product which results from the photodegradation process is the demethylated tertiary amine analog (CL 84,760) of AVENGE. Since the photolytic demethylation occurs relatively rapidly and since CL 84,760 is classified as only slightly toxic (LD_{50}= 1350 mg/kg), this mechanism provides a major process for AVENGE detoxification in the environment. It also provides the explanation for the observation that AVENGE disappears from both plant (Exhibit 9) and soil (Exhibit 11, 12) surfaces without leaving significant non-AVENGE residues. (See Figure, page 8).

Leachability in Soils and Runoff Tests

Leaching studies have been carried out in soil types varying from agricultural sand to clay loam by the soil column technique (Exhibit 19). These studies have shown that no appreciable leaching of radioactivity occurs from either fresh (ranging from 0.7% in clay loam to 2.6% in sandy loam) or aged (0.47% in sandy loam) deposits of AVENGE. This finding is supported by the results of runoff tests (Exhibit 18) which were designed to allow collection of leachate as well as runoff water and sediment; <0.01, 0.01 and 0.04% of the dose, respectively, were found in these fractions. Further support is found in the results of soil metabolism studies (Exhibits 17, 12) which show that most of the applied radioactivity remains in the top-most layer of the soil.

Volatilization Studies

By virtue of its quaternary salt nature, AVENGE is so nonvolatile that conventional techniques [Eggersten et al; Anal. Chem. 41:1175 (1969)] are unable to detect any vapor pressure. Experiments with a differential scanning calorimeter (Exhibit 14) have shown no weight loss when AVENGE is held at 140°C (melting/decomposition occurs at 146-148°C) for one hour while the demethylated analog, CL 84,760, showed a loss of about 6% under these conditions.

Behavior in Biological Systems

AVENGE is essentially inert metabolically. It is not degraded by soil microorganisms (Exhibit 3), rats (Exhibit 4), goats (Exhibits 5, 6), fish (Exhibit 7) or barley plants (Exhibits 8, 9). It is rapidly excreted intact by rats and goats and does not accumulate in rat, goat, fish, chicken (Exhibits 10, 45) or cattle tissues (Exhibit 46).

Under field conditions (Exhibit 9), residues of the compound rapidly disappear from plants ($t_{1/2}$ =4 days) without leaving significant residues of metabolites (below 0.05 ppm, including unextractables, in foliage at harvest); parent AVENGE is the only significant component (97-99%) of the residue on treated plant foliage at all time intervals and residues in this study are well below the proposed tolerance for grain (less than 0.005 ppm versus 0.2 ppm). Under greenhouse conditions (Exhibit 8), the rate of disappearance from plant foliage is slower than under field conditions, but the pattern is qualitatively the same.

A study of spray droplet size and drift (Exhibit 52) from aerial applications of 1 lb of AVENGE per acre in 3, 5 and 10 gallons of total volume spray per acre, was conducted in Casselton, North Dakota. (Exhibit 52). For droplet size and drift determination, white Kromekite cards were mounted in the spray pattern (under one wing) at 100 foot intervals for 1,000 feet (total of 11 cards). After application, cards were picked up, labeled and sent to Princeton for examination and calculations of droplet sizes. Drift residues were also collected in 2 quart Pyrex baking dishes filled with water. After application the water was sent to Princeton for analysis of AVENGE residues. The total amounts of AVENGE accounted for when applied at the rate of 1 lb ai/A were 325.6, 323.4, 289.4 grams. When sprayed in the respective volumes of 3, 5 and 10 gpa, these amounts account for 78, 78 and 70%, respectively of the total AVENGE deposited in a 1,000 x 40 ft. swath.

