



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF  
PREVENTION, PESTICIDES  
AND TOXIC SUBSTANCES

**MEMORANDUM**

Date: 5/15/02

Subject: Clethodim. Registration on Mint. Summary of Analytical Chemistry and Residue Data.

DP Barcode: D283279

PC Code: 121011

40 CFR: 180.458

MRID: 45571901

Case No.: 294661

Submission: S508696

Petition No.: 2E06396

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**Executive Summary**

Clethodim (Select®) is a cyclohexenone herbicide used for control of annual and perennial grass weeds in broad leaf crops. Clethodim is a post-emergence herbicide against a wide range of annual and perennial grasses.

Clethodim products are currently registered for a variety of use sites including agricultural crops and non-crop areas. The labels for two clethodim products, Select EC® (12 % active ingredient or ai, EPA Reg. No. 59639-78) and Select 2 EC (26 % ai, EPA Reg. No. 59639-3) permit application to commercial and residential sites and on other non-crop or non-planted areas including rights of way such as railroads, highways, roads, dividers, medians, pipelines, public utility lines, pumping stations, transformer stations and substations, around airports, electric utilities, commercial buildings, manufacturing plants, storage yards, rail yards, fence lines, parkways, ornamental gardens, walkways, patios, greenhouse benches, along driveways and around golf courses.

The formulation used to apply clethodim to mint was Prism 0.94EC, containing 12.6% clethodim

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by weight (the active ingredient) and 87.4% inert ingredients as an emulsifiable concentrate. Two broadcast foliar applications at a maximum rate of 0.25 pound active ingredient per acre (2.0 pints per acre) per application can be made per season, for a total seasonal application rate of 0.5 pound active ingredient per acre (except on Long Island, NY; applications there are restricted to a maximum of 0.25 pound active ingredient per acre per season). The minimum retreatment interval was 14 days, with a minimum pre-harvest interval of 14 days. The label for Prism 0.94EC recommends that a crop oil concentrate, consisting of a minimum 80% oils and 15% emulsifier, always be used as an adjuvant with this herbicide, usually at a concentration of 1% volume/volume in the finished spray volume. All six trials did include crop oil concentrate, although in one case the emulsifier content was well below 15%.

Metabolism studies for clethodim in/on carrots, soybeans, and cotton have been conducted and reviewed (PP#9F3743, MRIDs 41030137 & 41030138, M. Nelson, 3/12/90). The available metabolism studies on soybean, cotton, and carrots included soybean foliage, cotton foliage, and carrot leaves. The metabolism in soybean, cotton, and carrots, including soybean foliage, cotton foliage, and carrot leaves is similar. HED previously concluded that additional metabolism data may be required for future petitions on crops other than root crops and oil seed crops. However, metabolism data for soybean foliage, cotton foliage, and carrot leaves can support the proposed use on mint for this petition. The residues of concern are clethodim and its metabolites containing the 5-(2-ethylthiopropyl) cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones.

Metabolism studies of [propyl-1-<sup>14</sup>C]-clethodim in lactating goats and laying hens were previously reviewed (PP#9F3743, MRID# 41030139 & 41030140, M. Nelson, 3/12/90). The nature of the residue in ruminants and poultry is adequately understood for the purposes of the subject petition. HED previously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety. However, discussion of residues in livestock is not relevant to this petition as there are no livestock feed items associated with mint.

Permanent tolerances have been established under 40 CFR §180.458(a)(1), (4), and (5) for the combined residues of the herbicide clethodim and its metabolites containing the 2-cyclohexen-1-one moiety in/on the fat, meat, and mbyop of cattle, goats, hogs, horses, poultry, and sheep at 0.20 ppm, milk at 0.05 ppm, eggs at 0.20 ppm, cottonseed at 1.0 ppm, potatoes at 0.5 ppm, soybeans at 10.0 ppm, potato flakes and granules at 1.0 ppm, cottonseed meal 2.0 ppm.

