PC 108201

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Memorandum:

SUBJECT: PP#5E4499. Diflubenzuron. Geographical Expansion For Use of Dimilin 25W and Dimilin 2F Formulations in/on Rangeland Grass. Grasshopper Control. MRID#'s 436579-01 and 436579-02. CBTS#15731. DP Barcode#D216357.

FROM: Jerry B. Stokes, Chemist
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THRU: Elizabeth T. Haeberer, Section Head
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Elizabeth T. Haeberer 2/28/96

TO: Hoyt Jamerson, PM #43
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William L. Biehn, Project Coordinator, Interregional Research Project No.4, State Agricultural Experiment Station, Rutgers University, New Brunswick, NJ on behalf of the IR-4 Project and the Agricultural Experiment Station of New Mexico requests in this petition, PP#5E4499, that 1) the current tolerance for diflubenzuron in/on rangeland grass be increased from 3.0 ppm to 5.0 ppm, (40 CFR §180.377), 2) both Dimilin 25W and Dimilin 2F formulations be authorized for the proposed use, and 3) the geographical treatment areas be expanded for proposed use. A letter dated 02/28/95 from SOLVAY DUPHAR B.V. has been submitted in this petition, whereby EPA is authorized to use the company's data for the technical diflubenzuron to support the IR-4 proposal.

The petitioner has submitted field trial residue data for treated rangeland grass (MRID#'s 436579-01 and 436579-02). These trials were conducted using the Dimilin 25W and Dimilin 2F formulations.

Conclusions:

1a. According to the petitioner's submission, problems were encountered when the spray mixture was prepared for some of the aerial treatments. As a result the 2F formulation was applied with diesel oil only; the 25W formulation was applied with "blend" and diesel oil. Apparently water was not used in the mix because of gelling in the spray tank. The proposed labels do not match these mixing/spraying directions. The petitioner must clearly define workable mixing/spraying directions. A revised Section B is needed.

1b. CBTS does not consider the label restriction on grazing rangeland grass practical, therefore CBTS considers the higher rate (i.e., 0.50 lb a.i./A/year) the maximum application per acre per year, and the residue data should reflect this rate. (See comments Magnitude of the Residue, this memo). A revised Section B is needed.

2. CBTS does not consider rangeland grass a minor crop. The proposed labels should include a restriction stating that applications can only be made or authorized by Federal, state, and local government agents in the grasshopper control program. A revised Section B should be submitted.

3. A clarification is needed of total geographical area to be treated and intended use patterns. The following issues require resolution:

   a. A clear definition of the geographical area in which the grasshopper control is needed, i.e., are the areas of the states of New Mexico, Colorado, Texas, and Oklahoma registered for use against the range caterpillar to also be considered for the use on the grasshopper?

   b. The petitioner must clarify his intention concerning areas already authorized for treatment against the range caterpillar. Will this area still be on the label? Does the petitioner propose that the 2F formulation be used against the range caterpillar? A revised Section B may be needed.

4a. The metabolism of diflubenzuron in rangeland grass is adequately understood for the proposed use. The residue of regulatory concern is parent diflubenzuron.

4b. The metabolism of diflubenzuron in ruminants is adequately understood for the proposed use. The residues of regulatory

concern are parent diflubenzuron and its metabolites p-chloroaniline (PCA) and 4-chlorophenylurea (CPU). (See conclusion 7a below).

5. The available analytical methodologies are adequate for the determination of diflubenzuron residues in/on rangeland grass and livestock commodities of meat, meat byproducts, and milk.

6. The field trial residue data are adequate to support the proposed use against the grasshopper. However, the proposed 5.0 ppm tolerance should be increased to 6.0 ppm to adequately reflect diflubenzuron residues on fresh and dried rangeland grass. A revised Section F should be submitted.

7a. According to the HED Metabolism Committee the tolerance expression for diflubenzuron needs to be rewritten to include the ruminant metabolites PCA and CPU. Any secondary diflubenzuron residues (combined parent and PCA and CPU) that might occur from these proposed labels will be adequately covered by the established tolerances (0.05 ppm) for livestock meat, fat, and milk (0.05 ppm). However, the 0.05 ppm tolerance for meat byproducts would not cover the combined residues of parent diflubenzuron and its chlorophenyl metabolites PCA and CPU. A tolerance of 0.1 ppm would have to be established. A revised Section F is needed to increase the meat byproduct tolerance and to include the PCA and CPU metabolites in the tolerance expression for all animal commodities.

