UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

**MEMORANDUM**

**DATE:** 2/1/2006

**SUBJECT:** **Clothianidin. Tolerance Petition Requesting Food Use of the Insecticide Clothianidin on Grapes, Potatoes, Sorghum, and Cotton (Section 3 Registration). Summary of Analytical Chemistry and Residue Data.**

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|---|---|
| **Petition Numbers:** | **4F6869, 3F6792, 5F6908** |
| **PC Code:** | **044309** |
| **DP Barcode:** | **D303164, D309473, D309474, D312449, D314533, D318496** |
| **Regulatory Citation:** | **40CFR §180.586** |
| **EPA Registration Numbers:** | **66330-40, 66330-52, 264-789, 264-XXX** |
| **Chemical Class:** | **Neonicotinoid (Chloronicotinyl) & Nitroguanidine Insecticide** |
| **MRID Numbers:** | **46346801 & -02, 46357301 & -02, 46144901 & -02, 46482308** |
| **Trade Names:** | **Clutch™ 50WDG, Belay™ 16WSG, Poncho™ 600, AE1283742** |

**FROM:** William T. Drew, Chemist
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This residue chemistry summary document was originally prepared under contract #EP-W-04-052 by Dynamac Corporation (1910 Sedwick Road, Building 100; Durham, NC 27713). It has been reviewed by HED and revised to reflect current OPP policies.

**Executive Summary**

Clothianidin, with CAS Registry Number 210880-92-5 and CAS Name [*C(E)*]-*N*-[(2-Chloro-5-thiazolyl) methyl]-*N'*-methyl-*N''*-nitroguanidine, is a systemic, broad-spectrum, neonicotinoid insecticide. Clothianidin is a major metabolite of thiamethoxam. It is currently registered (40CFR §180.586) for use on various crops.

Arvesta Corporation has submitted a petition (PP#4F6869) proposing the use of clothianidin on grapes and potatoes. The formulations being proposed for use include a 50% active ingredient (ai) water-dispersible granule (WDG) and a 16% ai water-soluble granule (WSG). The 16% WSG formulation is proposed for a single early-season soil application (in-furrow at planting or side-dress at hilling) to potatoes at a rate of up to 0.20 pounds ai per acre (lb ai/A), and for one or two soil applications (drip-irrigation during berry development) to grapes at rates totaling 0.20 lb ai/A per season, with a 30-day pre-harvest interval (PHI) for grapes. The PHI for potatoes was not specified. The 50% WDG formulation is proposed for up to three foliar broadcast applications to potatoes at rates totaling 0.14 lb ai/A per season, with a 14-day PHI, and for two foliar broadcast applications to grapes at rates totaling 0.2 lb ai/A per season, with a 0-day PHI. For foliar applications, the minimum re-treatment interval (RTI) is 7 days for potatoes and 14 days for grapes; the RTI for soil applications to grapes was not specified. In conjunction with these uses, Arvesta has proposed the establishment of permanent tolerances for residues of clothianidin *per se* in/on grapes (at 0.50 ppm), raisins (1.0 ppm), and potatoes (0.10 ppm).

Bayer CropScience has submitted a petition (PP#3F6792) proposing the use of clothianidin on sorghum and another petition (PP#5F6908) proposing the use of clothianidin on cotton for early-season control of certain insect pests. The formulation being proposed for use on sorghum is a 48% ai flowable concentrate (FC), while that proposed for use on cotton is a 14% ai FC (with 33% imidacloprid as co-active). Both uses are proposed seed treatments, with the 48% FC applied to sorghum at a rate of up to 0.25 lb ai/100 lb seeds, and the 14% FC applied to cotton at up to 0.15 lb ai/100 lb seeds. They are intended for use in commercially available equipment designed for liquid or slurry seed treatment only. The products are not for utilization in hopper-box, slurry-box, or similar seed treatment applications used at planting. In conjunction with these uses, Bayer CropScience has proposed the establishment of permanent tolerances for residues of clothianidin *per se* in/on sorghum grain, forage, and stover (at 0.01 ppm), as well as cottonseed and gin byproducts (0.01 ppm).

Additionally, Bayer CropScience has requested label amendments (for the 48% FC formulation) allowing plant-back intervals (PBIs) to be reduced to 30 days for potatoes and 8 months for sugarcane after the planting of corn, rapeseed, or canola that received seed treatment with clothianidin. Also, Gustafson has submitted a request for label amendments (48% FC) reducing the maximum application rate for sweet corn to 0.25 mg ai/seed, allowing the PBI to be reduced to 30 days for root and tuber vegetables (Crop Group 1), and allowing the PBI to be reduced to 4 months for all other rotated crops after the planting of sweet corn, canola, rapeseed, or sorghum that received seed treatment with clothianidin.

The nature of the residue has been adequately delineated in plants based on the acceptable corn, sugar beet, apple, and tomato metabolism studies. The HED Metabolism Assessment Review Committee (MARC) has determined that the parent compound is the only residue of concern (ROC) in primary crops for both tolerance setting and risk assessment purposes (MARC Decision Memo, D282449, Yan Donovan, 4/25/2003). The nature of the residue in livestock is also understood based on the acceptable goat and hen metabolism studies.

For ruminants, the MARC concluded that the ROCs for risk assessment include parent and the metabolites TZU, TZG, TZNG, and ATMG-Pyruvate; for poultry, the MARC concluded that the ROCs for risk assessment include parent and the metabolites TZU, TZG, TZNG, and ATG-Acetate. However, only parent needs to be included in the tolerance expression.

Adequate LC/MS/MS methods are available for both collecting data and enforcing tolerances for clothianidin residues in plant (Bayer Methods 00552 and 109240-1) and animal (Bayer Method 00624) commodities. The validated limit of quantitation (LOQ) for clothianidin in plant commodities is 0.010 ppm, except for wheat straw (0.020 ppm), and the validated LOQs are 0.010 ppm in milk and 0.020 ppm in animal tissues. All three of these methods have been reviewed by BEAD's Analytical Chemistry Laboratory (ACL), approved for tolerance enforcement, and forwarded to FDA for inclusion in PAM Volume II. In addition, Arvesta has submitted another LC/MS/MS method (Morse Method #Meth-164) for enforcing tolerances and collecting data on residues of clothianidin and TMG in grape and potato commodities. This newer method is similar to Method 00552 and involves extraction of residues with acetonitrile/water, cleanup using solid phase extraction (SPE) cartridges, and the separate analysis of clothianidin and TMG by LC/MS/MS. The validated LOQ for each analyte is 0.020 ppm in all grape and potato matrices, except for potato chips and raisins (with LOQs of 0.040 ppm). The method was adequately validated in conjunction with the field trials and processing studies and has undergone a successful independent laboratory validation (ILV) trial.

Samples of sorghum and cotton commodities were analyzed for clothianidin using an LC/MS/MS method developed by Bayer (Bayer Method 109240-1), which is essentially Method 00552 with the use of an internal standard for quantitation. Methods 00552 and 109240-1 have been reviewed by the Agency and approved for tolerance enforcement, as noted above. The validated LOQ for clothianidin residues is 0.010 ppm in sorghum forage, stover, and grain; the LOQ is also 0.010 ppm in cottonseed and gin byproducts. This method was adequately validated in conjunction with the field trials.

Adequate storage stability data are available indicating that clothianidin and TMG are stable at -20°C or less for intervals of up to 5.3 months in grapes and 6 months in potatoes. These data support the maximum storage durations (3 to 5 months) from the grape and potato field trials. Samples of processed commodities from the grape and potato processing studies were stored frozen for no more than 1 month prior to analysis. Samples of sorghum and cotton commodities were stored frozen from collection to analysis for durations of up to 11 months. Storage stability data are available on corn, sugar beet, and canola matrices indicating that clothianidin is stable in frozen storage for intervals of up to 24 months (MRID #45422611). These data will support the current sorghum and cotton field trials.

With the proposed uses on potatoes, sorghum, and cotton there is the potential for increased exposure of livestock through clothianidin residues in sorghum and cotton commodities, and potato culls. Based on current and proposed uses, the recalculated maximum theoretical dietary burdens (MTDBs) for livestock are 0.321 ppm for dairy cattle, 0.287 ppm for beef cattle, 0.020 ppm for poultry, and 0.035 ppm for swine. Considering data from the available ruminant feeding study and the above MTBDs, the current tolerance for clothianidin residues in milk is adequate and tolerances are not required for meat, meat-byproducts or fat from cattle, goats, hogs, horses, or sheep. Data from the poultry metabolism study also indicate that a poultry feeding study and tolerances for poultry commodities are not required for the current petitions.

The available field trial data are adequate and will support the proposed use patterns on

sorghum, cotton, grapes, and potatoes. The number and geographic distribution of the field trials are adequate for all formulations. For grapes, residues of clothianidin were 0.040 to 0.278 ppm and averaged 0.139 ppm in grapes harvested immediately following (0 days after last treatment, or DAT) the last of two foliar applications of clothianidin (50% WDG) totaling roughly 0.2 lb ai/A (1X the proposed maximum seasonal use rate). HAFT residues of clothianidin in grapes treated with 50% WDG were 0.277 ppm. Residues of clothianidin were less than 0.020 ppm (the LOQ) in all grape samples harvested 30 DAT following a single drip-irrigation application of clothianidin (16% WSG) at a rate of roughly 0.20 lb ai/A (1X the proposed maximum seasonal use rate). Residues of the metabolite TMG were less than 0.020 ppm (the LOQ) in all grape samples from both treatment regimes. Arvesta has proposed a tolerance on grapes of 0.50 ppm, but HED is recommending a tolerance of 0.60 ppm, based on calculated results from HED's *Tolerance/MRL Harmonization Spreadsheet* (the data set, log-normal probability plot, and tolerance selection summary are appended to this report following the IRL Status sheet).

