Primary Evaluator	William T. Drew, Chemist RAB2/HED (7509C)	Date: 8/15/2005
Approved by	Richard A. Loranger, Branch Senior Scientist RAB2/HED (7509C)	Date: 12/28/2005

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). It has been reviewed by HED and revised to reflect current OPP policies.

STUDY REPORT

MRID #46346802. Sandra J. Carringer (2003) *Magnitude of the Residue of TM-444 and its Metabolite in Grape Raw Agricultural and Processed Commodities*. Study #TCI-03-076. Unpublished study prepared by Arvesta Corporation, Morse Laboratories Incorporated, and The National Food Laboratory Incorporated. 393 pages. {OPPTS Residue Chemistry Test Guideline 860.1500}

EXECUTIVE SUMMARY

Twelve grape field trials with clothianidin were conducted throughout the US during 2003. With the exception of the two field trial sites in New York, side-by-side tests were conducted at each trial site comparing the use of clothianidin as either a single drip-irrigation application (to soil) of a water-soluble granule (WSG) formulation or as two foliar broadcast applications of a water-dispersible granule (WDG) formulation. The soil application (Belay™ 16WSG) was made at a total rate of 0.197 to 0.199 pounds of active ingredient per acre (lb ai/A), while the two foliar broadcast applications (Clutch™ 50WDG) were made 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 (essentially 1X the proposed maximum seasonal use rate of 0.2 lb ai/A). Both the drip-irrigation and foliar applications were applied during fruit development, with a re-treatment interval (RTI) of 13 to 14 days between 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 Belay™ 16WSG 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 of 0.198 lb ai/A per season (1X). Grapes were harvested at commercial maturity, 30 days after treatment (DAT) at the drip-irrigation trials, or immediately following the second application (0 DAT) at the foliar broadcast trials. 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 determine residue decline. Single control and duplicate treated samples were collected at each trial site. Samples were stored frozen from collection to analysis for up to 3 months, a duration supported by storage stability data on grapes.

The LC/MS/MS methods (Morse Methods #Meth-157 and #Meth-164) used to determine residues of clothianidin and its metabolite, TMG, in grapes were adequately validated in conjunction with the field trial analyses. For both methods, residues are extracted with ACN/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™ solid phase extraction (SPE) columns, respectively. Residues are concentrated, reconstituted in 1% acetic acid, and analyzed by LC/MS/MS. The validated limit

of quantitation (LOQ) for both analytes is 0.020 ppm in grapes, and the limit of detection (LOD) is 0.007 ppm.

Following either one or two drip-irrigation applications of clothianidin (Belay™ 16WSG) totaling roughly 0.2 lb ai/A, residues of clothianidin were less than 0.020 ppm (the LOQ) in all 24 grape samples harvested 30 DAT. Following 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 highest average field trial (HAFT) residues were 0.277 ppm. Residues of metabolite TMG were no more than 0.007 ppm (at or below the LOD) in all grape samples regardless of the application regime.

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

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the grape field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming US EPA Residue Chemistry Summary Document (DP Barcodes D309473 and D309474).

COMPLIANCE

Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.

A. BACKGROUND INFORMATION

Clothianidin (also known by its development code numbers, TM-444, TI-435, or V-10066) is a systemic insecticide, belonging to the chloronicotinyl (and nitroguanidine) class of chemicals, which 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 transmission of stimuli and eventually inhibiting reproduction of the insect. Clothianidin is a major metabolite of thiamethoxam. It is currently registered (40CFR §180.586) for use on various crops.

Arvesta has submitted a petition (PP#4F6869) requesting the establishment of tolerances for residues of clothianidin in/on grape and potato commodities. The 50% ai water-dispersible granule (WDG) formulation is proposed for foliar applications to grapes and potatoes (Clutch™ 50WDG, EPA Registration #66330-40). The 16% ai water-soluble granule (WSG) formulation is proposed for soil applications to grapes and potatoes (Belay™ 16WSG, EPA Registration #66330-52).