In addition, permanent tolerances are established under 40 CFR §180.458(a)(3) and (6) for the combined residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim, in/on dry bulb onions at 0.20 ppm, radish, tops at 0.70 ppm, sugar beet roots at 0.20 ppm, sugar beet tops and molasses at 1.0 ppm, the tuberous and corm vegetables crop subgroup 1c, fruiting vegetables crop group, root vegetables (except sugar beets) crop subgroup 1b, leaves of root and tuber vegetables (excluding sugar beets, crop group 2), sugar beet, tops and sugar beet, molasses at 1.0 ppm, leaf petioles crop subgroup 4b at 0.6 ppm, melon crop subgroup 9a at 2.0 ppm, squash/cucumber crop

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subgroup 9b and cranberry at 0.5 ppm, sugar beets, roots at 0.20 ppm, sunflower seed at 5.0 ppm, strawberry at 3.0 ppm, sunflower, meal and clover, forage at 10.0 ppm, clover, hay at 20.0 ppm, green onion and leaf lettuce at 2.0 ppm, the Head/stem Brassica Crop Subgroup 5-A at 3.0 ppm, mustard, flax and canola, seed at 0.5 ppm, and flax and canola, meal at 1.0 ppm.

Time-limited tolerances (set to expire on 4/30/03) are established under 40 CFR §180.458(a)(2) for the combined residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim, in/on alfalfa forage at 6 ppm, alfalfa hay at 10 ppm, dry beans at 2 ppm, peanuts and peanut hay at 3 ppm, peanut meal at 5 ppm, tomato paste at 3 ppm, and tomato puree at 2 ppm.

HED has recently evaluated the residue data of clethodim in/on the leafy *Brassica* greens subgroup 5-B, turnip greens, dry bean, peanuts, peanut hay, peanut meal, and alfalfa hay and forage; and recommended for the establishment of tolerances for the residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones at 3.0 ppm for peanuts, peanut hay, the leafy *Brassica* greens subgroup 5-B and turnip greens, 2.5 ppm for dry bean, 5.0 ppm for peanut meal, and 6.0 ppm for alfalfa hay and forage.

To support the proposed use, the petitioner conducted five field trials were conducted on plots located in Region 5 (2 trials, WI) and Region 11(3 trials, WA) in 1998 following two broadcast foliar applications at a maximum rate of 0.25 pound active ingredient per acre (2.0 pints per acre) per application, for a total seasonal application rate of 0.5 pound active ingredient per acre. The minimum retreatment interval was 14 days, with a minimum pre-harvest interval of 14 days.

Adequate methodology is available for enforcement of the proposed tolerances. The analytical method used to assay clethodim residues in/on mint was RM-26B-3 (a modification of RM-26B-2), which was validated for the analyses of residues of clethodim sulfoxide and its metabolite (5-hydroxy clethodim sulfone) in/on green onions, leaf lettuce, and cabbage. The validated LOQ for residues of DME and DME-OH is 0.50 ppm each in/on mint; and 0.078 ppm and 0.076 ppm for residues of DME and DME-OH, respectively, in mint oil.

The available mint residue data are adequate for a permanent registration using the Prism 0.94EC formulation based on OPPTS 860.1500. The available mint residue data are adequate to support the proposed tolerance of 2.0 ppm for the combined residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones.

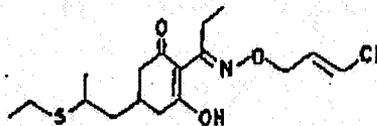
### Residue Chemistry Deficiencies

There were no data gaps associated with these field trials and processing studies with respect to the requirements of Residue Chemistry Test Guidelines, OPPTS 860.1500 and OPPTS 860.1520.