For potatoes, residues of clothianidin were 0.021 ppm or less and averaged 0.011 ppm (less than the LOQ) in potatoes harvested 13 to 14 days following the last of three foliar applications of clothianidin (50% WDG) totaling roughly 0.20 lb ai/A (approximately 1.4X the proposed maximum seasonal use rate). Residues of clothianidin were 0.033 ppm or less and averaged 0.014 ppm (less than the LOQ) in potatoes harvested at maturity following a single in-furrow application (at planting) of clothianidin (16% WSG) at a rate of roughly 0.20 lb ai/A (1X the proposed maximum seasonal use rate). HAFT residues of clothianidin in potatoes treated with 16% WSG were 0.031 ppm. Residues of the metabolite TMG were less than 0.020 ppm (the LOQ) in all potato samples from both treatment regimes. Arvesta has proposed a tolerance on potatoes of 0.10 ppm, but HED is recommending a tolerance of 0.05 ppm, based on calculated results from HED's *Tolerance/MRL Harmonization Spreadsheet* (the data set, log-normal probability plot, and tolerance selection summary are appended to this report following the IRL Status sheet).

In sorghum, following a single treatment of sorghum grain with 48% FC, residues of clothianidin were less than 0.010 ppm (the LOQ) in all samples of sorghum forage, stover, and grain (n = 24 per matrix). In cotton, following a single treatment of cottonseed with 14% FC, residues of clothianidin were less than 0.003 ppm, the limit of detection (LOD) in all samples of cottonseed (n = 24) and less than 0.005 ppm (the LOD) in all gin byproducts (n = 12).

The available sorghum, grape, and potato processing studies are adequate. Samples were analyzed using adequate methodology and are supported by the available storage stability data. For grapes, residues of clothianidin concentrated slightly in juice (1.1X) and by 1.6X in raisins. Based on the HAFT residues from the grape field trials (0.277 ppm), the maximum expected residues of clothianidin in raisins would be 0.443 ppm. As this residue level is below the recommended 0.60 ppm tolerance for grapes, a separate tolerance for raisins is not required.

For potatoes, processing factors determined from the two processing studies were similar for each matrix. Residues of clothianidin were reduced in wet peel (0.5X), but concentrated in granules (2.3X) and chips (1.4X). Based on HAFT residues of 0.031 ppm for whole tubers, the maximum expected residues in granules/flakes and chips would be 0.071 and 0.043 ppm, respectively. As the maximum expected residue level in chips is less than the recommended 0.05 ppm tolerance on potatoes, a separate tolerance is not required on chips. Based on the maximum expected residues in potato granules/flakes, HED is recommending a tolerance be established at 0.08 ppm on this processed food.

In sorghum, residues in three samples of grain harvested at maturity (after treatment at

2X the proposed label's maximum use rate) were non-detectable (less than 0.003 ppm). Considering that residues were less than a third of the LOQ (0.010 ppm) in grain treated at a 2X rate, and that the application to sorghum is made as a seed treatment, residue data on aspirated grain fractions derived from sorghum are not required. In addition, the Agency does not currently require processing data on sorghum's processed commodity, flour.

In cotton, residues in three samples of undelinted cottonseed (harvested at maturity and ginned following treatment at 5X the proposed label's maximum use rate) were all less than the LOQ (0.010 ppm). Considering that residues were less than the LOQ in cottonseed treated at a 5X rate, and that the application to cotton is made as a seed treatment, residue data on processed commodities derived from cotton were not generated. The registrant submitted a request for waiver of the requirement for a cotton processing study.

Adequate confined and limited field rotational crop studies are available to support the proposed maximum seasonal use rates on sorghum, cotton, and potatoes. The metabolism of clothianidin in primary and rotational crops is similar. The MARC concluded that parent, TZNG and MNG are the ROCs in rotational crops and that only parent needs to be included in the tolerance expression. Residue data from the available limited field rotational crop studies, conducted at 0.7X to 0.9X the proposed maximum seasonal rates (0.20 lb ai/A), adequately support the current tolerances for inadvertent residues in selected rotational crops.

**Regulatory Recommendations and Residue Chemistry Deficiencies**

No major residue chemistry deficiencies were noted in the subject petitions that would preclude the establishment of permanent tolerances for clothianidin on sorghum, cotton, grapes, and potatoes; however, the following labeling issues should be resolved prior to establishing permanent tolerances.

(1) Because the field trials supporting foliar applications of 50% WDG did not include the use of any spray adjuvants, directions (for use on grapes) on the label of the 50% WDG formulation should prohibit the use of wetting agents or other adjuvants. HED does not object to the use of adjuvants on potatoes in light of the exaggerated-rate data from the processing studies showing tuber residues below the recommended 0.05 ppm tolerance. Alternatively, HED would not object to conditional registration of the 50% WDG formulation (for use on grapes) allowing the adjuvants, contingent upon submission of data showing that residues, with and without the use of such agents, are comparable.

(2) Based on the current tolerances on rotational crops, the proposed labels for potatoes should be amended to include a plant-back restriction of 30 days for cereal grain crops, grasses, nongrass animal feeds (such as alfalfa), soybeans, and dry beans. A plant-back restriction of 1 year is required for all other rotated crops. If plant-back intervals of less than 1 year are desired by the petitioner, then extensive field rotational crop trials will be required.

(3) The label amendments requested by Bayer CropScience and Gustafson should be approved. The label for 48% FC (Poncho™ 600) should be amended to read as follows:

> Areas planted with treated seed may be replanted immediately with corn, rapeseed, canola, and sorghum. These areas may also be replanted after 30 days with cereal grains, grasses, nongrass animal feeds, soybeans, dried beans, or root and tuber vegetables. These areas may also be replanted after 8 months with sugarcane. Do not plant any other crop in the treated

area for at least 1 year after treated field corn or popcorn seeds are planted. Do not plant any other crop in the treated area for at least 4 months after treated sweet corn, canola, rapeseed, or sorghum seeds are planted.

The registrant has requested a waiver of the requirement for a cotton processing study. HED recommends that the waiver be granted; residue data from the cotton field trial conducted at a 5X exaggerated rate indicate that a processing study for cotton is unnecessary.

Residue data support tolerances for clothianidin of 0.01 ppm in/on sorghum forage, stover, and grain; 0.01 ppm in/on cottonseed and gin byproducts; 0.60 ppm in/on grapes; 0.05 ppm in/on potatoes and 0.08 ppm in/on potato granules/flakes. A separate tolerance for raisins is not required. A summary of the proposed and recommended tolerances, along with the correct commodity definitions for the requested commodities, is presented in Table 8. The registrant should submit a revised Section F to reflect these changes. A recommendation regarding tolerances will be made in HED's forthcoming human health risk assessment.

**Background**

Clothianidin is a systemic, broad-spectrum insecticide belonging to the neonicotinoid (chloronicotinyl) and nitroguanidine classes of chemicals. Clothianidin enters the transpiration stream through the roots and cotyledons of newly germinating seedlings and protects below- and above-ground plant parts from insect damage. It binds (via ingestion and contact routes) with the nicotinic acetylcholine receptor sites, interfering with neural transmission of stimuli and eventually inhibiting reproduction of the insect. Clothianidin is a major metabolite of thiamethoxam. It is currently registered to Bayer CropScience and Gustafson for use as a seed treatment on corn and canola, and to Arvesta Corporation for use as a foliar application on pome fruit.

Tolerances are established for residues of clothianidin in/on canola seed and corn commodities at 0.01 to 0.10 ppm , and at 0.01 ppm in milk. Permanent tolerances were also recently established (*70 FR 7886*, 2/16/2005) for residues of clothianidin in/on pome fruit at 1.0 ppm.

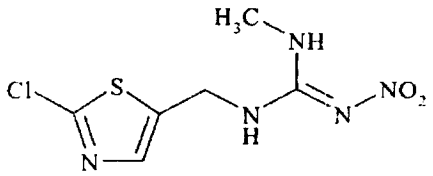
Arvesta has submitted a petition (PP#4F6869) proposing the use of clothianidin on grapes and potatoes. The products being proposed for use on grapes and potatoes include a 50% WDG and a 16% WSG formulation. These formulations are proposed for either soil (16% WSG) or foliar (50% WDG) applications. Arvesta is also proposing the establishment of permanent tolerances for residues of clothianidin in/on the following plant commodities:

Grapes ..... 0.5 ppm,
Raisins ..... 1.0 ppm,
Potatoes ..... 0.1 ppm.

Bayer CropScience has submitted a petition (PP#3F6792) proposing the use of clothianidin on sorghum and another petition (PP#5F6908) proposing the use of clothianidin on cotton. The formulation being proposed for use on sorghum is a 48% FC, while that proposed for use on cotton is a 14% FC (with 33% imidacloprid as co-active). Both are proposed for use as seed treatments. Bayer CropScience is also proposing the establishment of permanent tolerances for residues of clothianidin in/on the following plant commodities:

Sorghum Grain ..... 0.01 ppm,
Sorghum Forage ..... 0.01 ppm,
Sorghum Stover ..... 0.01 ppm,

Cotton Seed ..... 0.01 ppm,
Cotton Gin Byproducts ..... 0.01 ppm.

| **TABLE 1** | **Nomenclature of Test Compound.** |
|---|---|
| Compound |  |
| Empirical Formula | $C_6H_8ClN_5O_2S$ |
| Common Name | Clothianidin |
| Company Experimental Names | TM-444, TI-435, V-10066 |
| IUPAC Name | *(E)*-1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine |
| CAS Name | [*C(E)*]-*N*-[(2-Chloro-5-thiazolyl) methyl]-*N'*-methyl-*N''*-nitroguanidine |
| CAS Number | 210880-92-5 (formerly 205510-53-8) |
| Chemical Class | Chloronicotinyl (Neonicotinoid) |
| Known Impurities of Concern | None |
| End-Use Products (EUPs) | Clutch™ 50WDG, EPA Registration #66330-40<br>Belay™ 16WSG, EPA Registration #66330-52<br>Poncho™ 600, EPA Registration #264-789<br>AE1283742, EPA Registration #264-XXX (not yet registered) |

| **TABLE 2** | **Physicochemical Properties (from MRID #45422301).** |
|---|---|
| **Parameter** | **Value** |
| Molecular Weight | 249.7 |
| Melting Point (°C) | 176.8 |
| pH at 23°C | 6.24 [1% solution/suspension] |
| Density (g/cm$^3$) at 20°C | 1.61 [PAI], 1.59 [TGAI] |
| Water Solubility (g/L) at 20°C | 0.327 |
| Solvent Solubility (g/L) at 25°C | n-Heptane <0.00104<br>Xylene 0.0128<br>1-Octanol 0.938<br>Dichloromethane 1.32<br>Ethyl Acetate 2.03<br>Methanol 6.26<br>Acetone 15.2 |
| Vapor Pressure (Pa) at 25°C | $1.3 \times 10^{-10}$ |
| Dissociation Constant ($pK_a$) at 20°C | 11.09 |
| Octanol/Water Partition Coefficient (Log $K_{OW}$) at 25°C | 0.7 |
| UV/Visible Absorption Spectrum, Maximum (nm) | 265.5 [acidic, neutral sol'ns], 246.0 [basic sol'n]. |

