1-19-76

EEE BRANCH REVIEW

DATE:	IN ____ OUT ____	IN 11/24/75 OUT 1/19/76	IN ____ OUT ____
	FISH & WILDLIFE	ENVIRONMENTAL CHEMISTRY	EFFICACY

FILE OR REG. NO. 241-ELN

PETITION OR EXP. PERMIT NO. 6F1703

DATE DIV. RECEIVED

DATE OF SUBMISSION

DATE SUBMISSION ACCEPTED 3 C1D status = yes 2b

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

PRODUCT MGR. NO. Mountfort (23)

PRODUCT NAME(S) Avenge Wild Oat Herbicide

COMPANY NAME American Cyanamid

SUBMISSION PURPOSE Registration

CHEMICAL & FORMULATION Difenzoquat methyl sulfate
1,2-dimethyl-3,5-diphenyl-1H
pyrazolium methyl sulfate

1. Introduction

Applicant proposes registration of difenzoquat methyl sulfate for use on barley and wheat.

Previous environmental chemistry evaluations of this chemical are dated 2-15-74, 12-6-74, 1-21-75, and 10-16-75.

2. Directions for Use

Use 2.5 - 4 pints Avenge (0.625 - 1.0 lb.) per acre depending on wild oat density.

Tank mixes

a) Avenge at recommended rate plus MCPA amine or ester at recommended rate 0.25 - 1.0 acid equivalent per acre

b) Avenge at recommended rate plus bromoxynil at 0.375 - 0.5 lb. active ingredient per acre per label directions.

c) Avenge at recommended rate plus bromoxynil at 0.25 - 0.5 lbs. active ingredient plus MCPA at 0.25 - 0.5 lb acid equivalent per acre per label directions.

Application may be ground or aerial.

Do not make more than one application of Avenge per growing season. Rotation of other crops can be made the following year.

Use Avenge on

a) barley and Fall-seeded wheat varieties throughout U.S.

b) Spring-seeded wheat all varieties in Arizona, New Mexico, California, Utah, Nevada, Idaho, Oregon and Washington

c) Spring-seeded wheat (North Central States): only spring wheat varieties ERA and Red River 68 and durum wheats Bono, Hercules, Leeds, Rolette, Ward, Wells in Montana, North and South Dakota and Minnesota.

3. Discussion of Data - Section H-PP6F1703

Exhibit 1:

Avenge: Solubility and Stability of Aqueous Solutions. American Cyanamid Company Memo. W. C. Groth Oct. 3, 1975.

Difenzoquat is very water soluble, being 76.5% at room temperature. In nonpolar solvents, solubility is less than 0.1%, while in polar solvents difenzoquat is soluble.

Exhibit 2 Section H PP6F1703

Chemodynamic Properties of Avenge difenzoquat: Determination of Partition Coefficient Report C-802 October 9, 1975

P-values of difenzoquat in octanol-water partitions were 0.11 and 0.03 at concentrations of 8 and 8000 ppm. In another solvent system p-values ranged from 0.22 through 24.1 to 137 in chloroform/water, /saturated aqueous sodium chloride, 1 aqueous 0.1 M sodium perchlorate, respectively.

Exhibit 11 Section H PP6F1703

Avenge difenzoquat: Fate on Soil under Field Conditions (Fort Collins, Colorado), PD-M 12, p 1149-72, October 8, 1975.

Colorado sandy loam (sand, silt, clay 56.4, 28.8, 14.8 pH 7.2, CEC 27.6, organic matter 2.5, moisture content 4.61%, 1/3 bar 13.7%) was treated with equivalent of 1.1b. active ingredient as N-methyl ^{14}C of cation and as 3-^{14}C of pyrazolium ring. Disappearance of both labels followed under field conditions. Recovery or percent remaining based upon 0 day sample rather than calculated amount applied. Analyses by counting of TLC plates.

Results

Only top one inch of soil analyzed, since another study Report C-540 showed 90-98% of the ^{14}C in top one inch over extended sample intervals.