Fate in Soils

A. Surface Application

Since AVENGE is used as a postemergence spray on plants at the 3-5 leaf stage, any AVENGE reaching the soil as a result of spray droplets missing the plants will be deposited as a thin film on the surface. Because of very strong adsorption of the compound by soil particles, the deposit will remain immobilized at the surface. Under realistic conditions in the field (Exhibits 11 and 12), AVENGE applied to the soil surface disappears at a moderate rate (about half of dose lost during 16-week period) as a result of thermal or photolytic demethylation (13) to form a compound (CL 84,760) which is classified as only slightly toxic (1350 mg/kg) and which is lost readily by volatilization. Side-by-side comparisons (Exhibit 11) using both ring- and N-methyl labeled tracers have shown that the disappearance rates are essentially identical for both tracers. At all time intervals studied, up to and including twelve months after treatment, there is no significant bound radioactivity (less than 5% of that present) and parent AVENGE is by far, the main component (greater than 96%) in the extract (Exhibits 12, 15) although traces of other compounds are seen. These compounds are also found in various photodegradation experiments and have been characterized as hydroxylated quaternary salt derivatives of AVENGE (Exhibit 16). The results of these studies with radiotracers parallel very closely the results of nontracer field disappearance studies in soils (Exhibits 24 through 32). Only occasionally can any residue be found in the soil at the beginning of the next growing season. In fact, realistic follow-crop studies have been difficult to conduct because so few of the field studies still showed soil residues at the time of follow-crop planting.

B. Surface Application - Tank-Mix Combinations

AVENGE is effectively used as a tank-mix combination with broadleaf weed killers - MCPA, bromoxynil and bronate (MCPA plus bromoxynil) for selective control of both wild oats and certain broadleaf weeds in barley and wheat. Data taken from field trials (Exhibits 33 through 38) indicate that the apparent AVENGE residues in soil are not significantly altered when used as a tank-mix combination with MCPA, bromoxynil or bronate (MCPA plus bromoxynil). The apparent MCPA or bromoxynil residues in soil are not significantly altered when used as tank-mix combinations with AVENGE.

C. Application by Incorporation

Although AVENGE is not used as a soil-incorporated product, studies using incorporation (Exhibit 17) have been conducted as part of the conventional development program. When AVENGE is protected from sunlight by incorporation into the soil, the thermal and/or photolytic demethylation mechanism is attenuated and other mechanisms are emphasized. These other mechanisms are relatively unimportant under realistic conditions and are relatively inefficient compared with demethylation-volatilization. As a result, the compound disappears at a much slower rate (10-25% of dose lost after two years) but the time scale is such that elucidation of the mechanisms responsible for this loss is beyond existing technology.

Laboratory soil metabolism studies (Exhibits 3, 17) have shown that microorganisms are ineffective in metabolizing AVENGE and that the behavior of the compound is the same under both aerobic and anaerobic conditions; no production of $^{14}CO_2$ or other radiolabeled volatiles is found in the absence of strong irradiation. AVENGE does not significantly alter the metabolic integrity of microorganisms (Exhibit 23). By far the major non-AVENGE product formed on long-term aging of soil-incorporated AVENGE is an extremely polar material which appears by gel permeation chromatography to have a molecular weight several times that of AVENGE and which behaves as a fulvic acid when subjected to a standard fractionation scheme for soil organic matter [Federal Register 40 (123):26893-26894 (1975)]. The radioactivity cannot be released from this material as discrete molecules even by extremely vigorous chemical treatments. Very small amounts of several other extractable very polar compounds are found in older samples; these compounds appear to be the same as the very polar compounds, characterized as hydroxylated quaternary derivatives of AVENGE, which appear in photolysis studies (Exhibit 16). Whether these arise as a result of slow photochemical processes brought about by the small amount of light diffusing into the soil or are formed by other physical or chemical processes in the soil is not known.