## 860.1200 Directions for Use

**TABLE 3 Summary of Proposed Directions for Uses of Clothianidin.**

| Application Type; Timing; Equipment | Formulation | Maximum Application Rate | Maximum Number per Season | Maximum Seasonal Rate | PHI (Days) | Use Directions and Limitations |
|---|---|---|---|---|---|---|
| **Grapes[1]** | | | | | | |
| Drip-irrigation to soil; during fruit development; using chemigation. | 16% WSG | 0.2 lb ai/A | 2 | 0.20 lb ai/A | 30 | Do not apply 50% WDG following soil application of 16% WSG. A 14-day RTI is specified for the foliar applications. A minimum application volume is not specified. Regardless of formulation or application type, do not apply more than 0.20 lb ai/A per season of clothianidin per crop. |
| Foliar broadcast; during fruit development; ground or aerial equipment. | 50% WDG | 0.094 lb ai/A | 2 | 0.19 lb ai/A | 0 | |
| **Potatoes[1]** | | | | | | |
| In-furrow to soil (at planting) or side-dress to soil (during hilling); ground equipment. | 16% WSG | 0.2 lb ai/A | 1 | 0.20 lb ai/A | NA[2] | Do not apply 50% WDG following soil application of 16% WSG. A 7-day RTI is specified for the foliar applications. A minimum application volume is not specified. Regardless of formulation or application type, do not apply more than 0.20 lb ai/A/season of clothianidin per crop. |
| Foliar broadcast; during tuber development; ground or aerial equipment. | 50% WDG | 0.047 lb ai/A | 3 | 0.14 lb ai/A | 14 | |
| **Sorghum** | | | | | | |
| Seed treatment; prior to planting; commercial seed-treatment equipment. | 48% FC | 0.25 lb ai/100 lb seeds | 1 | 0.25 lb ai/100 lb seeds | NA | For use by commercial seed treaters only. Not for use in farm applicators used at planting. Treated seed must be conspicuously colored. |
| **Cotton** | | | | | | |
| Seed treatment; prior to planting; commercial seed-treatment equipment. | 14% FC | 0.15 lb ai/100 lb seeds | 1 | 0.15 lb ai/100 lb seeds | NA | For use by commercial seed treaters only. Not for use in farm applicators used at planting. Treated seed must be conspicuously colored. |

1. Both labels specify a 12-hour restricted entry interval (REI). PBIs for rotated crops are not specified.
2. NA = Not Applicable.

***Conclusions:*** Provided that amendments are made pertaining to the use of adjuvants and rotational crop restrictions, the proposed label directions are adequate and are supported by the available sorghum, cotton, grape, and potato field trial data. Because the field trials supporting foliar applications of 50% WDG did not include the use of any spray adjuvants, directions (for use on grapes) on the label of the 50% WDG formulation should prohibit the use of wetting agents or other adjuvants. HED does not object to the use of adjuvants on potatoes in light of the exaggerated-rate data from the processing studies showing tuber residues below the recommended 0.05 ppm tolerance. Alternatively, HED would not object to conditional registration of the 50% WDG formulation (for use on grapes) allowing the adjuvants, contingent upon submission of data showing that residues, with and without the use of such agents, are comparable.

**860.1300 Nature of the Residue - Plants**

**MARC Decision Memo, D282449, Yan Donovan, 4/25/2003**
**Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003**

Adequate plant metabolism studies are available reflecting the application of [$^{14}$C]-clothianidin as a seed treatment to corn and sugar beets, as foliar applications to apples, and as soil and foliar applications to tomatoes. Based on these metabolism studies, the MARC concluded that the nature of the residue has been adequately delineated, and that parent only is the ROC to be used in risk assessment and the tolerance expression for primary crops. However, the MARC also determined that future new uses on root crops and/or leafy vegetables will require analysis of TMG along with parent in field trial samples. The metabolic profiles in the tested primary crops were similar in that the highest level residue was the parent, clothianidin, with the exception of mature sugar beet tops.

**860.1300 Nature of the Residue - Livestock**

**MARC Decision Memo, D282449, Yan Donovan, 4/25/2003**
**Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003**

The nature of clothianidin residues in livestock is understood based on the adequate goat and hen metabolism studies. In these studies, a goat was dosed orally for 3 days with [$^{14}$C]-clothianidin at levels equivalent to roughly 200 ppm in the diet, and hens were dosed orally for 3 days with [$^{14}$C]-clothianidin at levels equivalent to 140 ppm in the diet. For ruminants, the MARC concluded that the ROCs include parent, TZU, TZG, TZNG, and ATMG-Pyruvate and that these residues should by included in risk assessments. For poultry, the MARC concluded that the ROCs include parent, TZU, TZG, TZNG and ATG-Acetate for risk assessment purposes. However, for purposes of tolerances, the MARC recommended that only parent needs to be included in the tolerance expression.

**860.1340 Residue Analytical Methods - Plants**

**DER for MRID #46346801 (Residue Analytical Method for Plant Commodities)**

Adequate LC/MS/MS methods (Bayer Methods 00552 and 109240-1) are available for determining residues of clothianidin in plant commodities. For both, the validated method LOQ is either 0.010 or 0.020 ppm, depending on the matrix. These methods have been approved for tolerance enforcement by ACL (PMV Results Memo, D282448, Patricia Schermerhorn, 7/17/2003) and have been forwarded to FDA for inclusion in PAM Volume II.

In the current petition, Arvesta has proposed an LC/MS/MS method for enforcing tolerances of clothianidin and its metabolite, TMG, in grape and potato commodities. The

method, entitled *Determination of TM-444 and TMG in Grape and Potato Raw Agricultural and Processed Commodities* (Morse Method #Meth-164), was used for the analysis of residues in the grape and potato field trials and processing studies and was adequately validated in conjunction with these analyses. The method is similar to the current enforcement method (Method 00552).

For Morse Method #Meth-164, residues are extracted with acetonitrile/water/guanidine-HCl (20:80:1 vol/vol/wt), filtered, and concentrated. Residues of clothianidin and TMG are then cleaned up separately using ChemElut liquid/liquid extraction (LLE) or ENVI-Carb™ SPE columns, respectively. Residues are concentrated, reconstituted in 1% acetic acid, and analyzed by LC/MS/MS. The validated LOQ for each analyte is 0.020 ppm in all grape and potato matrices, except for potato chips and raisins (with LOQs of 0.040 ppm). The LOD for each analyte is 0.007 ppm for all grape and potato matrices, except for chips and raisins (with LODs of 0.013 ppm). Method validation data for the LC/MS/MS method demonstrated adequate method recoveries of clothianidin and TMG from all grape and potato commodities Clothianidin recoveries averaged 75 to 92%, with low standard deviations (± 4 to 14%), and TMG recoveries averaged 77 to 102%, also with low standard deviations (± 5 to 11%). The fortification levels and samples used in method validation are adequate to bracket expected residue levels.

A successful ILV trial was conducted using the above method with samples of grapes fortified at 0.020 and 0.040 ppm. Although the LC/MS/MS method was not validated at the proposed tolerance level for grapes (0.50 ppm), as required by Agency guidance, the available ILV trial will be considered adequate as the ILV data together with the method validation data from the developing laboratory indicate that recoveries of both clothianidin and TMG are likely to be acceptable at the proposed 0.50 ppm tolerance.

Samples of sorghum commodities were analyzed using an LC/MS/MS method entitled *Modification M001 of the Method 00552 for the Determination of Residues of TI-435 in/on Plant Materials* (Bayer Method 109240-1). It and the original method (Method 00552) have been validated by the Agency and accepted for tolerance enforcement. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum forage, stover, and grain. The LOD is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain. Average concurrent method recoveries were 85 ± 10% from forage samples, 87 ± 3% from stover samples, and 91 ± 8% from grain samples fortified with clothianidin at 0.010 ppm.

Samples of cotton commodities were analyzed using the same method as for sorghum, with minor modifications. The validated LOQ for clothianidin residues is 0.010 ppm for cottonseed and gin byproducts. The LOD is 0.003 ppm for cottonseed and 0.005 ppm for gin byproducts. In the current study, the method was validated in conjunction with the analysis of field trial samples using control samples of cottonseed fortified with clothianidin at 0.010 and 0.050 ppm and gin byproducts fortified with clothianidin at 0.010 and 0.500 ppm. Average concurrent method recoveries were 95 ± 8% (0.010 ppm spike) and 97 ± 4% (0.050 ppm spike) from cottonseed samples fortified with clothianidin, while recoveries were 96 ± 13% (0.010 ppm spike) and 92 ± 5% (0.500 ppm spike) from gin byproducts samples fortified with clothianidin.

**860.1340 Residue Analytical Methods - Livestock**

An adequate LC/MS/MS method (Bayer Method 00624) is available for determining residues of clothianidin, TZU, TZG, TZNG and ATMG-pyruvate in milk. The method LOQ is 0.010 ppm for each analtye in milk. This method has been approved for tolerance enforcement by ACL (PMV Results Memo, D282448, Patricia Schermerhorn, 7/17/2003) and has been forwarded to FDA for inclusion in PAM Volume II.