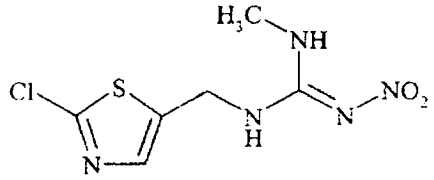
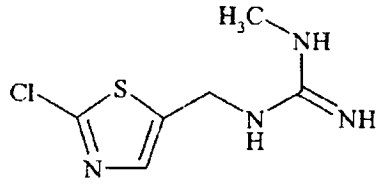
TABLE A.1 Nomenclature of Test Compound and its Metabolite.	
Compound	
Empirical Formula	$C_9H_8ClN_5O_2S$
Common Name	Clothianidin
Company Experimental Names	TM-444, TI-435, V-10066
IUPAC Name	*(E)*-1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine
CAS Name	[*C(E)*]-*N*-[(2-Chloro-5-thiazolyl)methyl]-*N'*-methyl-*N''*-nitroguanidine
CAS Number	210880-92-5 (formerly 205510-53-8)
Chemical Class	Chloronicotinyl
Known Impurities of Concern	None
End-Use Product (EUP)	Clutch™ 50WDG, EPA Registration #66330-40 Belay™ 16WSG, EPA Registration #66330-52
Metabolite	
Common Name	Metabolite TMG
Company Experimental Name	TMG
CAS Name	[*C(E)*]-*N*-[(2-Chloro-5-thiazolyl)methyl]-*N'*-methylguanidine

TABLE A.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 Xylene 0.0128 1-Octanol 0.938 Dichloromethane 1.32 Ethyl Acetate 2.03 Methanol 6.26 Acetone 15.2
Vapor Pressure (Pa) at 25°C	1.3×10^{-10}
Dissociation Constant (pK_a) at 20°C	11.09

TABLE A.2 Physicochemical Properties (from MRID #45422301).	
Parameter	**Value**
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].

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Details on soil characteristics were not included in the report; these data should be provided for studies such as MRID #46346802, reviewed in this data evaluation record (DER), which include soil applications. A summary of weather conditions was provided for each field trial site (see Table B.1.1), including average monthly minimum and maximum temperatures, and precipitation (rainfall and/or irrigation) during the field trial, compared with average historical values for the same months. No unusual meteorological or other conditions were reported that would affect the integrity of the study. The treatment regimes (drip-irrigation or foliar broadcast) used in the grape field trials are reported in Table B.1.2.

B.1.1 Trial Site Conditions

Trial Identification (City, State/Year)	Soil Characteristics				Meteorological Data		
	Type	%OM	pH	CEC	Monthly Precipitation (Inches)[1]	Average Monthly Temperature (°C)	
						Min	Max
North Rose, NY/2003	Sand	NR[2]			2.9	11	22
Dundee, NY/2003	Gravelly Silt Loam	NR			3.9	11	22
Madera, CA/2003	Loamy Sand	NR			1.6-3.9	16-17	34-37
Hughson, CA/2003	Sandy Loam	NR			4.4-5.3	17	32-33
Poplar, CA/2003	Loam	NR			0.8-3.0	10-15	28-33
Lindsay, CA/2003	Loam	NR			1.0-3.0	16-17	33-34
Dinuba, CA/2003	Loam	NR			4.0-18.0	16-17	34-35
Plainview, CA/2003	Loamy	NR			8.1-10.8	10-15	28-33
Richgrove, CA/2003	Clay	NR			8.0-10.1	11-18	28-36
Delano, CA/2003	Sandy loam	NR			12.7-14.5	17-18	34-36
George, WA/2003	Very Fine Sandy Loam	NR			0.0-0.7	5-10	19-27
Ephrata, WA/2003	Sandy Loam	NR			2.6-6.4	5-13	19-32

1. Rainfall and irrigation are included in the precipitation values.
2. NR = Not Reported.

TABLE B.1.2 Study Use Pattern on Grape.