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## Background

### Clethodim



The Interregional Research Project No. 4 (IR-4), on behalf of the Michigan Agricultural Experiment Stations, has submitted a petition for the establishment of permanent tolerances for residues of the herbicide clethodim (Select<sup>®</sup> Herbicide 0.94EC (also called Prism, EPA Reg. Nos 59639-73). The proposed tolerances for the combined residues of clethodim [(E)-(±)-2-[1-[[[3-chloro-2-propenyl]oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one] and its metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-[2-(ethylthio)propyl]-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones in/on mint is 5.0 ppm

Tolerances are currently established for the combined residues of clethodim and its metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones in/on various raw and processed food commodities under 40 CFR 180.458(a)(3). Tolerances are established for residues of clethodim and its metabolites containing the 2-cyclohexen-1-one moiety in milk and the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep under 40 CFR 180.458(a)(1). Several time-limited tolerances are listed under 40 CFR §180.458(a)(2).

## 860.1200 Directions for Use

Table 1. Summary of Directions for Use of Mint.						
Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Mint						
Apply PRISM Herbicide postemergency to actively growing grasses. Broadcast foliar application using ground or aerial equipment.	Prism 0.94EC [59639-78]	0.25	2	0.5	14	Use a crop oil concentrate containing at least 15% emulsifier at 1% v/v to finished spray volume unless tank mix instructions indicate otherwise. Ground application use a minimum of 5 gals. of spray solution per acre. Air application use a minimum of 3 gals. of spray solution per acre. Do not apply more than 68 fl. oz of Prism herbicide(0.5 lb ai) per acre per season. Application on Long Island, NY is restricted to no more than 34 fl oz of Prism herbicide(0.25 lb ai) per acre per season.

## 860.1300 Nature of the Residue - Plants

Metabolism studies for clethodim in/on carrots, soybeans, and cotton have been conducted and reviewed (PP#9F3743, MRIDs 41030137 & 41030138, M. Nelson, 3/12/90). The available metabolism studies on soybean, cotton, and carrots included soybean foliage, cotton foliage, and carrot leaves. The metabolism in soybean, cotton, and carrots, including soybean foliage, cotton foliage, and carrot leaves is similar. HED previously concluded that additional metabolism data may be required for future petitions on crops other than root crops and oil seed crops. However, metabolism data for soybean foliage, cotton foliage, and carrot leaves can support the proposed use on mint for this petition. The residues of concern are clethodim and its metabolites containing the 5-(2-ethylthiopropyl) cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones.

## 860.1300 Nature of the Residue - Livestock

Metabolism studies of [propyl-1-<sup>14</sup>C]-clethodim in a lactating goat and laying hens were previously reviewed (PP#9F3743, MRID# 41030139 & 41030140, M. Nelson, 3/12/90). The nature of the residue in ruminants and poultry is adequately understood for the purposes of the subject petition. HED previously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety. As no livestock feed commodities are associated with the use of clethodim on mint, information on the nature of clethodim residues in livestock is not relevant to this petition.

#### **860.1340 Residue Analytical Methods**

Adequate methodology is available for enforcement of the proposed tolerances. The analytical method used to assay clethodim residues in/on the spinach leaves was RM-26B-3 (a modification of RM-26B-2), which was validated for the analyses of residues of clethodim sulfoxide and its metabolite (5-hydroxy clethodim sulfone) in/on green onions, leaf lettuce, and cabbage. The validated LOQ for residues of DME and DME-OH is 0.50 ppm for each residue in/on mint; and 0.078 ppm and 0.076 ppm for residues of DME and DME-OH, respectively, in mint oil.

#### **860.1360 Multiresidue Methods**

The petitioner has previously submitted data (1991; MRID 43166406, and 1992; MRID 43166407) describing the testing of clethodim and its metabolites through FDA Multiresidue Methods. These data, which have been forwarded to FDA for review, and indicate that adequate recoveries of clethodim, clethodim sulfoxide, and 5-OH clethodim sulfone have been obtained under FDA's multiresidue protocols (PP#9F3743, M. Nelson's memo of 3/12/90).