**860.1360 Multiresidue Methods**

Multiresidue method testing of clothianidin and its metabolites MNG, TZG, TZNG, TZU, and ATMG-Pyr have been submitted (Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003).

***Conclusions:*** Clothianidin and its major metabolites are not adequately recovered using any of the multiresidue methods. These data were forwarded to the US FDA for further evaluation.

**860.1380 Storage Stability**

**DER for MRID #46346802 (Grape Field Trials)**
**DER for MRID #46357301 (Potato Field Trials)**
**DER for MRID #46144901 (Sorghum Field Trials)**
**DER for MRID #46482308 (Cotton Field Trials)**

Adequate storage stability data are available indicating that clothianidin is stable at -18°C for intervals of up to 24 months in sugar beet roots, corn (grain, forage, and straw), and canola seed (Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003). Data are also available indicating that clothianidin is stable in frozen apples and apple juice for intervals of up to 15 months (Residue Chemistry Summary Document, D287182, William Cutchin, 7/13/2004).

In conjunction with the current grape and potato field trials, the petitioner conducted studies examining the stability of clothianidin and TMG in grapes and potatoes. Control samples of grapes and potatoes were fortified separately with clothianidin and TMG (each at 0.500 ppm), then stored at -20°C for intervals of up to 6 months. Corrected recoveries of clothianidin and TMG were 100% and 99% in grapes after 5.3 months of storage, and 104% and 96% in potatoes after 6 months of storage. In the current field trials, samples of grapes were stored frozen for durations of up to roughly 3 months and samples of potatoes were stored frozen for durations of up to roughly 5 months prior to analysis. In the grape processing studies, whole fruit were stored frozen for approximately 2 months, while juice and raisins were stored frozen for no more than 30 days prior to analysis. In the potato processing studies, whole tubers and all processed fractions were stored frozen for no more than 17 days prior to analysis.

Samples of sorghum commodities were stored frozen from collection to analysis for durations of up to 11 months. Samples of cotton commodities were stored frozen from collection to analysis for durations of up to 10 months. Storage stability data are available on corn, sugar beet and canola matrices indicating that clothianidin is stable in frozen storage for intervals of up to 24 months (MRID #45422611). These data will support the current cotton and sorghum field trials.

***Conclusions:*** The available storage stability data are adequate and support the current sorghum, cotton, grape, and potato field trials and processing studies.

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

As there are no significant livestock feed items associated with grapes, the proposed use on grapes will not alter the previously estimated dietary exposure of livestock to clothianidin. However, the proposed uses on sorghum, cotton, and potatoes may lead to residues in sorghum and cotton commodities, and potato culls, which are potentially significant livestock feed items. Based on the current and proposed tolerances, the MTDBs of clothianidin residues for livestock are calculated below (see Table 4). Because clothianidin is also a metabolite of thiamethoxam, the previously calculated MTDBs (Residue Chemistry Summary Document, D282446, Yan

Donovan, 5/1/2003) also considered the potential contribution of clothianidin resulting from the use of thiamethoxam. The previously estimated values for corn commodities were included in the residues in Table 4. The recalculated MTDBs are 0.321 ppm for dairy cattle, 0.287 ppm for beef cattle, 0.020 ppm for poultry, and 0.035 ppm for swine.

**TABLE 4 Calculation of MTDBs of Clothianidin Residues for Livestock.**

| Feed Commodity | % Dry Matter[1] | % of Diet[1] | Residues (ppm)[2] | Dietary Contribution (ppm)[3] |
|---|---|---|---|---|
| **Dairy Cattle** | | | | |
| Corn, Field (Forage) | 40 | 50 | 0.140 | 0.175 |
| Corn, Sweet (Forage) | 48 | 50 | 0.140 | 0.146 |
| **TOTAL BURDEN** | | 100 | | **0.321** |
| **Beef Cattle** | | | | |
| Corn, Field (Forage) | 40 | 40 | 0.140 | 0.140 |
| Corn, Sweet (Forage) | 48 | 40 | 0.140 | 0.117 |
| Corn, Field (Stover) | 83 | 20 | 0.125 | 0.030 |
| **TOTAL BURDEN** | | 100 | | **0.287** |
| **Poultry** | | | | |
| Corn, Field (Grain) | NA[4] | 80 | 0.020 | 0.016 |
| Corn, Pop (Grain) | NA | 20 | 0.020 | 0.004 |
| **TOTAL BURDEN** | | 100 | | **0.020** |
| **Swine** | | | | |
| Potato Culls | NA | 50 | 0.050 | 0.025 |
| Corn, Field (Grain) | NA | 50 | 0.020 | 0.010 |
| **TOTAL BURDEN** | | 100 | | **0.035** |

1. From OPPTS Residue Chemistry Test Guideline 860.1000, Table 1 (August 1996).
2. The residues in corn forage and stover include the proposed tolerance plus estimated residues of clothianidin resulting from the use of thiamethoxam, of which clothianidin is a metabolite.
3. Dietary Contribution = [(Residues ÷ %DM) x %Diet]. NOTE: %DM is only used for cattle.
4. NA = Not Applicable.

An adequate ruminant feeding study is available and was reviewed in conjunction the petition for tolerances on corn and canola (PP#1F6315). In this study, dairy cows were dosed daily with clothianidin for 28 consecutive days at levels equivalent to 0.26 ppm, 0.80 ppm, and 2.56 ppm in the diet. These dose levels are equivalent to 0.8X, 2.5X and 8X the MTDB for dairy cattle, and 0.9X, 2.8X and 9X the MTBD for beef cattle. Samples of milk were collected throughout the dosing period, and samples of muscle, kidney, liver, and fat were collected from each animal at sacrifice. Samples of milk from all three dose groups were analyzed for residues of clothianidin, TZU, TZG, and ATMG-pyruvate using the LC/MS/MS method (Method 00624), which has been recommended for tolerance enforcement. Samples of tissues from only the two highest dose groups were analyzed using the same method. The method LOQ for each analyte is 0.010 ppm in milk and 0.020 ppm in each tissue.

Residues of clothianidin and the three metabolites were each below the LOQ (less than

0.020 ppm) in all tissues samples from the 0.80 and 2.56 ppm dose groups, while residues of the three metabolites were also below the LOQ (less than 0.010 ppm) in all samples of milk from all three dose groups. Residues of clothianidin were no more than 0.012 ppm in milk from the highest dose and were below the LOQ in all milk samples from the low and middle dose levels.

Based on the current MTDBs for dairy and beef cattle (0.321 and 0.287 ppm) and the above residue data, the current 0.10 ppm (LOQ) tolerance for residues in milk is adequate and tolerances are not required for meat, meat-byproducts, or fat of cattle, goats, horses, or sheep. Based on the MTDB for swine (0.035 ppm) and the residue data from the highest dose group (72X the MTDB for swine), separate tolerances are not required for hog commodities.

A poultry feeding study has not been conducted. However, considering the TRR levels in eggs and tissues from the poultry metabolism study, in which hens were dosed at 140 ppm (roughly 7000X the MTDB), quantifiable residues of clothianidin and its regulated metabolites are unlikely to occur in hens dosed at up to 10X the MTDB (40CFR §180.6[a][3]). Therefore, a poultry feeding study and tolerances for poultry commodities are not required for the current petitions.

***Conclusions:*** The current tolerance for clothianidin residues in milk is adequate and tolerances are not required for meat, meat-byproducts, nor fat from cattle, goat, hogs, horses, or sheep. A poultry feeding study and tolerances for residues in poultry tissues and eggs are not required at the present time.

## 860.1500 Crop Field Trials

**DER for MRID #46346802 (Grape Field Trials)**
**DER for MRID #46357301 (Potato Field Trials)**
**DER for MRID #46357302 (Potato Field Trials)**
**DER for MRID #46144901 (Sorghum Field Trials)**
**DER for MRID #46482308 (Cotton Field Trials)**

To support tolerances on grapes and potatoes, Arvesta has submitted grape and potato field trial data from throughout the US (with one potato field trial in Canada) using both the 50% WDG and 16% WSG formulations. To support tolerances on sorghum and cotton, Bayer CropScience has submitted sorghum and cotton field trial data from throughout the US using the 48% FC and 14% FC formulations on sorghum and cotton, respectively. The results of the sorghum, cotton, grape, and potato field trials are summarized in Table 5 and discussed below.

**TABLE 5 Summary of Residue Data from Crop Field Trials with Clothianidin.**

| Commodity | Formulation | Application Type | Total Use Rate | Analyte | PHI (Days)[1] | Residues (ppm)[2] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | n | Min. | Max. | HAFT[3] | Mean | Std. Dev. |
| **Grape (MRID #46346802)** | | | | | | | | | | | |
| Fruit | 50% WDG | Foliar Broadcast | 0.196-0.203 lb ai/A | Clothianidin | 0 | 24 | 0.040 | 0.278 | 0.277 | 0.139 | 0.098 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | 16% WSG | Drip-Irrigation Soil | 0.197-0.199 lb ai/A | Clothianidin | 30 | 20 | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| **Potato (MRID #46357301)** | | | | | | | | | | | |
| Tuber | 50% WDG | In-Furrow Soil | 0.200-0.202 lb ai/A | Clothianidin | 84-145 | 4 | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | Foliar Broadcast | 0.201 lb ai/A | Clothianidin | 0-28 | 20 | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | 16% WSG | In-Furrow Soil | 0.196-0.198 lb ai/A | Clothianidin | 84-145 | 4 | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | Side-Dress Soil | 0.194-0.197 lb ai/A | Clothianidin | 48-110 | 4 | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| **Potato (MRID #46357302)** | | | | | | | | | | | |
| Tuber | 50% WDG | Foliar Broadcast | 0.194-0.207 lb ai/A | Clothianidin | 13-14 | 29 | <0.020 | 0.021 | 0.021 | 0.011 | 0.004 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |
| | 16% WSG | In-Furrow Soil | 0.196-0.204 lb ai/A | Clothianidin | 85-134 | 30 | <0.020 | 0.033 | 0.031 | 0.014 | 0.007 |
| | | | | TMG | | | <0.020 | <0.020 | <0.020 | <0.020 | 0 |