Location (City, State/Year)	Application							
	EUP	Method [1]; Timing [2]	Volume (GPA) [3]	Single Rate (lb ai/A) [4]	Number	RTI (Days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
North Rose, NY/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	50-51	0.100, 0.101	2	14	0.201	None
Dundee, NY/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	98-100	0.099, 0.098	2	13	0.197	None
Madera, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	151-152	0.100, 0.100	2	14	0.200	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA [5]	0.198	None
Hughson, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	57	0.102, 0.098	2	14	0.200	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.199	1	NA	0.199	None
Poplar, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	69-71	0.098, 0.101	2	14	0.199	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.199	1	NA	0.199	None
Lindsay, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	70	0.098, 0.099	2	14	0.197	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.197	1	NA	0.197	None
Dinuba, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	191-192	0.099, 0.099	2	14	0.198	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
Plainview, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	195-197	0.099, 0.100	2	14	0.199	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
Richgrove, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	69-71	0.098, 0.098	2	14	0.196	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
	Belay™ 16WSG	Drip-irrigation; bud break and fruit development.	NA	0.099, 0.099	2	90	0.198	None

TABLE B.1.2 Study Use Pattern on Grape.

Location (City, State/Year)	Application							
	EUP	Method [1]; Timing [2]	Volume (GPA) [3]	Single Rate (lb ai/A) [4]	Number	RTI (Days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
Delano, CA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	116-166	0.099, 0.104	2	14	0.203	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
George, WA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	60-61	0.099	2	14	0.198	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
Ephrata, WA/2003	Clutch™ 50WDG	Broadcast foliar; fruit development.	151	0.099, 0.100	2	14	0.199	None
	Belay™ 16WSG	Drip-irrigation; fruit development.	NA	0.198	1	NA	0.198	None
	Belay™ 16WSG	Drip-irrigation; bud break and fruit development.	NA	0.099, 0.099	2	101	0.198	None

1. All applications were made using ground equipment or irrigation systems. No tank mix adjuvants were used for any applications at any of the field trials.
2. The first (or only) application was made at fruit development for Clutch™ 50WDG and Belay™ 16WSG (single application at 1X rate) treatment regimes; the first application was made at bud break for the Belay™ 16WSG (2 applications, each at 0.5X rate) treatment regime.
3. GPA = Gallons Per Acre.
4. The target single application rate was 0.198 lb ai/A for the drip-irrigation treatment and 0.099 lb ai/A for the foliar treatments. The target total application rate was 0.198 lb ai/A for all treatment regimes.
5. NA = Not Applicable.

TABLE B.1.3 Grape Field Trial Numbers and Geographical Locations.

NAFTA Growing Region[1]	Submitted[2]	Requested	
		Canada	US
1	2	NA[3]	2
2	--	NA	--
3	--	NA	--
4	--	NA	--
5	--	NA	--
6	--	NA	--
7	--	NA	--
8	--	NA	--
9	--	NA	--
10	8	NA	8
11	2	NA	2
12	--	NA	--
Total	12	NA	12

1. Regions 13 to 21 and 1A, 5A, 5B, and 7A were not included as the proposed use is for the US only.
2. Each field trial included side-by-side tests, using Clutch™ 50WDG as a foliar application and Belay™ 16WSG as a drip-irrigation application, for a total of 24 tests.
3. NA = Not Applicable.

B.2. Sample Handling and Preparation

Grapes were harvested at commercial maturity, immediately following the final foliar application (0 DAT) or at 30 DAT for the drip applications. 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. A single control and duplicate treated samples (12 bunches each) were collected from each trial and placed in frozen storage at the test facility for 5 to 48 days. Samples were then shipped by ACDS freezer truck to the analytical laboratory, Morse Laboratories in Sacramento, California. At Morse Laboratories, all grape samples were homogenized and stored frozen (at -20 ± 5°C) prior to analysis. Samples were stored frozen from collection to analysis for durations of up to 3 months.

B.3. Analytical Methodology

Grapes were analyzed for residues of clothianidin and its metabolite, TMG, using two related LC/MS/MS methods entitled *Determination of TM-444 and TMG in Potatoes* (Morse Method #Meth-157) and *Determination of TM-444 and TMG in Grape and Potato Raw Agricultural and Processed Commodities* (Morse Method #Meth-164). Method #Meth-164 is a more current version of Method #Meth-157 that includes procedures for the analysis of grapes and processed potato fractions. A detailed description of Method #Meth-164 is presented in the DER for MRID #46346801, in conjunction with an independent laboratory validation (ILV) of that method.