Follow-Crop Studies

Under artificial conditions (Exhibit 22) designed to force the maximum uptake of residues from soil by follow-crops (AVENGE incorporated into the soil, aged only four months under relatively mild conditions in the greenhouse), red beets and alfalfa took up considerably more radioactivity than did follow-crop plants growing in the field under realistic conditions (Exhibit 15), but even under these severe conditions, residues were only about 0.25 ppm in beet roots and foliage at maturity and even less (0.12 ppm) in mature alfalfa (22). Essentially all of the radioactivity could be extracted readily and consisted of parent AVENGE plus several very polar materials which appear to be the photodegradation products observed in water-photolysis

experiments (Exhibit 16) and characterized as hydroxylated quaternary derivatives of AVENGE. Whether these materials are formed in the soil and taken up by the roots of the plants or are actually formed from AVENGE by metabolic processes in the roots of the plants cannot be determined. In any event, the conditions of this experiment were so artificial and the results so different from those found in both field metabolism experiments (Exhibit 15) and field follow-crop residue studies that their validity and applicability to the elucidation of the fate of AVENGE in the environment is highly suspect.

Studies have been conducted under realistic field conditions (Exhibit 15) to determine the degree to which following crops might take up radioactive residues from the soil. The plot used for these studies was the one in which the initial field soil metabolism studies (Exhibit 12) were done. In this plot an unusually high proportion of the initially applied radioactivity (about 35%, equivalent to about 0.35 lb/acre) remained in the soil at the time of follow-crop planting. About two-thirds of the radioactivity remaining in the soil was AVENGE and the rest consisted of small quantities of several photodegradation products. Barley straw at maturity contained less than 0.05 ppm of radioactivity and mature seeds contained essentially none (about 0.002 ppm). At maturity, red beet roots and foliage also contained essentially no radioactivity (about 0.004 ppm). Unchanged AVENGE was the major extractable radiocomponent in the barley plants at four weeks and in the mature straw. Radioactivity levels in the other samples were too low for characterization. These findings are in excellent agreement with the results of follow-crop studies under actual use conditions using conventional nonradiotracer techniques. Data from grower field trials (Exhibits 38 through 44) where barley, wheat, red beets, sugar beets and pinto beans were grown as follow-crops on soil treated with AVENGE indicate that the apparent residues of CL 84,777 in these plants (including red beet and sugar beet roots) were below the sensitivity of the analytical methods used.

Fish and Wildlife

CL 84,777 does not persist in an aquatic environment (Exhibit 20) and has a low order of acute toxicity to fish (LC50 to bluegills and trout at 96 hours after treatment are 696 ppm and 694 ppm, respectively (Exhibit 47). Bluegill fingerlings exposed to water containing 1.0 ppm radioactive CL 84,777 for 28 days, did not accumulate the chemical (Exhibit 7).

CL 84,777 is non-toxic to honey bees to the extent that no bees were killed when a dose equivalent to 36 lb/A was administered (Exhibit 51).

CL 84,777 is relatively non-toxic to duck and quail. The 8-day dietary LC_{50} for duck and quail were 10,388 ppm and greater than 4640 ppm, respectively (Exhibits 49, 50).