**TABLE 5 Summary of Residue Data from Crop Field Trials with Clothianidin.**

| Commodity | Formulation | Application Type | Total Use Rate | Analyte | PHI (Days)[1] | Residues (ppm)[2] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | n | Min. | Max. | HAFT[3] | Mean | Std. Dev. |
| **Sorghum (MRID #46144901)** | | | | | | | | | | | |
| Grain | 48% FC | Seed Treatment | 0.25 lb ai/100 lb Seeds | Clothianidin | 97-167 | 24 | <0.010 | <0.010 | <0.010 | <0.010 | 0 |
| Forage | | | | | 42-112 | | <0.010 | <0.010 | <0.010 | <0.010 | 0 |
| Stover | | | | | 97-167 | | <0.010 | <0.010 | <0.010 | <0.010 | 0 |
| **Cotton (MRID #46482308)** | | | | | | | | | | | |
| Cottonseed | 14% FC | Seed Treatment | 0.35 lb ai/100 lb Seeds | Clothianidin | 116-213 | 24 | <0.010 | <0.010 | <0.010 | <0.010 | 0 |
| Gin Byproducts | | | | | 116-175 | 12 | <0.010 | <0.010 | <0.010 | <0.010 | 0 |

1. For foliar applications of 50% WDG, the proposed PHIs are 0 and 14 days for grapes and potatoes, respectively. For the drip-irrigation application to grapes of 16% WSG, the PHI is 30 days. No PHI is specified for the early season application of 16% WSG to potatoes for either in-furrow or side-dress application.
2. The LOQ is 0.020 ppm for each analyte in both grapes and potatoes, and the LOD is 0.007 ppm. For calculation of the mean and standard deviation (for trials where some sample residues were below the LOQ and others were above it), half the LOQ was used for samples with residues less than the LOQ.
3. HAFT = Highest Average Field Trial.

## Grape

**DER for MRID #46346802 (Grape Field Trials)**

Twelve grape field trials were conducted during 2003 throughout the US. With the exception of the two trial sites in NY, side-by-side tests were conducted at each site comparing the use of clothianidin as either a single drip-irrigation application using 16% WSG at a rate of 0.197to 0.199 lb ai/A (essentially 1X the proposed maximum seasonal use rate of 0.20 lb ai/A), or as two foliar broadcast applications using 50% WDG at a rate of 0.098 to 0.101 lb ai/A per application, for a total rate of 0.196 to 0.203 lb ai/A per season (1X rate). Both the drip-irrigation and foliar applications were applied during fruit development, with an RTI of 13 to 14 days for the two foliar applications. No adjuvants were added to the spray tank at any of the field trials for either type of application. Two of the field trials (California and Washington) also included another test in which the 16% WSG formulation was applied as two drip-irrigation applications during fruit development, at a rate of 0.099 lb ai/A, with an RTI of 90 to 101 days, for a total rate of 0.198 lb ai/A per season (1X rate). Grapes were harvested at commercial maturity, 0 DAT for the foliar treatment and 30 DAT for the drip-irrigation treatment. Additional grape samples from one trial site were harvested at 7, 14, and 21 DAT (foliar treatment), and at 23, 37, and 44 DAT (drip treatment) to examine residue decline. Single control and duplicate treated samples were collected from each test. Samples were stored frozen from collection to analysis for up to 3 months, a duration supported by storage stability data on grapes.

Residues of clothianidin and its metabolite, TMG, were determined using LC/MS/MS methods (Morse Methods #Meth-157 and #Meth-164) which were adequately validated in conjunction with the sample analyses. For both methods, the validated LOQ for both analytes is 0.020 ppm in grapes, and the LOD is 0.007 ppm.

Following either one or two drip-irrigation applications of clothianidin (16% WSG) totaling roughly 0.20 lb ai/A, residues of clothianidin were less than 0.020 ppm (the LOQ) in all 24 grape samples harvested 30 DAT. For the two foliar broadcast applications, residues of clothianidin were 0.040 to 0.278 ppm in 24 grape samples harvested 0 DAT. For the foliar applications, average residues of clothianidin were 0.139 ppm and HAFT residues were 0.277 ppm. Residues of metabolite TMG were no more than 0.007 ppm (the LOD) in all grape samples regardless of the application regime.

In the decline trial, clothianidin residues in grapes treated with 16% WSG were less than 0.020 ppm (the LOQ) at all intervals. For the 50% WDG treatment, the clothianidin residues in grapes treated foliarly decreased steadily from 0 DAT (0.136 to 0.139 ppm) to 21 DAT (0.056 to 0.066 ppm).

## Potato

**DER for MRID #46357301 (Potato Field Trials)**

In preliminary trials conducted at two sites in the US and Canada during 2002, side-by-side tests were conducted comparing applications of the 50% WDG and 16% WSG formulations of clothianidin. A total of four treatments were used at each site. In two of these tests, clothianidin (50% WDG) was applied as either a single in-furrow application (at planting) at a rate of 0.20 lb ai/A (1X rate for soil treatment) or as three foliar broadcast applications (during tuber development) at a rate of 0.066 to 0.068 lb ai/A per application, with RTIs of 7 days, for a total rat of 0.20 lb ai/A per season (roughly 1.4X the proposed maximum seasonal use rate for foliar treatment). In the other two tests, clothianidin (16% WSG) was applied at a rate of 0.194 to 0.198 lb ai/A (1X rate) as either a single in-furrow application (at planting), or as a single

side-dress application on either side of the hill (after crop emergence). Potato tubers were harvested at commercial maturity, 84 to 145 DAT for the in-furrow application and 48 to 110 DAT for the side-dress treatment. For the foliar applications, tuber samples were harvested at 14 days following the final application, with additional samples collected at 0, 7, 21, and 28 DAT in order to investigate residue decline. Single control and duplicate treated samples were collected from each test. Samples were stored frozen from collection to analysis for up to 5 months, a duration supported by the available storage stability data on potato tubers.

Residues of clothianidin and metabolite TMG were determined using an LC/MS/MS method (Morse Method #Meth-157) which was adequately validated in conjunction with the sample analyses. The validated LOQ for both analytes is 0.020 ppm in potatoes, and the LOD is 0.007 ppm.

Regardless of the application regime, residues of both clothianidin and metabolite TMG were less than 0.020 ppm (the LOQ) in all samples of potato tubers harvested following either a single soil application or multiple foliar applications totaling roughly 0.20 lb ai/A. Detectable residues below the LOQ (0.010 to 0.019 ppm) were observed in only 4 samples from the Canadian trial site treated with either the 50% WDG or 16% WSG formulations as an in-furrow application at planting.

**DER for MRID #46357302 (Potato Field Trials)**

Fifteen potato field trials were conducted during 2003 throughout the US. At each site, side-by-side tests were conducted comparing the use of clothianidin as either a single in-furrow application (at planting) using the 16% WSG formulation at a rate of 0.194 to 0.207 lb ai/A (1X rate), or as three foliar broadcast applications using a 50% WDG formulation at a rate of 0.064 to 0.069 lb ai/A per application, for a total rate of 0.196 to 0.204 lb ai/A per season (roughly 1.4X rate). The foliar applications were made during tuber development with RTIs of 6 to 8 days; no spray adjuvants were used for any of the applications at any of the field trials. Potato tubers were harvested at commercial maturity, 85 to 134 DAT for the in-furrow tests and 13 to 14 DAT for the foliar tests. Additional tuber samples from two trial sites were harvested at 121, 128, and 135 DAT (in-furrow treatment) and at 0, 21, and 28 DAT (foliar treatment) to examine residue decline. Single control and duplicate treated samples were collected from each test. Samples were stored frozen from collection to analysis for up to 3 months, a duration supported by storage stability data on potato.

Residues of clothianidin and metabolite TMG were determined using LC/MS/MS methods (Morse Methods #Meth-157 and #Meth-164) described above, which were adequately validated in conjunction with the sample analyses. For both methods, the validated LOQ for both analytes is 0.020 ppm in potatoes, and the LOD is 0.007 ppm.

Residues of metabolite TMG were non-detectable (less than 0.007 ppm) in all potato samples from all trials using either formulation. For the in-furrow application using 16% WSG, residues of clothianidin in tubers harvested 85 to 134 DAT were less than 0.020 ppm (the LOQ) in 21 out of 30 samples, and were 0.020 to 0.033 ppm in the remaining 9 samples. For the foliar applications using 50% WDG, residues of clothianidin in tubers harvested 13 to 14 DAT were less than 0.020 ppm (the LOQ) in 27 out of 29 samples, and were 0.020 and 0.021 ppm in the remaining 2 samples. Average residues of clothianidin were 0.014 ppm for the in-furrow applications and 0.011 ppm for the foliar applications, while HAFT residues for clothianidin were 0.031 ppm following the in-furrow application and 0.021 ppm following the foliar application. Because residues of clothianidin were less than the LOQ in all samples from the

two field trials having repeated sampling intervals, residue decline could not be reliably determined.

**Sorghum**

**DER for MRID #46144901 (Sorghum Field Trials)**

In a total of 12 sorghum field trials conducted in 2001, clothianidin formulated as the 48% FC was applied as a single seed treatment to grain sorghum at 0.25 lb ai/100 lb seeds using commercial seed treatment equipment. Based on the seeding rates used at the various field trial sites (roughly 38,000 to 133,000 seeds/A, which are typical for sorghum production), the actual field use rates were equivalent to 0.006 to 0.026 lb ai/A. Sorghum forage was harvested at 42 to 112 days after planting (DAP), while sorghum stover and grain were harvested at commercial maturity, 97 to 167 DAP. A single control and duplicate treated samples were collected from each trial. Samples were stored frozen from collection to analysis for up to 11 months, a duration supported by available storage stability data.

The LC/MS/MS method used to determine clothianidin residues in/on sorghum forage, stover, and grain (Bayer Method 109240-1) is a current tolerance-enforcement method and was adequately validated in conjunction with the field trial analyses. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum forage, stover, and grain. The LOD is 0.005 ppm for forage, 0.010 ppm for stover, and 0.003 ppm for grain.