7b. Since rangeland grass, fresh or dried, is not a poultry feedstuff, the existing 0.05 ppm tolerance is adequate for eggs.

Recommendations:

CBTS **cannot recommend for** the requested tolerance increase and expanded use for diflubenzuron in/on rangeland grass because of conclusions 1, 2, 3a, 3b, 6, and 7a. Revised Sections B and F are needed along with clarification of the areas to be treated.

NOTE TO PM: According to the HED Metabolism Committee the residues of regulatory concern are parent diflubenzuron and its metabolites p-chloroaniline (PCA) and 4-chlorophenylurea (CPU) (See memo of 03/22/96, S. Knizner). The tolerance expression for diflubenzuron needs to be rewritten to include the ruminant metabolites PCA and CPU.

Detailed Considerations:

Proposed Use

The proposed use is to control grasshoppers in rangeland grass areas.

DIMILIN®25W Formulation (25% a.i.)

Apply 0.5 to 1.0 fl.oz./A (ca. 0.125 to 0.25 lb a.i./A) DIMILIN®25W with 5 - 30 gallons of water/A for ground application and 1 - 5 gallons/A for aerial application. Label restrictions: Do not exceed 1.0 fl. oz./A/year if grass is to be used for feed or grazing. Do not make more than 2 applications per year. If a second application is made, it should be applied 2 - 3 weeks after the first application. Do not plant food or feed crops in DIMILIN treated soils within 6 months following last application, unless DIMILIN is authorized for use on these crops.

Registered treatment areas: A regional use is authorized in the states of New Mexico, Colorado, Texas, and Oklahoma for control of the **range caterpillar**, a pest localized mainly in New Mexico and in adjacent counties in the surrounding states.

Proposed treatment areas : Use only in Colorado, Montana (South of Missouri River), Nebraska (West of State Highway 183), North Dakota (West of Missouri River), South Dakota (West of Missouri River), and Wyoming.

DIMILIN®2F Formulation (24% a.i.)

Apply 0.5 to 1.0 fl.oz./A (ca. 0.125 to 0.25 lb a.i./A) DIMILIN®2F with 5 - 30 gallons of water/A for ground application and 1 - 5 gallons/A for aerial application. For ULV in an oil carrier, use a total volume of 16 to 32 fl. oz./A. Label restrictions: Do not exceed 1.0 fl. oz./A/year if grass is to be used for feed or grazing. Do not make more than 2 applications per year. If a second application is made, it should be applied 2 - 3 weeks after the first application. Do not plant food or feed crops in DIMILIN treated soils within 6 months following last application, unless DIMILIN is authorized for use on these crops.

This formulation is **not** registered for control of the **range caterpillar.**

Proposed treatment areas : Use only in Colorado, Montana (South of Missouri River), Nebraska (West of State Highway 183), North Dakota (West of Missouri River), South Dakota (West of Missouri River), and Wyoming.

Included on the summary page of Section D of this submission (MRID#436579-02) are the following comments from the petitioner:

"In 1988, EPA established a tolerance of 3.0 ppm for residues of diflubenzuron in/on range grass (for regional registration in CO, NM, OK, and TX)."....."EPA indicated they would consider expansion of the range grass use if additional residue data were submitted." ....."The study discussed herein and the supporting data was collected to obtain additional residue data on range grass for use in acquiring full registration of the products."

CBTS has reviewed the previous decision concerning control of the range caterpillar [including RD comments to IR-4, letter dated 04/22/88, H. Jamerson (RD) to G. Markle (IR-4)], and this proposed use to combat grasshoppers in rangeland grass. CBTS, in review of PP#5E3174, **only** assessed the use of diflubenzuron in/on rangeland grass to control the **range caterpillar**, an insect localized in northwestern New Mexico and surrounding counties in the adjacent states of CO, Ok, and TX. CBTS did not review or comment on the use of diflubenzuron against grasshopper infestations in the NM area, nor in other areas within the US. The petitioner has commented in this summary about full registration on rangeland grass. This petition request now comes from IR-4, in behalf of the state of New Mexico and USDA. The proposed label restricts the use to an area which does not include the state of New Mexico. A clarification is needed of the intended treatment areas. CBTS does not consider the rangeland grass a minor crop. Documentation is needed verifying that the grasshopper is limited to the geographical area described on the proposed label. The petitioner has not clearly expressed his intentions as to the areas already authorized for treatment against the range caterpillar. Does the petitioner propose the use of the 2F formulation against the range caterpillar?