For both methods, residues of clothianidin and TMG in grapes are both extracted with ACN/water/guanidine-HCl (20:80:1 vol/vol/wt) and filtered through Celite. The filtrate is

concentrated and diluted with water. Separate aliquots are then taken for further cleanup and determination of clothianidin and TMG. Residues of clothianidin are cleaned up using a ChemElut™ LLE column eluted with cyclohexane/ethyl acetate (1:1 vol/vol). Residues of TMG are cleaned up using an ENVI-Carb™ SPE cartridge eluted with methanol/water/acetic acid (80:20:1 vol/vol/vol). The purified residues are concentrated and re-dissolved in 1% acetic acid for separate determination by LC/MS/MS. The HPLC system consists of a C_{18} column with a mobile phase gradient of water to methanol, each containing 1% formic acid. The retention times for clothianidin and TMG are approximately 7.3 and 4.5 minutes, respectively. The monitored transitions are m/z 250 to 169 for clothianidin and m/z 205 to 132 for TMG. The validated LOQ for each analyte is 0.020 ppm in grapes and the LOD is 0.007 ppm.

Prior to analysis of field trial samples, the method was validated using triplicate control samples of grapes fortified with clothianidin at 0.020 and 0.500 ppm. The method was also validated concurrently with the field trial samples using control samples of grapes fortified with clothianidin at 0.020 to 1.00 ppm.

B.4. Storage Stability

In conjunction with analysis of the field trial samples, a storage stability study was conducted to support the sample storage durations for the field samples. Control samples of frozen, homogenized grapes were separately fortified with clothianidin or TMG at 0.500 ppm and placed in frozen storage at -20°C. Duplicate or triplicate subsamples were analyzed immediately following fortification (Day 0) and again after intervals of 30 and 162 days of frozen storage. Duplicate freshly fortified samples were analyzed along with the stored samples.

C. RESULTS AND DISCUSSION

The number and geographic representation of the grape field trials are adequate. A total of 12 grape field trials were conducted during 2003. With exception of the two field trial sites in New York, side-by-side tests were conducted at each trial site comparing the use of clothianidin as either a single drip-irrigation application using the Belay™ 16WSG formulation at a rate of 0.197 to 0.199 lb ai/A, or as two foliar broadcast applications using the Clutch™ 50WDG formulation at a rate of 0.098 to 0.101 lb ai/A/application (for a total application rate of 0.196 to 0.203 lb ai/A per season). Both the drip-irrigation and foliar broadcast applications were applied during fruit development, with an RTI of 13 to 14 days between the two foliar applications. In addition, two field trials (California and Washington) included another test in which the Belay™ 16WSG 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 application rate of 0.198 lb ai/A per season (essentially 1X the proposed maximum seasonal use rate). Grapes were harvested at commercial maturity, immediately following (0 DAT) the second foliar application or at 30 DAT for the drip applications. 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 determine residue decline. Single control and duplicate treated samples were collected from each trial.

The LC/MS/MS methods (Morse Methods #Meth-157 and #Meth-164) used to determine residues of clothianidin and TMG in grapes are adequate for data collection. Average concurrent method recoveries were 86 ± 4% for the 14 grape (fruit) samples fortified with clothianidin at 0.020 to 1.00 ppm and 93 ± 6% for the 14 grape (fruit) samples fortified with metabolite TMG at

0.020 to 1.00 ppm (see Table C.1). Apparent residues of clothianidin and TMG were less than the LOD in all control samples. The validated LOQ for each analyte is 0.020 ppm for grapes; the LOD for both is 0.007 ppm. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for durations of up to approximately 3 months (see Table C.2). Concurrent storage stability data are available indicating that clothianidin and TMG are stable in frozen grapes stored for intervals of up to 5 months (see Table C.3). These data will support the current grape field trials.

TABLE C.1 Summary of Method Validation and Concurrent Recovery Results for the LC/MS/MS Methods from Grapes.

Analyte	Crop [Matrix]	Spiking Level (mg/kg)	Sample Size	Recoveries (%)	Mean Recovery ± Std Dev (%)
Method Validation Recoveries					
Clothianidin	Grape [Fruit]	0.020	3	87-90	92 ± 4
		0.500	3	92-97	
TMG	Grape [Fruit]	0.020	3	92-106	102 ± 6
		0.500	3	100-106	
Concurrent Method Recoveries					
Clothianidin	Grape [Fruit]	0.020	5	81-85	86 ± 4
		0.100	3	78-88	
		0.200	2	84-87	
		0.500	2	92-93	
		1.00	2	86-90	
TMG	Grape [Fruit]	0.020	12	84-98	93 ± 6
		1.00	2	100-104	

TABLE C.2 Summary of Freezer Storage Conditions.