Recovery of ^{14}C as % of
Zero-time Sample
Analysis by Combustion

Weeks	Methyl label	Ring Label
0	-	94.8
1	93.0	93.0
2	75.9	92.7
4	72.0	62.5
8	60.2	54.8
16	55.4	

Of the gross radioactivity 95-98% was extractable in organic solvents at all sample intervals, and by TLC analyses 96%-98% of all extractable ^{14}C was identifiable as parent compound. Therefore binding does not occur in the top one inch layer of soil. Since soil samples below 1 inch were not analyzed, 45% of zero-sample ^{14}C was not accounted. This 45% could be loss due to leaching below one inch, or degradation followed by volatilization of degradate as postulated by applicant.

This study is compromised by the lack of adequate analysis of the 1 - 4 inch soil layer. It is apparent that more ^{14}C was present than was accounted by the procedures employed.

Exhibit 13 Section H PP6F1703

Avenge: The Identification of Volatile Metabolite or Degradation Products Isolated from Soil, Water and Thin Films. PD-M12 pages 1023-1044, October 3, 1975.

Pond water containing parent compound exposed to high intensity artificial light for 19-1/2 days. At this time 70% was parent and 30% degradates. Methylene chloride extracts of pond water were placed in glass trays as thin film, covered and uncovered, in greenhouse with artificial light. Extracts also subjected to sublimation in microsublimation apparatus. Another study used ^{14}C-parent as thin film in petri dishes. Another study used ^{3}H and ^{14}C parent sprayed on loam soil exposed to artificial light in covered trays and one tray used polyurethane sponge as trap for volatile material.

Results - Petri dishes with thin films of ^{14}C parent and CL 84,760 (demethylated parent).

Lids of petri dishes over thin films showed only CL 84760 as volatile with 1/3 of applied CL 84760 on lid after 24 hours. In dish with parent compound, only degradate CL 84760 found on lid over one-week sampling interval.

Results - Soil trays

Again only CL 84760 (degradate) found on lid of tray. When volatile material trapped in polyurethane foam sponge, demethyl parent was shown as major ^{14}C material, with small traces of parent.

Results - Pond Water extractable as a thin film

Uncovered tray showed 30% loss over 7 days while covered tray showed only 1% loss. Covered tray lid showed CL 84760 only by TLC but 3 compounds by GLC, one of which was CL 84760.

Results - Microsublimation

Only ^{14}C-material sublimed was CL 84760 as shown by TLC. GLC showed numerous peaks but major peak was CL 84760.

Conclusions

Demethylated parent compound (known as CL 84760) is volatile from a variety of media or surfaces, while parent compound shows almost no indication of volatility.

Exhibit 14 Section H PP6F1703

The relative volatility of CL 84760 and difenzoquat as determined in a differential scanning calorimeter. Report F-345 September 18, 1975.

The demethylated degradation product of difenzoquat was volatilized more readily than parent compound at 140°C for one hour. Degradate showed about 5 - 7% volatility loss (depending on apparatus design) compared to essentially 0.00% loss of parent compound under similar conditions.

Exhibit 15 Section H PP6F1703

Uptake of 3-^{14}C-difenzoquat wild oat herbicide derived residues from soil by barley and red beets grown as follow crops. Report C-707 October 8, 1975.

Colorado sandy loam treated at rate equivalent to 1 pound active ingredient per acre using 3-^{14}C-difenzoquat in field plot. Plot was treated in May and soil sampled through September. Following spring top 4 inches of soil hand tilled and planted to barley and red beets which were grown to maturity.

Results

Soil samples in spring time about 1 year after treatment showed 35% of initial ^{14}C still present with 95% of remaining ^{14}C as extractable and 66% of extractable as parent compound.

^{14}C in Follow Crops

Plant Part	Interval	^{14}C-ppm	Extractable %	Parent
Barley whole	4	0.035	91	65%
Barley straw	12	0.048	94	39%
Barley seed	12	0.002	-	-
Barley trash	12	0.004	-	-
Red Beets foliage	4	0.043	90	-
Red Beets roots	12	0.005	100	-
Red Beets foliage	12	0.004	86	-

Conclusion

^{14}C studies with difenzoquat demonstrate that little or no difenzoqual is taken up by barley or red beets as follow crops after field weathering of soil residues for about one year.

