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RAB2/HED (7509C)

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RAB2/HED (7509C) *R. Loranger*

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 #46144902. F. K. Duah (2002) *TI-435 600 FS - Magnitude of the Residue in Sorghum Processed Commodities (Request for Waiver of the Study for the Magnitude of the Residue in Sorghum Aspirated Grain Fractions and Processed Commodities)*. Bayer Study #T519SO02, Bayer Report #200244, Gustafson Project #0104002. Unpublished study prepared by Bayer Corporation Agricultural Division, Gustafson Research and Development Center (GRDC), and Texas A&M University Food Protein Research and Development Center (FPRDC). 67 pages. {OPPTS Residue Chemistry Test Guideline 860.1520}

EXECUTIVE SUMMARY

Clothianidin formulated at 5 pounds active ingredient per gallon as a flowable concentrate (5 lb ai/gal 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 label 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 per acre (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 days after planting (DAP). Prior to analysis, sorghum raw agricultural commodity (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. Briefly, residues are extracted with ACN/water, filtered, concentrated, and cleaned up using a ChemElutTM column. Residues are then analyzed by LC-MS/MS and quantified using deuterated clothianidin as an internal standard. The validated limit of quantitation (LOQ) for clothianidin residues is 0.010 ppm in/on sorghum grain, and the limit of detection (LOD) is 0.003 ppm.

The residue data on sorghum grain are adequate. Residues in/on 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 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.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the sorghum processing 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 Barcode D303164).

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 as a seed treatment for corn and canola.

Bayer CropScience has also requested tolerances for clothianidin residues in/on sorghum commodities in conjunction with a proposed seed treatment use on sorghum (PP#3F6792). The 5 lb ai/gal FC formulation of clothianidin (Poncho™ 600, EPA Registration #264-789) is proposed for use on grain sorghum as a single seed treatment application at up to 0.25 lb ai/100 lb seeds, using commercial seed treatment equipment.

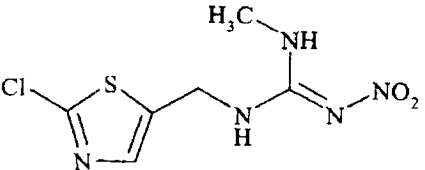
TABLE A.1 Nomenclature of Test Compound.	
Compound	
Empirical Formula	C ₆ H ₈ ClN ₅ O ₂ S
Common Name	Clothianidin
Company Experimental Names	TM-444, TI-435, V-10066
IUPAC Name	(E)-1-(2-Chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine
CAS Name	[C(E)]-N-[(2-Chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitroguanidine
CAS Number	210880-92-5 (formerly 205510-53-8)
Chemical Class	Chloronicotinyl
Known Impurities of Concern	None
End-Use Product (EUP)	Poncho™ 600, EPA Registration #264-789

TABLE A.2 Physicochemical Properties (from MRID #45422301).	
Parameter	Value
Molecular Weight	249.7
Melting Point (°C)	176.8

TABLE A.2 Physicochemical Properties (from MRID #45422301).	
Parameter	Value
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
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. Application and Crop Information

The sorghum seed was treated at the GRDC in McKinney, Texas, using a Hege 11 commercial seed treater. For application, clothianidin (5 lb ai/gal FC) was diluted with water to form a slurry, and was applied at a rate of 0.50 lb ai/100 lb seeds. The treated seeds were then shipped to the field trial site for planting (see Table B.1).

TABLE B.1 Study Use Pattern on Sorghum.							
Location (City, State/Year)	Application						
	EUP	Method ¹ /Timing	Seeding Rate (Seeds/A) ²	Single Rate (lb ai/A) ³	Number	RTI ⁴ (Days)	Total Rate (lb ai/A)
Benoit, MS/2001	Poncho™ 600	Seed treatment/prior to planting.	72,906	0.024	1	NA ⁵	0.024

1. The application was made using a commercial seed-treater (Hege 11 treater) at GRDC in McKinney TX; no tank mix adjuvants were used.
2. Typical seeding rates for grain sorghum range from 50,000 to 150,000 seeds/A.
3. Seeds were treated at a rate of 0.50 lb ai/100 lb seeds; the equivalent field use rate was 0.024 lb ai/A based on the actual seeding rate.
4. RTI = Re-Treatment Interval.
5. NA = Not Applicable.

B.2. Processing Procedures

A single control and duplicate treated samples (500 lb each) of grain were harvested at commercial maturity (134 DAP), placed in frozen storage at the test facility within 3 hours, and stored frozen for durations of 1 to 117 days. Samples were then shipped by freezer truck to Texas A&M University FPRDC in Bryan, Texas, and triplicate subsamples of sorghum grain (RAC) were placed in frozen storage. All samples were then shipped frozen to the analytical



Clothianidin/264-789/PC Code 044309/Bayer CropScience AG/264
 DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIA 8.3.1, 8.3.2, 8.3.3
 Processed Food and Feed - Sorghum

laboratory, Residue Analysis Laboratory at the Bayer Research Park (BRP) in Stilwell, Kansas, where they were homogenized and stored frozen (at less than -15°C) prior to analysis. Analysis of processed commodities was not performed.