Grape Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)[1]	Limit of Demonstrated Storage Stability (Months)[2]
Fruit	-20 ± 5	~3	5.3

1. Extracts were stored frozen for 0 to 13 days prior to analysis.
2. Concurrent storage stability data for grapes are available indicating that clothianidin is stable under frozen conditions for intervals of up to 5.3 months (162 days).

TABLE C.3 Stability of Clothianidin and Metabolite TMG in Frozen Grapes.

Analyte	Spike Level (ppm)	Storage Interval (Days)	Freshly Fortified Recovery (%)	Stored Sample Residues (ppm)	Corrected [1] Stored Sample Residues (ppm)	Average Corrected Recovery (%)
Clothianidin	0.500	0	97, 97, 92 (95) [2]	NA [3]	NA	100
		30	96, 108 (102)	0.488, 0.482	0.478, 0.473	95
		162	96, 97 (96)	0.502, 0.454	0.523, 0.473	100
TMG	0.500	0	106, 106, 100 (104)	NA	NA	100
		30	93, 100 (96)	0.470, 0.482	0.490, 0.502	99
		162	97, 98 (98)	0.490, 0.475	0.500, 0.485	99

1. Residues were corrected for average concurrent recovery from freshly fortified samples.
2. Average recoveries are in parentheses.
3. NA = Not Applicable.

Following either one or two drip-irrigation applications of clothianidin (as the Belay™ 16WSG formulation) totaling roughly 0.2 lb ai/A, residues of clothianidin were less than 0.020 ppm (the LOQ) in all 24 grape samples harvested 30 DAT (see Table C.4), while all residues of TMG were less than 0.007 ppm (the LOD). For the two foliar broadcast applications of clothianidin (as the Clutch™ 50WDG formulation), residues of clothianidin were 0.040 to 0.278 ppm in 24 grape samples harvested immediately following the final application (0 DAT), while residues of TMG were no more than 0.007 ppm. Average residues of clothianidin were 0.020 ppm for the drip applications and 0.139 ppm for the foliar applications (see Table C.5). HAFT residues for clothianidin were 0.277 ppm following the foliar applications.

In the decline trial, clothianidin residues in grapes treated via Belay™ 16WSG drip-irrigation were less than 0.020 ppm (the LOQ) at all sampling intervals. For the trials with treatment via Clutch™ 50WDG foliar broadcast, the clothianidin residues in grapes decreased steadily from 0.136 to 0.139 ppm at 0 DAT to residues of 0.056 to 0.066 ppm at 21 DAT.

Common cultural practices were used to maintain plants, and the weather conditions, maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

TABLE C.4 Residue Data from Grape Field Trials with Clothianidin.

Trial ID (City, State/Year)	EPA Region	Variety	Grape Matrix	Treat-ment Regime	Total Rate (lb ai/A)	PHI [1] (Days)	Residues (ppm) [2]	
							Clothianidin	TMG
North Rose, NY/2003	1	Elvira	Fruit	Foliar	0.201	0	0.069, 0.098	ND [3], ND
Dundee, NY/2003	4	Concord	Fruit	Foliar	0.197	0	0.127, 0.104	ND, ND
Madera, CA/2003	10	Thompson Seedless	Fruit	Foliar	0.200	0	0.072, 0.074	ND, ND
				Drip	0.198	30	[0.008, 0.010] [4]	ND, ND
Hughson, CA/2003	10	Thompson Seedless	Fruit	Foliar	0.200	0	0.275, 0.278	ND, ND
				Drip	0.199	30	ND, ND	ND, ND

TABLE C.4 Residue Data from Grape Field Trials with Clothianidin.