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Exhibit 16 Section H PP# 6F1703

The Photolysis of ^{14}C-labeled difenzoquat in water exposed to natural or artificial light. PD-M 12, pages 972-997, October 3, 1975.

^{14}C methyl or ring label difenzoquat exposed to sunlight or artificial light for intervals up to 65 days, in pond water or distilled water. Analysis by GLC, TLC and radiometric procedures.

Results:

Regardless of ^{14}C-label, decomposition of difenzoquat occurred at same rate in pond and distilled water exposed to artificial light, but at faster rate than when exposed to natural sunlight. Under artificial light 30% of initial difenzoquat remains after 58 days exposure while in natural sunlight, 70-80% was still intact. With one exception, TLC analysis showed the same degradation pattern from both ^{14}C labels. The one exception, a unique TLC spot with ^{14}C-methyl label, appeared and dissipated over first 30 day interval. Other than the fact that this unique spot did not absorb short wavelength UV radiation, this spot is not identified. All other photodegradates did absorb short UV radiation.

In contrast to previous photolysis studies, no azomethane was detected in any sample with lower limit of detection at 0.5 ppm, while when the previously used material was retested.

The seven degradation products found in all samples to some extent were characterized by chemical reaction. Five of the seven were phenolic in nature.

Exhibit 17 Section H PP# 6F1703

"Fate of Carbon-14 label" difenzoquat incorporated into soils" PD-M, Vol. 12, pages 1045-1148, October 7, 1975.

Ring or N-methyl ^{14}C-difenzoquat were incorporated in field soils or in greenhouse experiments.

In the field tests, steel cylinders 12 inches long were driven 10.5 inches into soil. The top one inch of soil in cylinder removed and treated with ring-label difenzoquat at rate equivalent to 1.03 lbs. active ingredient per acre. Treated soil returned to cylinder and subjected to natural weathering conditions for 24 months. The soil in field plot was Princeton sandy loam.

In the greenhouse studies, small planters (7" i.d. x 8" or 4" x 4") were filled with appropriate soil and treated with low rate 0.6 lbs. a.i./A or high rate 5.162 lbs.

Soil Characteristics

Soil Type	Location	pH	1/3 Bar	Organic Matter	Sand	Silt	Clay	Cation Exchange Capacity
Sandy Loam	New Jersey[b]	5.1	16.9	3.6	68	24	8	6.1/100g
Silty Clay	North Dakota	6.5	45.6	6.0	8	40	52	41.6/100g
Loamy Sand	Delaware	4.8	7.6	2.2	86	12	2	4.3/100g
Silt Loam	Wisconsin	6.7	30.6	5.2	24	56	20	6.1/100g
	Montana							

Soil characteristics of Montana soil are unknown.

a.i./A. Treatment incorporated into top one inch of soil which was returned to planter:

Low rate: Princeton, Delaware and North Dakota soils
High rate: Princeton and North Dakota soils
Low rate: Montana
Metabolism Study: Wisconsin soil.

In the metabolism study aerobic and anaerobic biometer flasks were used to collect volatile materials.

Results - Field Study.

Over the 24 month interval under natural weathering conditions the recovery of total ^{14}C ranged from 105% at 1 month to 72.1% at 24 months, with most of the ^{14}C in the top 2-3 inches of soil. The 3-6 inch soil layer showed 5.2% ^{14}C at 1 month, increasing to 16.5% at 24 months, while 6-12 inch soil layer had 3.3%, 2.8%, 1.7%, 1.9% and 6.1% at 1, 3, 6, 12, and 24 months. Thus, the top 3 inches of soil had 50% of applied ^{14}C still present in field soil at 2 years.

In greenhouse studies ^{14}C equivalent to difenzoquat typically showed slower rates of dissipation with about 80% of applied ^{14}C equivalent to difenzoquat typically showed slower rates of dissipation with about 80% of applied ^{14}C still present at 24 months. In the anaerobic and aerobic soil metabolism studies, no $^{14}CO_2$ or other volatile material was found.

In the field study, non-extractable ^{14}C did not exceed 12% at any sample interval, indicating that binding is ~~not~~ significant.

Overall: in all soil samples the major ^{14}C moiety found was parent compound. Minor amounts of demethylated parent were found, probably as photoproduct.