Residues of clothianidin were less than 0.010 ppm (the LOQ) in all samples of sorghum forage, stover, and grain (n = 24 per matrix).

**Cotton**

**DER for MRID #46482308 (Cotton Field Trials)**

In a total of 12 cotton field trials conducted in 2003, clothianidin formulated as the 14% FC was applied to cottonseed as a single seed treatment at 0.35 lb ai/100 lb seeds using commercial seed treatment equipment. Based on the seeding rates used at the various field trial sites (roughly 41,000 to 78,000 seeds/A), the actual field use rates were equivalent to 0.034 to 0.060 lb ai/A. Cottonseed and gin byproducts were harvested at commercial maturity, 116 to 213 DAP. Single control and duplicate treated cottonseed samples were collected from each trial; gin byproducts samples were also collected from 6 trials, using either a mechanical picker (at 3 trials) or stripper (at the other 3 trials). Samples were stored frozen from collection to analysis for up to 10 months, a duration supported by available storage stability data.

The LC/MS/MS method used to determine clothianidin residues in/on cottonseed and gin byproducts (Bayer Method 109240-1) is a current tolerance-enforcement method and was adequately validated in conjunction with the field trial analyses. The validated LOQ for clothianidin residues is 0.010 ppm for cottonseed and gin byproducts. The LOD is 0.003 ppm for cottonseed and 0.005 ppm for gin byproducts.

Residues of clothianidin were less than 0.003 ppm (the LOD) in all samples of cottonseed (n = 24) and less than 0.005 ppm (the LOD) in all gin byproducts (n = 12).

***Conclusions:*** The available field trial data are adequate and will support the proposed use patterns for clothianidin on sorghum, cotton, grapes, and potatoes. The number and geographic distribution of the field trials are adequate, and the appropriate samples were collected at the proposed PHIs. The samples were analyzed using adequate analytical methods and the sample storage intervals are supported by the available storage stability data. The available field trial data indicate that residues will not exceed the proposed tolerances of 0.01

ppm on sorghum and cotton commodities, nor the recommended tolerances of 0.05 ppm on potatoes, 0.08 ppm on potato granules/flakes, or 0.60 ppm on grapes.

## 860.1520 Processed Food and Feed

**DER for MRID #46346802 (Grape Field Trials)**
**DER for MRID #46357302 (Potato Field Trials)**
**DER for MRID #46144902 (Sorghum Processed Food and Feed)**
**DER for MRID #46482309 (Cotton Processed Food and Feed)**

Arvesta has submitted data from grape and potato processing studies reflecting both foliar broadcast applications of clothianidin (with 50% WDG) and drip-irrigation applications (with 16% WSG) at exaggerated rates (roughly 5X for grapes and soil treatment to potatoes, roughly 7X for foliar treatment to potatoes). Because residues in grapes from the drip application were less than the LOQ, only results from the foliar application processing study are presented in Table 6. For the potatoes, processing factors were determined from both processing studies (see Table 7) and then averaged.

Bayer CropScience has submitted data from sorghum and cotton processing studies reflecting seed treatment of sorghum grain (2X rate) and cottonseed (roughly a 5X rate) with the 48% FC formulation. Residues in three samples of sorghum grain were non-detectable (less than 0.003 ppm). Residues in three samples of undelinted cottonseed were all less than the LOQ (0.010 ppm).

**TABLE 6 Residue Data from Grape Processing Study with Clothianidin.**

| Processed Commodity | Total Rate (lb ai/A) | PHI (Days) | Residues (ppm)[1] | | Processing Factor | |
|---|---|---|---|---|---|---|
| | | | Clothianidin | TMG | Clothianidin | TMG |
| Fruit (RAC) | 0.992 **5X Rate** | 0 | 0.738, 0.504 [0.621] | ND[2], ND [0.004] | NA[3] | NA |
| Juice | | | 0.712, 0.702 [0.707] | ND, 0.003 [0.004] | 1.1 | 1.0 |
| Raisins | | | 0.947, *1.02, 1.03*[4] 0.992, *1.05, 1.07* [1.02] | 0.352, *0.377, 0.396* 0.338, *0.362, 0.331* [0.359] | 1.6 | 90 |

1. The validated LOQ values for clothianidin residues are 0.040 ppm for raisins, and 0.020 ppm for whole fruit and juice. The LOD is 0.013 ppm for raisins, and 0.007 ppm for whole fruit and juice. Average residues are reported in brackets. For calculation of average residues, ½LOD was used for samples reported as ND.
2. ND = Not Detected (less than the LOD).
3. NA = Not Applicable.
4. Residues in *italics* are the replicate analyses of a single sample.

**TABLE 7 Residue Data from Potato Processing Study with Clothianidin.**

| Potato Processed Commodity | Treatment | Total Rate (lb ai/A) | PHI (Days) | Residues (ppm)[1] | | Processing Factor[3] | Average Processing Factor |
|---|---|---|---|---|---|---|---|
| | | | | Clothianidin[2] | TMG | | |
| Tuber [RAC] | In-furrow | 0.986 **5X Rate** | 124 | 0.030, 0.021 [0.026] | ND[4] | NA[5] | NA |
| | Foliar | 1.01 **7X Rate** | 14 | *0.013, 0.011 [0.012]* | ND | NA | |

| TABLE 7 Residue Data from Potato Processing Study with Clothianidin. | | | | | | | |
|---|---|---|---|---|---|---|---|
| Potato Processed Commodity | Treatment | Total Rate (lb ai/A) | PHI (Days) | Residues (ppm)[1] | | Processing Factor[3] | Average Processing Factor |
| | | | | Clothianidin[2] | TMG | | |
| Granules/ Flakes | In-furrow | 0.986 **5X Rate** | 124 | 0.051, 0.058 [0.055] | ND | 2.1 | 2.3 |
| | Foliar | 1.01 **7X Rate** | 14 | 0.033, 0.031 [0.032] | ND | 2.6 | |
| Chips | In-furrow | 0.986 **5X Rate** | 124 | *0.029, 0.039 [0.034]* | ND | 1.3 | 1.4 |
| | Foliar | 1.01 **7X Rate** | 14 | *0.019, 0.017 [0.018]* | ND | 1.5 | |
| Wet Peel | In-furrow | 0.986 **5X Rate** | 124 | *0.007, 0.007 [0.007]* | ND | 0.3 | 0.5 |
| | Foliar | 1.01 **7X Rate** | 14 | *0.007, 0.008 [0.008]* | ND | 0.7 | |

1. For each analyte, the LOQ is 0.040 ppm (potato chips), and 0.020 ppm (potato tubers, granules/flakes, and wet peel). The LOD is 0.013 ppm (potato chips), and 0.007 ppm (potato tubers, granules/flakes, and wet peel).
2. Residue values in *italics* are between the LOD and the LOQ [average residues are presented in brackets].
3. The processing factor was calculated using the average residues of Clothianidin only in the potato RAC and processed fractions.
4. ND = Not detected (less than the LOD).
5. NA = Not Applicable.

## Grape

**DER for MRID #46346802 (Grape Field Trials)**

Clothianidin was applied to grapes in two side-by-side tests in 2003 using either the 50% WDG or the 16% WSG formulation. The 50% WDG formulation was applied as two foliar broadcast applications (during fruit development) at a total rate of 0.99 lb ai/A (5X), and the 16% WSG formulation was applied (during fruit development) as a single drip-irrigation application at 0.992 lb ai/A (5X). Grapes, the raw agricultural commodity (RAC) were harvested at commercial maturity, 0 DAT for the foliar application, and 30 DAT for the drip application. A single bulk sample of grapes was collected for processing from each test, and duplicate treated samples for each matrix were collected either prior to (whole grapes) or after (juice and raisins) processing. Prior to analysis, whole fruit were stored frozen for roughly 2 months, a duration supported by the available storage stability data, while juice and raisin samples were analyzed within 1 month.

Residues of clothianidin and metabolite TMG were determined using an LC/MS/MS method (Morse Method #Meth-164) which was adequately validated in conjunction with the processing study. For each analyte, the validated LOQs are 0.020 ppm in grapes and juice, and 0.040 ppm in raisins; the LODs are 0.007 ppm for whole fruit and juice, and 0.013 ppm for raisins.

Residues of both clothianidin and TMG were each less than the LOQ in grapes, juice and raisins resulting from the drip-irrigation application at 5X; therefore, processing factors could not be calculated for these samples. However, residues were detectable in samples from the foliar application. For the 5X foliar applications, average residues of clothianidin were 0.621, 0.707, and 1.02 ppm in whole fruit, juice, and raisins, respectively, while average residues of TMG were less than 0.004, less than or equal to 0.004, and 0.359 ppm, respectively. Residues of

clothianidin concentrated by 1.1X in juice and 1.6X in raisin, and residues of TMG concentrated by 1X in juice and roughly 90X in raisins (it is possible that TMG is formed during raisin production). Based on the average combined residues (expressed in parent equivalents), concentration factors for the combined residues would be 1.1X in juice and 2.3X in raisins.

The reported processing factors do not exceed the maximum theoretical concentration factors of 1.2X and 4.7X for grape juice and raisins, respectively (from Tables 2 and 3 of OPPTS Residue Chemistry Test Guideline 860.1520).

## Potato

**DER for MRID #46357302 (Potato Field Trials)**

Clothianidin was applied to potatoes in side-by-side tests using the 50% WDG and 16% WSG formulations. The 16% WSG formulation was applied to potatoes as a single in-furrow application at 0.986 lb ai/A (5X rate) at planting, and the 50% WDG formulation was applied during tuber development as three foliar broadcast applications totaling 1.01 lb ai/A/season (7X rate). Potato tubers were harvested at commercial maturity, 124 DAT for the 16% WSG formulation, and 14 DAT for the 50% WDG formulation. Duplicate subsamples of potato tubers (the RAC) were collected and the remaining bulk samples were processed into granules, chips, and wet peel using simulated commercial procedures. Prior to analysis, whole tubers and each processed fraction were stored frozen for up to 17 days; therefore, supporting storage stability data are not required.