#### **860.1380 Storage Stability**

The maximum freezer storage interval for mint foliage field samples was 200 days, while the duration of the storage stability study was 209 days. For mint foliage, the mean recovery of the spiked clethodim sulfoxide in the three replicates was  $86 \pm 4\%$  and the mean recovery of the 5-hydroxy clethodim sulfone fortification was  $78 \pm 4\%$ .

#### **860.1400 Water, Fish, and Irrigated Crops**

As no water, fish, or irrigated crops issues are associated with the use of clethodim on mint, this guideline requirement is not relevant to the current petition.

#### **860.1460 Food Handling**

As there are no food handling uses for clethodim, this guideline requirement is not relevant to the current petition.

#### **860.1480 Meat, Milk, Poultry, and Eggs**

As no livestock feed commodities are associated with the use of clethodim on mint, information

on the transfer of clethodim residues to livestock is not relevant to this petition.

### 860.1500 Crop Field Trials

MRID No. 455719-01, Michael P. Braverman PhD, (19 December 2001), Clethodim: Magnitude of the Residue on Mint, IR-4 Study Number: A5235. New Jersey Agricultural Experimental Station Publication Number A-27200-93-01. 256 pages.

Table 2.4. Summary of Residue Data from Crop Field Trials in Mint with Clethodim.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Analyte	Residue Levels* (ppm)				
				Min.	Max.	HAFT**	Mean	Std. Dev.
Mint	0.50 ± 0.01	20 - 21	Clethodim	< 1.2	< 4.4	< 4.2	< 2.1	1.2

\*For values preceded by < symbol, the 5-Hydroxy Clethodim Sulfone component of residue was less than LOQ.

\*\*HAFT - Highest Average Field Trial

Five field trials were conducted on plots located in Region 5 (2 trials, WI) and Region 11 (3 trials, WA) in 1998 following two broadcast foliar applications at a maximum rate of 0.25 pound active ingredient per acre (2.0 pints per acre) per application, for a total seasonal application rate of 0.5 pound active ingredient per acre. The minimum retreatment interval was 14 days, with a minimum pre-harvest interval of 14 days.

Analyses of the mint foliage samples were performed at the Cornell Analytical Laboratories, New York State Agricultural Experiment Station, in the Department of Food Science and Technology of Cornell University in Geneva, New York. Method RM-26B-3 was used for the analyses. The combined residues of clethodim and its metabolites were <1.2 - <4.4 ppm in/on mint samples.

The number of crop field trials and geographic representation for mint is adequate for a permanent registration using the Prism 0.94EC formulation based on OPPTS 860.1500. The available spinach residue data are adequate to support the proposed tolerance of 5.0 ppm for the combined residues of clethodim and its metabolites in/on mint.

### 860.1520 Processed Food and Feed

MRID No. 455719-01, Michael P. Braverman PhD, (19 December 2001), Clethodim: Magnitude of the Residue on Mint, IR-4 Study Number: A5235. New Jersey Agricultural Experimental Station Publication Number A-27200-93-01. 256 pages.

Two field trials were conducted in Wisconsin and Washington for mint processing studies. Mint samples were treated with two broadcast foliar applications at a maximum rate of 0.25 pound active ingredient per acre (2.0 pints per acre) per application, for a total seasonal application rate of 0.5 pound active ingredient per acre. The minimum retreatment interval was 14 days, with a minimum pre-harvest interval of 21 days. Mint oil samples were distilled on-site from mint foliage. The mint foliage was held at ambient temperature until distillation of mint oil commenced. Time elapsed from harvest, through distillation, until the mint oil was transferred to

the storage freezer was 210 minutes. Analyses of the mint foliage and mint oil samples were performed at the Cornell Analytical Laboratories, New York State Agricultural Experiment Station, the Department of Food Science and Technology of Cornell University in Geneva, New York.