Conclusions:

Difenzoquat is persistent in various soils, in greenhouse or field trials, when treatment is soil incorporated. Half-life, when incorporated, exceeds 2 years, but normal treatment as surface spray is not as persistent.

Exhibit 21 Section H PP# 6F1703

"Stability of Azomethane in air and water using GLC methods" PD-M Volume 12, pages 950-971, October 3, 1975.

Previously submitted photolyses studies on difenzoquat indicated that azomethane was a photodegradate. GLC methods sensitive to 0.01 ppm in water and 0.05 ppm in air were used to define the stability of azomethane in water and air.

Results:

In air the half-life of azomethane was 1 1/2 hours while in water the halflife was 2 hours. In air 95% of azomethane degraded in 5 hours, and in water 80% degraded.

Exhibit 22 Section H PP# 6F1703

"Uptake and Residues of Radioactivity in Table Beet and Alfalfa Plants Grown on Soil with aged residues of ^{14}C-labeled difenzoquat." PD-M Volume 12, pages 1173-1196, October 9, 1975.

Ring labeled 3-^{14}C-difenzoquat and deuterated (one deuterium in meta position of each phenyl group) difenzoquat were used to treat Wisconsin silt loam soil at rate equivalent to 1 lb. active cation per acre. Treated soil was aged in greenhouse for four months, contained in 12" x 12" x 12" poly propylene tanks. Treated soil was top one inch of soil, other 11 inches in tank were untreated. After 4 months of aging, beets and alfalfa were seeded.

Results:

Months	Plant Part	ppm	% Extractable ^{14}C
1	Beet Foliage	0.146	94
2.5	Beet Foliage	0.162	98
2.5	Beet Roots	0.063	97
4	Beet Foliage	0.220	97
4	Beet Roots	0.244	98
6	Beet Foliage	0.238	95
6	Beet Roots	0.166	91
1	Alfalfa Foliage	0.087	91
2.5	" "	0.103	95
4	" "	0.124	88

The percent extractable ^{14}C indicates that the ^{14}C is not bound to plant constituents. The 4-month beet roots and foliage were examined for parent compound by separation-isolation techniques. Only 8-10% of extractable ^{14}C was identifiable as parent. The other material, although similar to materials found in other studies such as photolysis and soil, was not identified.

Exhibit 31 Section H PP# 6F1703

"Determination of difenzoquat residues in soil: Oklahoma, 1975." Report C-835, October 16, 1975.

There is a discrepancy concerning the date of treatment. One part of the report dates the treatment on 11-20-74 and another part dates treatment on 3-21-75.

Oklahoma clay loam soil treated on unknown date with 1.0 or 2.0 lbs. active ingredient. Soil samples taken at unknown interval after treatment.

Residues in both 0-3 and 3-6 inch soil sections were less than 0.10 ppm at both rates. Analytical method is for the parent compound *per se*.

Exhibit 32 Section H PP# 6F1703

"Determination of difenzoquat residues in soil: Texas, 1975". Report C-836, October 16, 1975.

Texas sandy loam treated at rates of 1.0 and 2.0 lbs. active ingredient per acre as surface spray. Soil samples taken 88 days later.

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Residues of parent compound in both 0-3 and 3-6 inch soil sections at both treatment rates were less than 0.1 ppm, the lower level of detectability of the method.

Exhibit 33 Section H PP# 6F1703

"The Gas Chromatographic Determination of MCPA and Bromoxynil in Fortified Soil"
Report C-796, October 6, 1975.

Two published methods for analysis of MCPA and Bromoxynil were validated by recovery data from fortified soil. For MCPA recoveries ranged from 69% to 91 at levels between 0.05 and 2.00 ppm, while for bromozynil values were 75% to 115% at levels between 0.05 to 1.0 ppm. Average MCPA recovery was 80.7% (standard deviation 8.8%) while for bromoxynil average was 89% (standard deviation 15%).

Exhibit 34 Section H PP# 6F1703

"Determination of difenzoquat, bromoxynil and MCPA residues in soil following ground applications of difenzoquat alone or in combinations with MCPA or bromoxynil."
Report C-843, October 15, 1975.

North Dakota sandy clay treated with difenzoquat and tank mixes of difenzoquat plus MCPA (1.0) bromoxynil (0.5).