Residues of clothianidin and metabolite TMG were determined using an LC/MS/MS method (Morse Method #Meth-164) which was adequately validated in conjunction with the processing study. For each analyte, the validated LOQs are 0.020 ppm in whole tubers, granules, and wet peel, and 0.040 ppm in chips; the LODs are 0.007 ppm for whole tubers, granules, and wet peel, and 0.013 ppm for chips.

Residues of metabolite TMG were non-detectable (less than 0.007 ppm, the LOD) in all samples of tubers and processed commodities from tests using either formulation. For the trial using the 16% WSG formulation, residues of clothianidin averaged 0.026 ppm in tubers, 0.055 ppm in granules, 0.034 ppm (less than the LOQ) in chips, and 0.007 ppm (less than the LOD) in wet peel. For the trial using the 50% WDG formulation, residues of clothianidin averaged 0.012 ppm (less than the LOQ) in tubers, 0.032 ppm in granules, 0.018 ppm (less than the LOQ) in chips, and 0.008 ppm (less than the LOQ) in wet peel. The calculated processing factors for each matrix were similar regardless of the treatment regime. Average processing factors were 2.3X for granules/flakes, 1.4X for chips and 0.5X for wet peel.

The reported processing factor for granules/flakes does not exceed the maximum theoretical concentration factor of 4.7X (from Table 2 of OPPTS Residue Chemistry Test Guideline 860.1520). The guidelines do not address concentration factors for chips nor wet peel.

## Sorghum

**DER for MRID #46144902 (Sorghum Processed Food and Feed)**

Clothianidin formulated as 48% FC was applied as a single seed treatment to grain sorghum at a rate of 0.50 lb ai/100 lb seeds (2X the proposed maximum use rate) using a commercial seed treater. The seeds were planted at a single field trial site in Mississippi during 2001; based upon the actual seeding rate of 72,906 seeds/A, the field use rate was equivalent to 0.024 lb ai/A. Bulk samples of sorghum grain were harvested at commercial maturity, 134 DAP. Prior to analysis, sorghum RAC samples were stored frozen for a maximum of approximately 9 months, a duration supported by available storage stability data.

The LC/MS/MS method used to determine clothianidin residues in/on sorghum forage, stover, and grain (Bayer Method 109240-1) is a current tolerance-enforcement method and was adequately validated in conjunction with the field trial analyses. The validated LOQ for clothianidin residues is 0.010 ppm in sorghum grain and the LOD is 0.003 ppm.

Residues in three subsamples of sorghum grain harvested at maturity were non-detectable (less than 0.003 ppm).

**Cotton**

**DER for MRID #46482309 (Cotton Processed Food and Feed)**

In cotton, residues in three samples of undelinted cottonseed (harvested at maturity and ginned following treatment at 5X the proposed label's maximum use rate) were all less than the LOQ (0.010 ppm). Considering that residues were less than the LOQ in cottonseed treated at a 5X rate, and that the application to cotton is made as a seed treatment, residue data on processed commodities derived from cotton were not generated. The registrant submitted a request for waiver of the requirement for a cotton processing study.

***Conclusions:*** The available processing data are adequate. Samples were analyzed using adequate methodology and are supported by the available storage stability data. For grapes, residues of clothianidin concentrated slightly in juice (1.1X) and by 1.6X in raisins. Based on the HAFT residues from the grape field trials (0.277 ppm) and the above processing factor for raisins, the maximum expected residues of clothianidin in raisins would be 0.443 ppm. As this residue level is below the recommended tolerance of 0.60 ppm on grapes, a separate tolerance for raisins is not required.

For potatoes, processing factors determined from the two processing studies were similar for each matrix. Residues of clothianidin were reduced in wet peel (0.5X), but concentrated in granules (2.3X) and chips (1.4X). Based on HAFT residues of 0.031 ppm for whole tubers, the maximum expected residues in granules/flakes and chips would be 0.071 and 0.043 ppm, respectively. As the maximum expected residue level in chips is less than the recommended tolerance of 0.05 ppm on potatoes, a separate tolerance is not required on chips. Based on the maximum expected residues in potato granules/flakes, HED is recommending a tolerance be established at 0.08 ppm on this processed food.

For sorghum, residues in three subsamples of grain harvested at maturity were non-detectable (less than 0.003 ppm). Considering that residues were less than a third of the LOQ in grain treated at 2X the proposed label's maximum use rate, and that the application to sorghum is made as a seed treatment, residue data on aspirated grain fractions derived from sorghum are not required. In addition, the Agency does not currently require processing data on sorghum's processed commodity, flour.

In cotton, residues in three samples of undelinted cottonseed (harvested at maturity and ginned following treatment at 5X the proposed label's maximum use rate) were all less than the LOQ (0.010 ppm). The registrant (Bayer CropScience) submitted a request for waiver of the requirement for a cotton processing study. HED recommends that the waiver be granted (no cotton processing data are required).

**860.1650 Submittal of Analytical Reference Standards**

An analytical reference standard for clothianidin has been submitted to the EPA National Pesticide Standards Repository.

## 860.1850 Confined Accumulation in Rotational Crops

**MARC Decision Memo, D282449, Yan Donovan, 4/25/2003**
**Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003**

Because sorghum, cotton, and potatoes are rotated crops, the potential for residues occurring in rotational crops must be considered for the proposed new uses. An adequate confined rotational crop study was submitted in conjunction with the petition for use on canola and corn (Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003). Rotational crops of turnips, Swiss chard, and wheat were planted approximately 1, 5, and 10 months following a single soil application of [$^{14}$C]-clothianidin at the rate of 0.293 lb ai/A (roughly a 1.5X rate) and samples of the appropriate RACs were harvested at maturity. The metabolism of clothianidin in rotational crops was similar to the primary crops and included:

(1) hydrolysis of clothianidin to form TZMU,
(2) de-nitrification of clothianidin to form TMG,
(3) loss of the thiazolyl-methyl moiety (C-N bond cleavage) from clothianidin to form MNG,
(4) de-nitrification of MNG and C-N bond cleavage of TMG to form MG,
(5) N-de-methylation of clothianidin to form TZNG,
(6) N-de-methylation of MNG and C-N bond cleavage of TZNG to form NTG, and
(7) N-de-methylation of TZMU and hydrolysis of TZNG to form TZU.

Based on the confined study, the MARC concluded that parent, TZNG and MNG are the ROCs in rotational crops and that only parent needs to be included in the tolerance expression.

## 860.1900 Field Accumulation in Rotational Crops

Adequate limited field rotational crop studies were submitted in conjunction with the petition for use on canola and corn (Residue Chemistry Summary Document, D282446, Yan Donovan, 5/1/2003). In these studies, trials were conducted in which mustard greens, turnips, and wheat were planted 1, 4, 8, and 12 months following a single seed treatment to corn at rates equivalent to 0.144 to 0.171 lb ai/A at 10 or 11 field trial sites.

Considering the proposed maximum use rates on potatoes (0.14 and 0.20 lb ai/A per season for foliar and soil treatments, respectively), these limited trials were conducted at 0.7X to 0.9X the maximum proposed use rate for potatoes and will be considered acceptable for supporting the use on potatoes. Also, given that the proposed maximum use rates for the sorghum and cotton seed treatments equate to field application rates of significantly less than 0.10 lb ai/A, the limited field rotational crop trials will support the uses on sorghum and cotton. Therefore, the Agency's earlier conclusions pertaining to rotational crop tolerances and planting restrictions will apply to the use on potatoes.

Bayer CropScience has requested label amendments (for the 48% FC formulation) allowing plant-back intervals (PBIs) to be reduced to 30 days for potatoes and 8 months for sugarcane after the planting of corn, rapeseed, or canola that received seed treatment with clothianidin. Justification for the reduced potato PBI is based on the residue profile (less than the LOQ of 0.010 ppm) in turnip root from the limited field rotational crop study, while the rationale for reducing the sugarcane PBI is based on the much greater biomass of sugarcane relative to wheat (roughly 18:1), leading to calculated residues of clothianidin in rotated sugarcane of no more than 0.001 ppm. Also, Gustafson has submitted a request for label amendments (48% FC) reducing the maximum application rate for sweet corn to 0.25 mg ai/seed, allowing the PBI to be reduced to 30 days for root and tuber vegetables (Crop Group 1), and allowing the PBI to be reduced to 4 months for all other rotated crops after the planting of

sweet corn, canola, rapeseed, or sorghum that received seed treatment with clothianidin. The justification for reducing the PBI for root and tuber vegetables is identical to that described above, while the rationale for reducing the PBI for all other rotated crops to 4 months following sweet corn, canola, rapeseed, or sorghum is based on the lowered application rate to sweet corn seed and the lower chemical loading (from the perspective of lb ai/A) for canola, rapeseed, and sorghum. The label for 48% FC (Poncho™ 600) should be amended to read as follows:

> Areas planted with treated seed may be replanted immediately with corn, rapeseed, canola, and sorghum. These areas may also be replanted after 30 days with cereal grains, grasses, nongrass animal feeds, soybeans, dried beans, and root and tuber vegetables. These areas may also be replanted after 8 months with sugarcane. Do not plant any other crop in the treated area for at least 1 year after treated field corn or popcorn seeds are planted. Do not plant any other crop in the treated area for at least 4 months after treated sweet corn, canola, rapeseed, or sorghum seeds are planted.

Based on the current tolerances on rotational crops, the proposed labels for grapes and potatoes should be amended to include a plant-back restriction of 30 days for cereal grain crops, grasses, nongrass animal feeds (such as alfalfa), soybeans, and dry beans. A plant-back restriction of 1 year is required for all other rotated crops. If plant-back intervals of less than 1 year are desired by the petitioner, then extensive field rotational crop trials will be required.

**860.1550 Proposed Tolerances**

The MARC has concluded that only parent needs to be included in the tolerance expression. A summary of the proposed and recommended tolerances, along with the correct commodity definitions for the commodities in petitions 4F6869, 3F6792, and 5F6908, is presented in Table 8 (below). The registrant should submit a revised Section F to reflect these changes.