Introduction

Summary

Exhibit

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Toxicological Studies

1	Acute Toxicology of Technical AC 84,777 to Rats, Mice, and Rabbits. American Cyanamid Report A-73-38.
2	Acute Inhalation Study of AVENGE 95-S in Rats, AMR Biological Research Contract No. 120-2059-83, September 13, 1973.
3	Acute Toxicology Studies With AVENGE 2A-S Formulations, American Cyanamid Reports A-73-139, A-73-138, and A-73-137.
3a	Acute Dermal Toxicity and Eye Sensitivity With AVENGE 2A-S American Cyanamid Company Report A-74-134.
3b	Acute Dermal Toxicity and Eye Sensitivity With AVENGE 2A-S Plus MCPA amine, American Cyanamid Company Report A-74-137.
3c	Acute Dermal Toxicity and Eye Sensitivity With AVENGE 2A-S Plus MCPA Ester, American Cyanamid Report A-74-138.
3d	Acute Dermal Toxicity and Eye Sensitivity With AVENGE 2A-S Plus Bromoxynil, American Cyanamid Company Report A-74-139.
3e	Acute Dermal Toxicity and Eye Sensitivity With AVENGE 2A-S Plus MCPA Ester (and Bromoxynil), American Cyanamid Report A-74-140.
4	Acute Oral Toxicity in Rats With Formulation (AC 2233-63-2). AMR Biological Research Contract No. 120-2059-73, September 10, 1973.
5	Acute Oral Toxicity of Formulation (AC 2233-63-2) in Rabbits. AMR Biological Research Contract No. 120-2059-83, September 13, 1973.
6	Primary Dermal Irritation of Formulation (AC-2233-63-2) in Rabbits. AMR Biological Research Contract No. 120-2059-83. September 11, 1973.
7	Acute Dermal LD_{50} Tests of Formulation (AC 2233-63-2) in Rabbits. AMR Biological Research Contract No. 120-2059-83. September 11, 1973.
8	Primary Eye Irritation of Formulation (AC 2233-63-2) in Rabbits. AMR Biological Research Contract No. 120-2059-83. September 11, 1973.
9	Acute Inhalation Study of CL 84,777-250A, Formulation (AC 2233-63-2) in Rats. AMR Biological Research Contract No. 120-2059-83. September 13, 1973.
10	Acute Inhalation Study of AVENGE 2A-S (Formulation) in Rats. AMR Biological Research Contract No. 122-2325-54. June 14, 1974.

Exhibit	
11	Repeated Application Dermal Toxicity Study in Rabbits With AC 84,777 Technical and AVENGE 2A Formulation. Biometric Testing, Inc. Experiment No. A-883. September 4, 1973.
✓12	Subacute (21-day) Dermal Toxicity Study in Rabbits With Herbicide AC 84,777, AVENGE 2A-S formulation. Food and Drug Research Laboratories, Inc. Laboratory No. 2106a. July 26, 1974.
✓13	Sub-Acute Oral Toxicity Studies - AC 84,777 and AC 92,390 Rats. (90-Day Feeding Study in Rats). Food and Drug Research Laboratories Inc. Laboratory No. 1626. September 12, 1973.
✓14	Final Report: Chronic Oral Toxicity Study in Rats With AC 84,777. (24 Month Long Term Feeding Study). Food and Drug Research Laboratories, Inc. Laboratory No. 1626a. September 19, 1975.
✓15	90-Day Feeding Study in Dogs With AC 84,777. Food and Drug Research Laboratories, Inc. Laboratory No. 1680. September 28, 197
✓16	Final Report: Eighteen-Month Mouse Carcinogenesis Study With AC 84,777. Pharmacopathics Research Laboratory, Inc.
✓17	Three-Generation Reproduction Study in Rats - AC 84,777 Final Report. Hazleton Laboratories, Inc. October 14, 1974.
✓18	Teratology Study in Rats - AC 84,777 Final Report. Hazleton Laboratories, Inc. July 22, 1974.
✓19	Dominant Lethal Study in Rats With AC 84,777. Food and Drug Research Laboratories, Inc. Laboratory No. 2088. September 3, 1974.
✓20	Acute toxicity of AC 84,777 to bluegill (Lepomis macrochirus) and rainbow trout (Salmo gairdneri). Bionomics, Inc. February, 1973.
✓21	Acute Toxicity of PROWL™ 3E, PROWL™ 4E, and AVENGE 2A-S to bluegill (Lepomis macrochirus) and rainbow trout (Salmo gairdneri). Bionomics, EG and G, Inc. May, 1974.
✓22	Eight-Day Dietary LC_{50} - Mallard Ducks - Technical AC 84,777, Final Report. Hazleton Laboratories, Inc. April 3, 1973.
✓23	Eight-Day Dietary LC_{50} -Bobwhite Quail - Technical AC 84,777 - Final Report. Hazleton Laboratories, Inc. April 3, 1974.
24	American Cyanamid Company Memo J. E. Fischer, ACCO Clinincal Developmen Laboratory to A. J. Tafuro, ACCO Program Administrator for Herbicides, Antidote Studies, 1975.
25	Neuromuscular Screen in Cat, Industrial Bio-Test Laboratories, Inc. Northbrook, Illinois, October 21, 1975.
26	Cardiovascular Study in Beagle Dog, Industrial Bio-Test Laboratories, Northbrook, Illinois, October 21, 1975.