Residues of bromoxynil applied 0.5 lbs. alone or in tank mix with difenzoquat were less than the level of detectability 0.05 ppm. at 0 day and 7 days posttreatment. No samples at longer intervals.

Residues of MCPA applied 1.0 lb. alone or in tank mix with difenzoquat were between 0.2 and 0.56 ppm at 0 day interval. By days 28 and 56 posttreatment residues of MCPA were less than the level of detectability 0.10 ppm.

Residues of difenzoquat applied at 1.0 lbs. alone or in tank mix with MCPA or bromoxynil showed slight increase from 0 day sample (0.17 ppm average) to 56 day sample (average 0.34 ppm). These residues are about the level of residues expected at these time intervals. There is no apparently significant trend toward either increased or decreased persistence of difenzoquat due to presence or absence of MCPA or bromoxynil.

No data submitted on tank mix of difenzoquat and 2,4-D, nor on triple tank mix of difenzoquat plus MCPA plus bromoxynil.

Exhibit 35 Section H PP# 6F1703

"Determination of difenzoquat bromoxynil, and MCPA residues in soil following ground application of difenzoquat alone and in combination with MCPA or bromoxynil."
Report No. C-844, October 15, 1975.

Oregon silt loam treated with difenzoqual alone or in tank mixes of difenzoquat plus MCPA or difenzoquat plus bromoxynil, or in triple tank mix of difenzoquat plus MCPA plus bromoxynil. Rates of application were:

difenzoquat	1.0 lb.
MCPA	0.75 lb.
bromoxynil	0.4 lb.
MCPA & bromoxynil	0.4 and 0.4.

Treatment was surface application. No data submitted on tank mix of difenzoquat plus 2,4-D although experimental design indicates this mixture was applied.

Results:

Residues of difenzoquat, MCPA and bromoxynil when applied alone or in various tank mixes were below the limit of detectability 0.10 ppm, 0.05, and 0.10 respectively, at all sample intervals from 0 days through 84 days . While application rates of MCPA and biomoxynil were low, these results are unexpected. For difenzoquat, the total lack of any apparent residue stretches credulity.

In a similar study, Exhibit 34 above, finite residues of difenzoquat were found at every sample interval between 0 and 56 days.

No explanation for these unexpected results is offered by applicant.

No data submitted on triple tank mix difenzoquat plus MCPA plus bromoxynil.

Exhibit 36 Section H PP# 6F1703

"Determination of difenzoquat, bromoxynil and MCPA residues in soil following ground application of difenzoquat alone and in combination with MCPA or bromoxynil.

Report No. C-845, October 13, 1975.

South Dakota silty clay loam treated with difenzoquat alone or in tank mixes of difenzoquat plus MCPA or difenzoquat plus bromoxynil or difenzoquat plus 2,4-D or triple tank mix of difenzoquat plus bromoxynil plus MCPA.

Rates of application were:

difenzoquat	1.0 lb.
MCPA	1.0 lb.
bromoxynil	0.38 lb.
2,4-D	0.50 lb.
MCPA + bromoxynil	0.25 + 0.25

Treatment was surface application. No data on tank mix of difenzoquat plus 2,4-D. No data on triple tank mixture of difenzoquat plus MCPA plus bromoxynil.

Residues of bromoxynil applied at 0.375 lbs. alone or in combination with difenzoquat were below the limit of detection 0.05 ppm at intervals between 0 and 14 days. No samples after 14 days.

It is noteworthy that bromoxynil residues are not detected above the limit of detection of 0.05 ppm in any of the three tank mix persistence studies.

Residues of MCPA alone or in combination with difenzoquat were about 0.5 ppm at 0 days. At seven days MCPA alone showed 0.10 ppm but when applied with difenzoquat showed 0.60 ppm. All other sample intervals to 84 days showed no measurable residues.

Residues of difenzoquat applied alone or in combination with MCPA or bromoxynil were quite variable. Over 84 day intervals, the average was 0.55 ppm with standard deviation of 0.36 ppm. No apparent effect on persistence from tank mixes with promoxynil or MCPA. The residues of difenzoquat showed little decline over the 84 day sample interval.