Trial ID (City, State/Year)	EPA Region	Variety	Grape Matrix	Treat-ment Regime	Total Rate (lb ai/A)	PHI[1] (Days)	Residues (ppm)[2]	
							Clothianidin	TMG
Poplar, CA/2003	10	Emperor	Fruit	Foliar	0.199	0	0.040, 0.042	ND, ND
				Drip	0.199	30	ND, ND	ND, ND
Lindsay, CA/2003	10	Autumn Royal	Fruit	Foliar	0.197	0	0.053, 0.050	ND, ND
				Drip	0.197	30	ND, ND	ND, ND
Dinuba, CA/2003	10	Ruby Red	Fruit	Foliar	0.198	0	0.080, 0.113	ND, ND
				Drip	0.198	30	ND, ND	ND, ND
Plainview, CA/2003	10	Crimson	Fruit	Foliar	0.199	0	0.136, 0.139	ND, ND
						7	0.092, 0.130	ND, ND
						14	0.073, 0.082	ND, ND
						21	0.066, 0.056	ND, ND
				Drip	0.198	23	ND, ND	ND, ND
						30	ND, ND	ND, ND
						37	ND, ND	ND, ND
						44	ND, ND	ND, ND
Richgrove, CA/2003	10	Ruby Seedless	Fruit	Foliar	0.196	0	0.073, 0.090	ND, ND
				Drip	0.198	30	ND, ND	ND, ND
				Drip	0.198	30	ND, ND	ND, ND
Delano, CA/2003	10	Thompson	Fruit	Foliar	0.203	0	0.121, 0.132	ND, ND
				Drip	0.198	30	ND, ND	ND, ND
George, WA/2003	11	Cabernet Sauvignon	Fruit	Foliar	0.198	0	0.220, 0.410	ND, [0.007][4]
				Drip	0.198	30	ND, ND	ND, ND
Ephrata, WA/2003	11	White Reisling	Fruit	Foliar	0.199	0	0.208, 0.330	ND, ND
				Drip	0.198	30	ND, ND	ND, ND
				Drip	0.198	30	ND, ND	ND, ND

1. PHI = Pre-Harvest Interval.
2. The LOQ is 0.020 ppm and the LOD is 0.007 ppm.
3. ND = Not Detected (less than the LOD).
4. Values in brackets are between the LOD and the LOQ.

TABLE C.5 Summary of Residue Data for Grape Field Trials Using Soil (Drip-Irrigation) or Foliar (Broadcast) Applications of Clothianidin.

Crop [Matrix]	Treat-ment	Total Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)[1]					
				n	Min.	Max.	HAFT[2]	Mean	Std. Dev.
Clothianidin Residues									
Grape [Fruit]	Foliar	0.196-0.203	0	24	0.040	0.278	0.277	0.139	0.098
	Drip	0.197-0.199[3]	30	20	<0.020	<0.020	<0.020	<0.020	0
	Drip	0.198[4]	30	4	<0.020	<0.020	<0.020	<0.020	0
TMG Residues									
Grape [Fruit]	Foliar	0.196-0.203	0	24	<0.020	<0.020	<0.020	<0.020	0
	Drip	0.197-0.199[3]	30	20	<0.020	<0.020	<0.020	<0.020	0
	Drip	0.198[4]	30	4	<0.020	<0.020	<0.020	<0.020	0

1. The LOQ is 0.020 ppm and the LOD is 0.007 ppm.
2. HAFT = Highest Average Field Trial.
3. Single application at 1X.
4. Two applications, each at ½X.

D. CONCLUSION

The grape field trial data are adequate. These data support the use of clothianidin on grapes as either one to two drip-irrigation applications utilizing the Belay™ 16WSG formulation during fruit development (at a total application rate of 0.2 lb ai/A per season), or the use of up to two foliar broadcast applications utilizing the Clutch™ 50WDG formulation during fruit development (at a rate of 0.1 lb ai/A per application, for a total application rate of 0.2 lb ai/A per season). Clothianidin residues resulting from the foliar broadcast applications of Clutch™ 50WDG are higher than from the drip-irrigation soil application of Belay™ 16WSG.

E. REFERENCES

Subject: *Independent Laboratory Validation for the Determination of TM-444 and TMG in Grapes*, Laboratory Study ID #Arvesta-1506
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F. DOCUMENT TRACKING

RDI: W. T. Drew (8/15/2005), R. A. Loranger (12/28/2005)
Petition Number: 4F6869
DP Barcode: D309473 and D309474
PC Code: 044309

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Chemical: Clothianidin

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