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S. Fredericks (for a ready reference)

AVENGE® (CL 84,777) WILD OAT HERBICIDE ON THE ENVIRONMENT

12 - AVENGE® difenzoquat: Fate on Soil Under Field Conditions. American Cyanamid Report No. C-540.

13 - CL 84,777: AVENGE® Wild Oat Herbicide: The Identification of Volatile Metabolites or Degradation Products Isolated from Soil, Water and Thin Films. PD-M 12, pp. 1023-1044.

14 - The Relative Volatility of CL 84,760 and AVENGE as Determined in a Differential Scanning Calorimeter. American Cyanamid Report F-345.

15 - AVENGE® difenzoquat: Uptake of 3-^{14}C CL 84,777 Wild Oat Herbicide Derived Residues from Soil by Barley and Red Beets Grown as Follow Crops. American Cyanamid Report No. C-797.

16 - CL 84,777: AVENGE® Wild Oat Herbicide: The Photolysis of ^{14}C Labeled CL 84,777 in Water Exposed to Natural or Artificial Light. PD-M 12, pp. 972-997.

17 - AVENGE® difenzoquat: Fate of Carbon-14 labeled CL 84,777 incorporated into soils. PD-M 12, pp. 1045-11

18 - Runoff Characteristics of ^{14}C-AVENGE® Applied to Silt Loam Soil Under Greenhouse Conditions. Bio/dynamics Report No. 74004-A. September 10, 1974.

19 - AVENGE* Wild Oat Herbicide: Soil-Leaching Studies of CL 84,777 [1,2-dimethyl-3,5-diphenyl-pyrazolium methyl sulfate]. PD-M 11, pp. 593-619.

20 - CL 84,777: AVENGE® Wild Oat Herbicide: Metabolic Studies of ^{14}C-Labeled CL 84,777 in Hydrolytic and Photolytic Environments. PD-M 11, pp. 620-660.

21 - AVENGE® Wild Oat Herbicide: Stability of Azomethane in Air and Water Using GLC Methods. PD-M 12, pp. 950-971.

22 - CL 84,777: Metabolism: Uptake and Residues of Radioactivity in Table Beet and Alfalfa Plants Grown on Soil With Aged Residues of C-14 labeled CL 84,777 (AVENGE® Herbicide). A Rotational Crop Study. PD-M 12, pp. 1173-1196.

23 - Studies of the Effects of Herbicide AC 84,777 on the Metabolic Activities of Microorganisms in Soil. Rutgers University.

24 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Soil. California. American Cyanamid Report No. C-838.

25 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-dimethyl-3,5-diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Soil. (California). American Cyanamid Report No. C-837.

26 - AVENGE® (CL 84,777): The Gas Chromatograph Determination of (1,2-dimethyl-3,5-diphenyl pyrazolium methyl sulfate) Residues in Soil (Undisturbed Soil Plot - Minnesota). American Cyanamid Report C-560.

27 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl Pyrazolium Methyl Sulfate) Residues in Soil. (Minnesota). American Cyanamid Report No. C-561.

28 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl Pyrazolium Methyl Sulfate) Residues in Soil. Oregon. American Cyanamid Report No. C-557.

29 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl Pyrazolium Methyl Sulfate) Residues in Soil (Montana). American Cyanamid Report No. C-558.

30 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl Pyrazolium Methyl Sulfate) Residues in Soil (South Dakota). American Cyanamid Report No. C-559.

31 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Soil, Oklahoma, 1975. American Cyanamid Report No. C-835.