According to the petitioner's submission, problems were encountered when spray mixture prepared for aerial treatments. As a result the 2F formulation in some of the field trials was applied with diesel oil only; the 25W formulation was applied with "blend" and diesel oil. Apparently water was not used in the mix because of gelling in the spray tank. The proposed labels do not match these mixing/spraying directions. The petitioner must clearly define workable mixing/spraying directions. A revised Section B may be needed.

The label restrictions now read: Do not exceed 1.0 fl. oz./A/year if grass is to be used for feed or grazing. Do not make more than 2 applications per year. The first statement implies that more than 1.0 fl. oz/A/year is allowed if the grass is not used as a feedstuff. Based on this statement, and the limit of 2 applications/year, 2.0 fl. oz./A/year (0.50 lb a.i./A/year) would be allowed on "ungrazed or hay/silage-cut" rangeland grass. **CBTS does not consider this restriction on grazing rangeland grass practical, therefore CBTS considers the higher rate the maximum application per acre per year, and the residue data should reflect**

this rate (See comments Magnitude of the Residue, this memo). A revised Section B is needed.

Previously CBTS requested that the label restrict the applicators: "Application must be made only by Federal, state, and local agents and not by private or commercial applicators." The United States has approximately 700 million acres of land area of which ca. 40% is classified as rangeland. The trend in the use of locally controlled land as rangeland has increased over the last twenty years. Consequently, range grass is not a minor crop, and is in fact a large source of forage for beef and dairy livestock. Therefore, we do not consider range grass to be a minor feedstuff. The proposed labels should state that applications can only be made or authorized by Federal, state, and local government agents in the grasshopper control program. A revised Section B must be submitted.

Nature of the Residue:

Plants: The metabolism of diflubenzuron in rangeland grass is adequately understood for the proposed use. The residue of regulatory concern is parent diflubenzuron.

Livestock: The metabolism of diflubenzuron in ruminants is adequately understood for the proposed use. According to the HED Metabolism Committee the residues of regulatory concern are parent diflubenzuron and its metabolites p-chloroaniline (PCA) and 4-chlorophenylurea (CPU) (See memo of 03/22/96, S. Knizner). The tolerance expression for diflubenzuron should be rewritten to include the ruminant metabolites PCA and CPU. A revised Section F is needed including these metabolites in the animal commodity tolerances.

Analytical Methodology:

The analytical methodology used for analysis of the rangeland grass samples, both fresh and dried is residue method RES 020 (July 1988), entitled "Liquid Chromatographic Determination of Diflubenzuron in Tea". This methodology involves extraction of a grass sample with boiling acetonitrile-water mixture (85:15), allowed to cool, filtration, concentration to small volume, extraction with hexane, evaporation to dryness, and the residuum solvent-dissolved with acetonitrile. The acetonitrile solution is applied to a Florisil® column as a clean-up procedure. Analysis for diflubenzuron is performed by reverse phase HLPC using UV detection at 254 nm. The limit of quantitation is 0.05 ppm. This method has not been validated by the EPA analytical laboratory in Beltsville. However a similar method for the determination of diflubenzuron in animal tissues, eggs, milk, and fish has been published in PAM, Vol II as Method III. Therefore, the methodology used to generate the residue data is adequate.

The recoveries of diflubenzuron in fresh and dried grass samples were spiked with 1.0 and 4.0 ppm of diflubenzuron. Percentage recoveries ranged from 90 to 105% (ave: 95%).

Recovery data:

Location	Sample ID; formulation; fresh vs.dried	Fortified level, in ppm	Percentage Recovery
PA	-031;2F;fr	1.0,4.0	94,86
"	-036;25W;"	"	92,88
FL	-423:2F;"	"	89,85
SD	-042;2F:dr"	"	86,77
"	-052;25W;fr	"	90,83
OK	-300;2F;fr	"	102,90
MT	-057;2F:fr	"	86,79
CA	-094;25W;fr	"	95,86
"	-067;25W;fr	"	114,90
NE	-004;25W;fr	"	93,80
"	-014;25W;dr	"	97,85
ND	-029;2F;fr	"	92,79
"	-034;25W;fr	"	80,80
WY	-044;25W;fr	"	85,80
"	-054;25W;dr	"	92,83
Average			91

Analytical Method No. 20 (MRID#00099683) is listed in PAM II as Method I. The enforcement method involves conversion of all diflubenzuron residues to 4-chloroaniline, followed by derivatization with heptafluorobutyric anhydride and analysis by GC/EC detection. This method is an adequate enforcement method in/on rangeland grass.