RAC	Processed Commodity	Field Trial Source of Processed Commodity	Total Rate (lbs ai/A)	PHI (days)	Residue in RAC (ppm) <sup>1</sup>	Residues in Oil (ppm)	Processing Factor
Mint	Mint Oil	Portage, WI	0.51	21	0.794	< 0.18	NA <sup>2</sup>
Mint	Mint Oil	White Swan, WA	0.49	21	1.588	< 0.18	NA

<sup>1</sup> Calculated as clethodim equivalents.

<sup>2</sup> Not Applicable.

The processing studies are acceptable. No concentration factor was applicable in this case, as the clethodim residue diminished in the RAC (mint foliage) to below the LOQ in the processed commodity (< 0.18 ppm in mint oil). No data gaps were associated with the study which would be impediments to registering clethodim with a permanent tolerance for treatment of mint plants destined for processing into mint oil.

#### 860.1650 Submittal of Analytical Reference Standards

The analytical reference standards for both DME and DME-OH (06/1993) have been submitted to the EPA National Pesticide Standards Repository.

#### 860.1850/1900 Confined and Field Accumulation in Rotational Crops

A confined rotational crop study of [ring-4,6-<sup>14</sup>C]-clethodim with carrots, lettuce, and wheat (MRID 41030211) was conducted. The study was reviewed by E. B. Conerly (EFGWB Science Chapter for Clethodim, 06/26/1990). Results indicated that there is no need for field rotational crop trials. A 1-month plantback interval for crops rotated with alfalfa was specified (D 236382, M. Collantes, et al, 2/10/98). The use directions submitted with the current petition do not specifically address rotational crops. The directions for use on fallow or nonproducing agricultural land state do not plant any crop for 30 days after application unless clethodim is registered for use on that crop.

#### 860.1550 Proposed Tolerances

The tolerance expression for clethodim in/on plants (40 CFR 180.458(a) (3) is the combined residues of clethodim and metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and

sulphones.

There are no established Codex maximum residue limits (MRLs) for residues of clethodim in/on mint; therefore, there are no questions with respect to Codex/U.S. tolerance compatibility. Codex MRLs are currently established on various crop and livestock commodities in terms of the sum of clethodim and its metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim.

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments
Mint	5.0	5.0	The available residue data is adequate for a permanent registration of the Prism 0.94 EC formulation.

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**References**

(PP#9F3734, MRID4138991, M.Nelson, 5/04/90)

CBTS No.: 12468  
DP Barcode: D194694  
Subject: PP# 9F3743 Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities. Evaluation of the Revised Compound Specific Residue Analytical Method, EPA-RM-26D-2, and the New Supporting Independent Laboratory Validation Data.  
From: F. Griffith  
To: J. Miller/D. Marlow/A. Kocialski  
Dated: 9/29/93  
MRID(s): None

CBTS Nos.: 13703, 13704, and 13705  
DP Barcode: D203378  
Subject: 4F4340. Clethodim in/on Sugar Beets and Onions (Dry Bulb). Evaluation of Residue Data and Analytical Methodology.  
From: J. Morales  
To: J. Miller/D. Kenny  
Dated: 2/8/95  
MRID(s): 43166400, 43166402, and 43166403-43166407.

CBTS Nos.: 16157, 16158, and 16442  
DP Barcodes: D219077, D219078 and D220698  
Subject: 5F4572/5H5729. Clethodim in/on Tomatoes and Tuberous and Corm Vegetables. Evaluation of Residue Data and Analytical Methodology.  
From: J. Morales  
To: J. Miller/D. Kenny  
Dated: 2/8/96  
MRID(s): 43757701-43757704

CBTS Nos.: None  
DP Barcodes: D258351  
Subject: OR990045. Clethodim. Section 24(c): Clover Grown for Seed.  
From: L. Cheung  
To: D. Kenny/ J. Miller  
Dated: 9/9/99  
MRID(s): None