32 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Soil. Texas, 1975. American Cyanamid Report No. C-836.

33 - The Gas Chromatographic Determination of MCPA (2-Methyl-4-Chlorophenoxyacetic acid) and Bromoxynil (3,5-Dibromo-4-Hydroxybenzonitrile) in Fortified Soil. American Cyanamid Report No. C-796.

34 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate), Bromoxynil (3,5-Dibromo-4-Hydroxylbenzonitrole) and MCPA (2-Methyl-4-Chloropheonxyacetic Acid) Residues in Soil Following Ground Application of AVENGE Alone and in Combination with MCPA or Bromoxynil (North Dakota). American Cyanamid Company Report C-843.

35 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate), Bromoxynil (3,5-Dibromo-40 Hydroxylbenzonitrile) and MCPA (2-Methyl-4-Chlorophenoxyacetic Acid) Residues in Soil Following Ground Application of AVENGE Alone and in Combination with MCPA or Bromoxynil (Oregon). American Cyanamid Report No. C-844.

36 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate), Bromoxynil (3,5-Dibromo-4-Hydroxylbenzonitrile) and MCPA (2-Methyl-4-Chlorophenoxyacetic Acid) Residues in Soil Following Ground Application of AVENGE alone and in Combination With MCPA or Bromoxynil (South Dakota). American Cyanamid Report No. C-845.

37 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-Pyrazolium Methyl Sulfate) Residues in Wheat and Barley Grain and Straw Grown in Soil Treated the Previous Year With AVENGE and Also treated With AVENGE in 1974 as a Postemergence Treatment. Minnesota, 1973-74. American Cyanamid Report No. C-574.

38 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Barley (Foliage), Table Beets (Foliage), and Soil. California. 1975. American Cyanamid Report No. C-798.

39 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Wheat (Foliage) and Soil. Minnesota, 1975. American Cyanamid Report No. C-852.

40 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Sugar Beets (Foliage) and Soil. Minnesota, 1975. American Cyanamid Report No. C-848.

41 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Barley (Foliage) and Soil. Minnesota, 1975. American Cyanamid Report No. C-849

42 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Sugar Beets (Foliage) and Soil. Minnesota, 1975. American Cyanamid Report No. C-850.

43 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Wheat (Foliage) and Soil. Minnesota, 1975. American Cyanamid Report No. C-851.

44 - AVENGE® (CL 84,777): Determination of CL 84,777 (1,2-Dimethyl-3,5-Diphenyl-1H-Pyrazolium Methyl Sulfate) Residues in Barley (Foliage), Pinto Beans (Foliage), and Soil. Montana, 1975. American Cyanamid Report No. C-799.

45 - AVENGE* Wild Oat Herbicide: Residues in Chicken Tissues (Muscle, Fat, Liver, Kidney and Skin) and Eggs. American Cyanamid Report No. C-447.

46 - AVENGE® Wild Oat Herbicide: Residues in Cattle Tissues (Muscle, Liver, Kidney and Fat). American Cyanamid Report No. C-777.

47 - Acute Toxicity of AC 84,777 to Bluegill (Lepomis Macrochirus) and Rainbow Trout (Salmo gairdneri). Bionomics, Inc.

48 - Acute Toxicity of PROWL™ 3E, PROWL™ 4E, and AVENGE 2A-S to Bluegill (Lepomis macrochirnus) and Rainbow Trout (Salmo gairdneri). Bionomics, EG and G, Inc.

49 - Eight-Day Dietary LC_{50} - Mallard Ducks Technical AC 84,777. Hazleton Laboratories, Inc.

50 - Eight-Day Dietary LC_{50} - Bobwhite Quail Technical AC 84,777. Hazleton Laboratories, Inc.

51 - Toxicity of Pesticides to Honey Bees. E. Lawrence Atkins, University of California.

52 - AVENGE® 2A-S Drift Study (North Dakota). American Cyanamid Report No. C-834.