Adequate methodology is available for livestock commodities of meat, meat byproducts, milk, eggs. These are listed as Methods II (GC/ECD) and III (HPLC/UV) in PAM II.

Storage stability:

All samples were stored frozen (-15±5 C) prior to analysis. Adequate storage stability data are available for the proposed use.

Magnitude of the Residue:

Field residue data (MRID#'s 436579-01 and 436579-02) in support of the proposed use against the rangeland grasshopper were submitted from sites in CA, FL, MT, ND, NE, OK, PA, SD, and WY using both the DIMILIN®25W and DIMILIN®2F formulations. A single application was made at rates of either 0.25 lb a.i. (1X proposed label rate) or 0.5 lb a.i. (2X proposed label rate). Fresh samples were collect and stored in the freezer until analyzed. Dried samples were field sun-dried for 1 - 3 days. Samples in the SD and MT trials, because of weather conditions, were removed fresh from the field, stored on dry ice, and then returned to the fields when the weather permitted and sun-dried for 3 days. The dried samples were also stored in the freezer until analyzed.

As discussed in the Proposed Use section of this memorandum, the proposed label would allow a maximum of 0.5 lb a.i./A/year on rangeland grass that is not to be grazed, or harvested for livestock feeding. CBTS does not consider this restriction practical, based on the vast acreage proposed to control the grasshopper. CBTS considers 0.5 lb a. i. the maximum application rate per acre per year. The field residue data using an application rate of 0.5 lb a.i./A show diflubenzuron residues slightly higher than the proposed 5.0 ppm tolerance in several field trials. Therefore, if the petitioner intends to allow a maximum of 0.5 lb a.i./A/year, then the tolerance must be established at 6.0 ppm, not at the proposed 5.0 ppm.

The field trial data submitted in support of the registered use against the range caterpillar used an applied rate approximately ½ the proposed rate against the grasshopper in this petition. These data have been considered in support of the current submission. The petitioner's field trial residue data are adequate to support the proposed use against the grasshopper. However, the proposed 5.0 ppm tolerance must be increased to 6.0 ppm to adequately reflect maximum diflubenzuron residues which may occur on fresh and dried rangeland grass from this proposed use. A revised Section F must be submitted.

Location	Plot size; ground/ aerial	Ground:air/ spray adjuvant	Application rate (lb a.i./A)	Diflubenzuron, in ppm,			
				Fresh grass		Dried grass	
				25W	2F	25W	2F
Germanville, PA	10 x 100 ft	ground/ water	0.25	2.3	2.0	--	--
			0.25	1.6	2.1	--	--
			0.50	2.7	3.5	--	--
			0.50	2.9	3.2	--	--
LaBelle, FL	12 x 100 ft	ground/ water	0.25	3.0	1.6	--	--
			0.25	3.8	3.0	--	--
			0.50	2.9	2.8	--	--
			0.50	5.5	4.3	--	--
Camp Crook, SD	60ft x 0.4 mi	aerial/ diesel oil	0.25	4.7	0.6	5.7	0.3
			0.25	4.6	0.6	4.5	0.3
			0.50	0.3	2.7	1.1	3.1
			0.50	0.3	3.1	0.6	3.5
Eakly, OK	24 x 60 ft	ground/ water	0.25	1.5	0.6	--	--
			0.25	1.5	0.8	--	--
			0.50	2.6	1.3	--	--