Canadian MRLs have also been established for residues of clothianidin at 0.01 mg/kg in milk, corn and canola (See attached IRL Status sheet), but there are no MRLs for cotton, sorghum, grapes, or potatoes.

**TABLE 8 Tolerance Summary for Clothianidin.**

| Commodity | Proposed Tolerance (ppm) | Recommended Tolerance (ppm) | Comments (*Correct Commodity Definition*) |
|---|---|---|---|
| Grape | 0.50 | 0.60 | *Grape* |
| Raisin | 1.0 | None | Because the maximum expected residue of clothianidin in raisins, 0.44 ppm, is below the recommended tolerance on grapes, a separate tolerance for raisins is not required. *Grape, Raisin* |
| Potato | 0.10 | 0.05 | *Potato* |

**TABLE 8 Tolerance Summary for Clothianidin.**

| Commodity | Proposed Tolerance (ppm) | Recommended Tolerance (ppm) | Comments (*Correct Commodity Definition*) |
|---|---|---|---|
| Potato Granules | None | 0.08 | Because the maximum expected residue of clothianidin in potato granules, 0.071 ppm, is above the recommended tolerance on potatoes, a separate tolerance for granules is required. *Potato, Granules/Flakes* |
| Sorghum Grain | 0.01 | 0.01 | *Sorghum, Grain* |
| Sorghum Forage | 0.01 | 0.01 | *Sorghum, Forage* |
| Sorghum Stover | 0.01 | 0.01 | *Sorghum, Grain, Stover* |
| Cottonseed | 0.01 | 0.01 | *Cotton, Undelinted Seed* |
| Cotton Gin Byproducts | 0.01 | 0.01 | *Cotton, Gin Byproducts* |

## References

DP Barcode: D282446
Subject: *PP#1F6315. TI-435 (Clothianidin) on Corn and Canola. Summary of Analytical Chemistry and Residue Data.*
From: Yan Donovan
To: Daniel Kenny/Meredith Laws
Dated: 5/01/2003
MRID #s: 45422527 to -35, 45422305 & -06, and 45422610 to -19

DP Barcode: D282448
Subject: *Method Review - PP#1F6315. New Chemical - Clothianidin (TI-435) in/on Corn and Canola. Original Request for Petition Method Validation.*
From: Patricia Schermerhorn
To: George Herndon/Meredith Laws
Dated: 7/17/2003
MRID #s: 45422536, -37, & -39, 45422606 & -08

DP Barcode: D287182
Subject: *Clothianidin. Petition for the Permanent Tolerances for the Uses on Apples and Pears and for the Use on Tobacco. Summary of Analytical Chemistry and Residue Data. Petition Number 1F6342.*
From: William Cutchin
To: William Cutchin
Dated: 7/13/2004
MRID #s: 46027101, 45480402 & -03

| INTERNATIONAL RESIDUE LIMIT STATUS | | | |
|---|---|---|---|
| **Chemical Name:** [C(E)]-N-[(2-Chloro-5-thiazolyl)methyl]-*N'*-methyl-N''-nitroguanidine | **Common Name:** Clothianidin | **X Proposed tolerancees**<br>☐ Reevaluated tolerance<br>☐ Other | **Date:** 4/19/2005 |
| Codex Status (Maximum Residue Limits) | | **US Tolerances (recommended)** | |
| X No Codex proposal step 6 or above<br>☐ No Codex proposal step 6 or above for the crops requested | | **Petition Numbers:** 4F6869, 3F6792, 5F6908<br>**DP Barcodes:** D303164, D309473, D309474, D312449, D314533, D318496<br>**Other Identifier:** PC Code 044309 | |
| Residue definition (step 8/CXL): NA | | **Reviewer/Branch:** William T. Drew/RAB2 | |
| | | **Proposed residue definition:** Clothianidin | |

| Crop(s) | MRL (mg/kg) | **Crops (proposed)** | **Tolerance (ppm)** |
|---|---|---|---|
| | | **Grape** | **0.50** |
| | | **Raisin** | **1.0** |
| | | **Potato** | **0.10** |
| | | **Sorghum grain** | **0.01** |
| | | **Sorghum forage** | **0.01** |
| | | **Sorghum stover** | **0.01** |
| | | **Cottonseed** | **0.01** |
| | | **Cotton gin byproducts** | **0.01** |
| | | | |

| Limits for Canada | Limits for Mexico |
|---|---|
| ☐ No Limits<br>X No Limits for the crops requested | X No Limits<br>☐ No Limits for the crops requested |
| Residue definition: Clothianidin | Residue definition: NA |

| Crops | MRL (mg/kg) | Crop(s) | MRL (mg/kg) |
|---|---|---|---|
| Field corn grain | 0.01 | | |
| Popcorn grain | 0.01 | | |
| Rapeseed (canola) | 0.01 | | |
| Sweet corn K+CWHR | 0.01 | | |
| Milk | 0.01 | | |

**NOTES:** per Stephen Funk, 4/16/2005. NA = Not Applicable.

Clothianidin

Summary of Analytical Chemistry and Residue Data

Barcodes: D303164, D309473, D309474, D312449, D314533, D318496

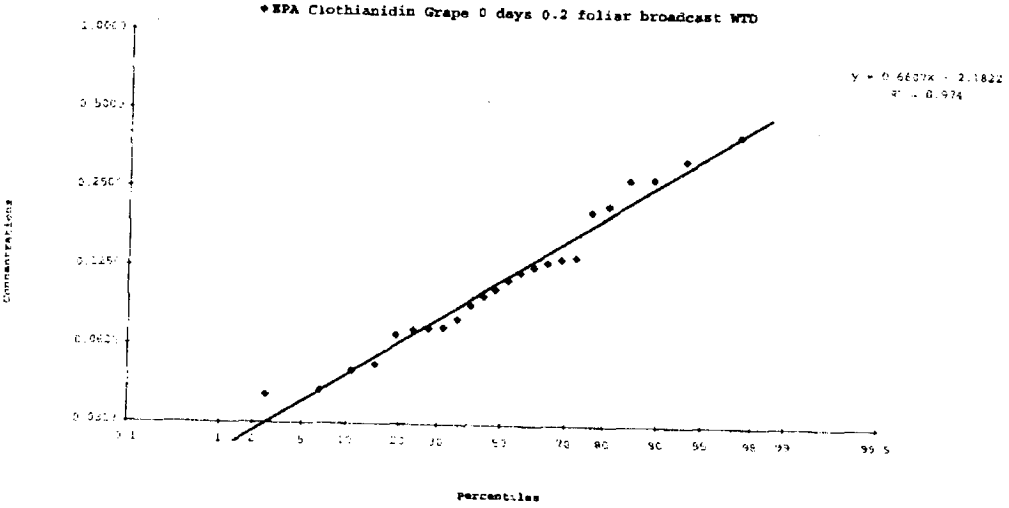
| EPA |
|---|
| Clothianidin |
| Grape |
| 0 days |
| 0.2 foliar |
| WTD |
| Residues |
| 0.069 |
| 0.098 |
| 0.127 |
| 0.104 |
| 0.072 |
| 0.074 |
| 0.275 |
| 0.278 |
| 0.040 |
| 0.042 |
| 0.053 |
| 0.050 |
| 0.080 |
| 0.113 |
| 0.136 |
| 0.139 |
| 0.073 |
| 0.090 |
| 0.121 |
| 0.132 |
| 0.220 |
| 0.410 |
| 0.208 |
| 0.330 |

| | |
|---|---|
| Regulator: | EPA |
| Chemical: | Clothianidin |
| Crop: | Grape |
| PHI: | 0 days |
| App. Rate: | 0.2 foliar broadcast |
| Submitter: | WTD |
| n: | 24 |
| min: | 0.04 |
| max: | 0.41 |
| median: | 0.11 |
| average: | 0.14 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| EU Method I Normal | 0.35 (0.40) | 0.40 (0.50) | 0.45 (--) |
| EU Method I Log Normal | 0.35 (0.60) | 0.60 (0.90) | 0.90 (--) |
| EU Method II Distribution-Free | 0.40 | | |
| California Method $\mu + 3\sigma$ | 0.45 | | |
| UPLMedian95th | 0.70 | | |
| Approximate Shapiro-Francia Normality Test | 0.9740<br>p-value > 0.05 : Do not reject lognormality assumption | | |

Lognormal Probability Plot

♦EPA Clothianidin Grape 0 days 0.2 foliar broadcast WTD



| EPA |
|---|
| Clothianidin |
| Potato (MLE) |
| 85 to 134 days |
| 0.2 in-furrow |
| WTD |
| Residues |
| 0.007 |
| 0.021 |
| 0.008 |
| 0.002 |
| 0.003 |
| 0.003 |
| 0.008 |
| 0.009 |
| 0.004 |
| 0.004 |
| 0.005 |
| 0.005 |
| 0.010 |
| 0.010 |
| 0.011 |
| 0.012 |
| 0.005 |
| 0.006 |
| 0.033 |
| 0.029 |
| 0.006 |
| 0.007 |
| 0.012 |
| 0.013 |
| 0.014 |
| 0.015 |
| 0.029 |
| 0.027 |
| 0.017 |
| 0.018 |

| | |
|---|---|
| Regulator: | EPA |
| Chemical: | Clothianidin |
| Crop: | Potato (MLE) |
| PHI: | 85 to 134 days |
| App. Rate: | 0.2 in-furrow |
| Submitter: | WTD |
| n: | 30 |
| min: | 0.00 |
| max: | 0.03 |
| median; | 0.01 |
| average: | 0.01 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| EU Method I Normal | 0.03<br>(0.04) | 0.04<br>(0.04) | 0.04<br>(--) |
| EU Method I Log Normal | 0.04<br>(0.05) | 0.05<br>(0.09) | 0.09<br>(--) |
| EU Method II Distribution-Free | | 0.04 | |
| California Method $\mu + 3\sigma$ | | 0.04 | |
| UPLMedian95th | | 0.06 | |
| Approximate Shapiro-Francia Normality Test | | 0.9901<br>p-value > 0.05 : Do not reject lognormality assumption | |

Lognormal Probability Plot