Difenzoquat Residues

Interval (days)	ppm	Average
0	0.31*, 0.88, 0.47*, 1.18**	0.71
7	0.16*, 0.43, 0.30*, 0.36**	0.31
14	0.57, 1.07*, 0.88**	0.84
28	0.15, 0.10*, 0.49**	0.25
56	1.38, <0.10*, 0.46**	0.65
84	0.54, 0.56*, 0.48**	0.53

* Tank mix with bromoxynil at 0.375 lb.
** Tank mix with MCPA at 1.0 lb.

Exhibit 38 Section H PP# 6F1703

"Determination of difenzoquat residues in barley (foliage), table beets (foliage) and soil. California, 1975."
Report No. C-798, September 12, 1975.

See attached Summary Table.

Exhibit 39 Section H PP# 6F1703

"Determination of difenzoquat residues in wheat (foliage) and soil. Minnesota, 1975."
Report No. C-852, October 7, 1975.

See attached Summary Table.

Exhibit 40 Section H PP# 6F1703

"Determination of difenzoquat residues in sugar beets (foliage) and soil. Minnesota, 1975."
Report No. C-848, October 16, 1975.

See attached Summary Table.

Exhibit 41 Section H PP# 6F1702

"Determination of difenzoquat residues in barley (foliage) and soil. Minnesota, 1975".
Report No. C-849, October 16, 1975.

See attached Summary Table.

Exhibit 42 Section H PP# 6F1703

"Determination of difenzoquat residues in sugar beets (foliage) and soil. Minnesota, 1975."
Report No. C-850, October 16, 1975.

See attached Summary Table.

Exhibit 43 Section H PP# 6F1703

"Determination of difenzoquat residue in wheat (foliage) and soil. Minnesota, 1975".
Report No. C-851, October 16, 1975.

See attached Summary Table.

Exhibit 44 Section H PP# 6F1703

Determination of difenzoquat residues in barley (foliage), pinto beans (foliage), and soil. Montana, 1975."
Report No. C-799, September 17, 1975.

See attached Summary Table.

Summary Table of Residues in Soil and Follow Crop

	Soil Residues						Crop Residues			
Exhibit Location	Rate	PTI	0 - 3	3 - 6	6 - 9	Soil Type	Crop	Part	PTI	ppm
38 California	1.0 0.75	83 172	0.17 *	* *	* *	Sandy loam	Barley Red beets		172 172	* *
39 Minnesota	1.0 ↓	320 386	0.29 *	0.34 *	* *	Clay loam	Wheat		401	*
40 Minnesota	1.0 ↓	324 389	0.24 *	* *	* *	Clay loam	Sugarbeets		402	*
41	1.0	350	*	0.19	*	Clay	Barley		398	*
Minnesota	↓	382	*	*	*	loam				
42 Minnesota	1.0 ↓	324 374	0.20 *	* *	* *	Clay loam	Sugarbeets		402	*
43 Minnesota	1.0 ↓	353 383	* *	0.15 *	* *	Clay loam	Wheat		398	*
44 Montana	1.0 ↓	306 417	0.42 *	* *	0.11 *	Silty clay	Barley Pinto beans		417 417	* *

* = less than 0.1 ppm

Root crops = tops and roots

Other crops = foliage

Exhibit 13 Section D1C PP# 6F1703

"Standard Operating Procedures - Residue Samples (General)."

This exhibit details general procedures for obtaining soil and crop residue samples. Procedures are adequate.

Exhibit 14 Section D1C PP# 6F1703

"Gas Chromatographic Determination of difenzoquat in Soil."
Report No. C-531, September 6, 1974.

This is validation of analytical procedure M-471 which is used for plants. Recovery data indicate that this procedure is a valid analytical method for parent compound only in soil samples. No recovery data on degradation or metabolic products were found.

4. Conclusions.

Environmental chemistry data requirements appear to be fulfilled at this time for the proposed use pattern.

5. Recommendations.

No adverse environmental chemistry comments at this time on the proposed use pattern.

REN 1/27/76

Ronald E. Ney, Jr. January 19, 1976
R. W. Cook RWCook 1-27-76 January 14, 1976

Environmental Chemistry Section
Efficacy and Ecological Effects Branch