B.3. Analytical Methodology

Samples 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 Ag Div report #109240-1 (MRID #45422537), which is essentially Method 00552 with the use of an internal standard for quantitation. Both methods have been validated by the Agency and accepted for tolerance enforcement. A brief description of the method follows.

Residues are extracted with ACN/water and filtered. The deuterated internal standard is added to the filtrate, which is then concentrated for cleanup using a ChemElut™ column eluted with cyclohexane/ethyl acetate. Residues are then analyzed by HPLC using a C₁₈ column, a gradient mobile phase of acidic water and ACN, and MS/MS quantitation (m/z 248 and 251 ions). Residues in grain were quantified using the deuterated clothianidin internal standard. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum grain, and the LOD is 0.003 ppm for grain.

C. RESULTS AND DISCUSSION

The LC/MS/MS method (Bayer Method 109240-1) used to determine clothianidin residues in/on sorghum grain is adequate for data collection. Average concurrent method recoveries were 94 ± 13% from 3 grain samples fortified with clothianidin at 0.010 ppm (see Table C.1). Apparent residues of clothianidin were less than the LOD in/on all control samples. The validated LOQ for clothianidin residues is 0.010 ppm for sorghum RACs, and the LOD is 0.003 ppm for sorghum grain. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for durations of up to 9 months (see Table C.2). Storage stability data are available for corn grain and canola seed indicating that clothianidin is stable in frozen storage for intervals of up to 24 months (MRID #45422611). These data will support the current sorghum processing study.

In the trial conducted in Mississippi during 2001, clothianidin (5 lb ai/gal FC) was applied as a single seed treatment application at 0.50 lb ai/100 lb seeds, which was equivalent to 0.024 lb ai/A. Bulk control and treated sorghum samples were harvested at commercial maturity, 134 DAP. Triplicate subsamples of sorghum grain (RAC) were collected.

Clothianidin residues were less than 0.003 (the LOD) ppm in 3 subsamples of sorghum grain (RAC) treated at 2X and harvested at maturity (see Table C.3). As residues were less than 0.003 ppm (the LOD) in all grain samples, the grain was not further processed.

TABLE C.1 Concurrent Recovery Results for the LC/MS/MS Method using Sorghum Grain.					
Analyte	Crop [Matrix]	Spiking Level (mg/kg)	Sample Size	Recoveries (%)	Mean Recovery ± Std Dev (%)
Clothianidin	Sorghum [Grain]	0.010	3	80-106	94 ± 13



TABLE C.2 Summary of Freezer Storage Conditions.			
Crop [Matrix]	Storage Temperature (°C)	Actual Storage Duration (Months) ¹	Limit of Demonstrated Storage Stability (Months) ²
Sorghum [Grain]	<-15	~9	24

1. Extracts were stored frozen for 1 day prior to analysis.
2. Storage stability data are available indicating that clothianidin is stable under frozen conditions in corn grain and canola seed for intervals of up to 24 months (MRID #45422611).

TABLE C.3 Residue Data from Sorghum Field Trials using Clothianidin as a Seed Treatment.					
Trial ID (City, State/Year)	Processed Commodity	Use Rate (lb ai/A) ¹	PHI ² (Days)	Residues (ppm) ³	Processing Factor
Benoit, MS/2001	Sorghum Grain (RAC)	0.024	134	ND ⁴ , ND, ND	NA ⁵

1. Seeds were treated at 0.50 lb ai/100 lb seeds; field use rate was based on actual seeding rate (72,906 seeds/A).
2. PHI = Pre-Harvest Interval (= DAP in this case, because use was as a seed treatment).
3. The LOQ is 0.010 ppm and the LOD is 0.003 ppm for sorghum grain.
4. ND = Not Detected.
5. NA = Not Applicable.

D. CONCLUSION

The residue data on sorghum grain are adequate. Following a seed treatment with clothianidin (5 lb ai/gal FC) at 0.50 lb ai/100 lb seeds (2X rate), residues in/on three subsamples of grain harvested at maturity were non-detectable (less than 0.003 ppm, the LOD). The Agency does not currently required a processing study on sorghum. Considering that residues were less than a third of the LOQ in grain treated at 2X, and that the application to sorghum is made as a seed treatment, residue data on aspirated grain fractions derived from sorghum are not required.

E. REFERENCES

Subject: *Modification M001 of the Method 00552 for the Determination of Residues of TI-435 in/on Plant Materials*, Bayer Ag Div Report #109240-1

Author: F. Nuesslein

Dated: 2000

MRID: 45422537

Subject: *Determination of the Storage Stability of TI-435 Residues in Fortified Analytical Samples of Plant Materials*, Bayer Ag Div Report #109734

Author: F. Nuesslein

Dated: 2001

MRID: 45422611

F. DOCUMENT TRACKING

RDI: W.T. Drew (7/27/2005), R.A. Loranger (12/28/2005)

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PC Code: 044309



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