Location	Plot size; ground/ aerial	Ground:air/ spray adjuvant	Application rate (lb a.i./A)	Diflubenzuron, in ppm,			
				Fresh grass		Dried grass	
				25W	2F	25W	2F
			0.50	2.3	1.2	--	--
Ekalaka, MT	60 ft x 0.5 mi	aerial/ diesel oil	0.25	1.1	0.8	0.8	0.9
			0.25	0.6	1.0	0.4	0.9
			0.50	1.1	1.1	1.5	1.2
			0.50	2.1	1.0	1.3	1.0
Hickman, CA	20 x 50 ft	ground/ water	0.25	2.0	2.3	--	--
			0.25	1.6	3.2	--	--
			0.50	2.8	3.0	--	--
			0.50	2.4	3.8	--	--
York, NE	50 x 400 ft	aerial/ diesel oil	0.25	0.4	0.7	1.1	1.9
			0.25	0.3	0.7	1.2	2,3
			0.50	0.6	0.7	1.9	2.6
			0.50	0.7	1.1	1.9	2.5
Hettinger, ND	75 x 3000 ft	aerial/ diesel oil	0.25	2.9	2.4	2.9	2.1
			0.25	2.2	2.1	2.6	2.2

Location	Plot size; ground/ aerial	Ground:air/ spray adjuvant	Application rate (lb a.i./A)	Diflubenzuron, in ppm,			
				Fresh grass		Dried grass	
				25W	2F	25W	2F
			0.50	4.7	4.6	5.1	3.7
			0.50	4.3	4.4	4.3	2.8
Hewlett, WY	75 x ca. 400 ft	aerial/not reported	0.25	0.9	2.5	1.1	3.6
			0.25	1.0	2.4	1.2	3.2
			0.50	4.3	0.5	2.0	1.2
			0.50	3.3	0.8	4.5	1.6
(total all trials)				71.5	72.5	45.7	40.9
(total 1X trials)				33.8	29.4	21.5	17.7
(total 2X trials)				37.7	43.1	24.2	23.2
(average 1X trials)				1.9	1.7	2.2	1.8
(average 2X trials)				2.1	2.4	1.0	1.0

Meat, Milk, Poultry, and Eggs:

Rangeland grass, both fresh and dried (hay), are feedstuffs.

A typical diet for beef and dairy cattle could contain 60% fresh grass or 60% grass hay, or a composite of both not to exceed 60% combined. The remaining 40% can be divided into portions of other feedstuffs such as corn grain, wheat middlings, and soybean hulls or cottonseed hulls. Tolerances are established for both oil seed hulls at 0.5 ppm. Contributions into the cattle diet from the oilseed hulls would only be <0.2 ppm. Therefore, based a diet that would give maximum exposure to diflubenzuron residues from the feeding of rangeland grass and oil seed hulls, an animal could consume approximately 15 ppm in its daily diet (60% forage X 6.0 ppm ÷ 25% DM ≈ 15 ppm).

Using this 15 ppm dietary exposure estimation, diflubenzuron residues (parent only) in ruminant liver would be <0.05 ppm. This limit is based on a 250 ppm goat metabolic study in which diflubenzuron was estimated at 7% of the total radioactivity residues (TRR: 6 ppm) in liver. Using this same 250 ppm metabolic study the measured amounts of PCA in goat liver was <0.03 ppm. Thus, for a dietary level of 15 ppm, the expected level of PCA would be <0.002 ppm. However, the level of CPU was estimated at 16% of the TRR and would translate into a CPU level of <0.06 ppm for the proposed use. Thus the estimated combined total in liver would >0.05 ppm, but <0.1 ppm.

Neither parent diflubenzuron (LOQ: 0.03 ppm) nor metabolite PCA (LOD: 0.001 ppm; LOQ: 0.005 ppm) have been found in milk in the ruminant study. However CPU (LOQ: 0.03 ppm) was estimated at 32-54% of the TRR in milk (0.22 ppm) in the 250 ppm metabolic study, and this translates into 0.007 ppm for a 15 ppm daily dietary exposure. Thus, the estimated combined diflubenzuron residues in milk would be well below the established 0.05 ppm tolerance.

Therefore any secondary combined diflubenzuron residues (parent and PCA and CPU) that might occur from these proposed labels would be adequately covered by the established tolerances (0.05 ppm) for livestock, meat, fat, and milk. However, the 0.05 ppm tolerance for meat byproducts would not cover the combined residues of parent diflubenzuron and its para-chloro metabolites PCA and CPU. A tolerance of 0.1 ppm would have to be established. A revised Section F is needed.

Since rangeland grass, fresh or dried, is not a poultry feedstuff, the 0.05 ppm tolerance is adequate for eggs.

cc: J. Stokes (CBTS); PP#5E4499; R.F.; Circu
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