



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

OPP OFFICIAL RECORD  
 HEALTH EFFECTS DIVISION  
 SCIENTIFIC DATA REVIEWS  
 EPA SERIES 361

MAY 18 1992

MEMORANDUM

*128845, 128887*

SUBJECT: PPOF3961. Thifensulfuron Methyl on oats grain/straw.  
 PPOF3962. Tribenuron Methyl on oats grain/straw.  
 Evaluation of Analytical Methods and Residue Data.

OFFICE OF  
 PESTICIDES AND TOXIC  
 SUBSTANCES

Chemistry Branch No.: 7812, 7813.  
 Chemical No. : 128845; 128887  
 DP Barcode: D162487  
 MRID : 41793401

FROM: R. W. Cook, Chemist *RWC*  
 Tolerance Petition Section I  
 Chemistry Branch I - Tolerance Support  
 Health Effects Division (H7509C)

THRU: Debra Edwards, Ph.D., Acting Chief *Debra Edwards*  
 Chemistry Branch I - Tolerance Support  
 Health Effects Division (H7509C)

TO: J. I. Miller, PM 23  
 Fungicide-Herbicide Branch  
 Registration Division (H7505C)

and

Toxicology Branch  
 Herbicide-Fungicide and Antimicrobial Support  
 Health Effects Division (H7509C)

The petitioner, Du Pont Agricultural Products, Wilmington, Delaware, proposes tolerances for residues of the herbicide thifensulfuron methyl {methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate} in or on the raw agricultural commodity oat grain at 0.05 ppm and oat straw at 0.1 ppm and tolerances for the herbicide tribenuron methyl {methyl 2-[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate} in or on the raw agricultural commodity oat grain at 0.05 ppm and oat straw at 0.1 ppm. The two chemicals are to be marketed together in a product named Harmony® Extra Herbicide. The active ingredient thifensulfuron methyl is also known by the company designation DPX-M6316 and is the sole active ingredient in Harmony® Herbicide. The active ingredient tribenuron methyl is also

known by the company designation DPX-L5300 and is the sole active ingredient in Express® Herbicide.

Tolerances are established under 40 CFR 180.439 for residues of thifensulfuron methyl on soybeans, barley straw, wheat straw at 0.1 ppm and in wheat grain and barley grain at 0.05 ppm. These tolerances were established under PP6F3431 and PP8F3663 (Du Pont Harmony® Herbicide EPA Reg No. 352-446). Temporary tolerances for residues of DPX-M6316 in or on soybeans has been established under PP8G3602 (Pinnacle® Herbicide EPA Experimental Use Permit 352-EUP-145). In addition, exemptions under Section 18 were considered under 87-VA-01 and 87-VA-02 (see M. Metzger, 1/27/87) for wheat and barley and in 89-LA-01 (see F. Suhre, 2/3/89) for oats. The Harmony® Herbicide increased application rate from 0.5 oz. a.i./A. to 0.75 oz. a.i./A. for wheat and barley. See C. Stanton / C. Olinger review of EPA Reg. No. 352-446 dated June 5, 1991.

A registration standard has been issued for thifensulfuron methyl (Harmony®, DPX-M6316). See registration standard dated 2/12/87 and sequel in this regard.

Tolerances are established under 40 CFR 180.451 for tribenuron methyl on barley and wheat grains at 0.05 ppm and on their straws at 0.1 ppm.

A new chemical review was written for Express® (DPX-L5300) which is now known by the common name tribenuron methyl (PP7F3540).

### Conclusions

- 1a. The nature of the residue resulting from the application of thifensulfuron methyl to oats is adequately understood. The residue of concern in plants is the parent compound per se.
- 1b. The nature of the residue resulting from the application of tribenuron methyl to oats is adequately understood. The residue of concern in plants is the parent compound per se.
- 2a. In animals, the nature of thifensulfuron methyl residues is adequately understood. The residue of concern in animals is thifensulfuron methyl per se.
- 2b. In animals, the nature of tribenuron methyl residues is adequately understood. The residue of concern in animals is tribenuron methyl per se.
- 3a. There are adequate enforcement methods for residues of thifensulfuron methyl and tribenuron methyl. The methods have been forwarded to FDA for inclusion in PAM II. In the interim, the methods can be received from Calvin Furlow, PIB/FOD.

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- 3b. Thifensulfuron methyl has not undergone testing by multiresidue methods. The petitioner should submit the results of analysis of thifensulfuron methyl by multiresidue methods.
- 3c. Tribenuron methyl DPX-L5300 has undergone testing by multiresidue methods. Multiresidue methods I, II, III, and IV will not detect tribenuron methyl residues.
4. We conclude that residues of thifensulfuron methyl and tribenuron methyl (each individually) are not likely to exceed the proposed tolerances of 0.05 ppm in oat grain and 0.1 ppm in oat straw when used in a single application at no more than 0.30 oz a.i./A. (comprised of 0.2 oz. a.i./A. thifensulfuron methyl and 0.1 oz a.i./A. tribenuron methyl) at the following application schedules (Winter Oats: after the crop is in the 2-leaf stage, but before the flag leaf is visible. Spring Oats: after the crop is in the 3-5 leaf stage, but before jointing).
5. Based upon current Branch guidance and in the absence of detectable residues in oat grain from exaggerated rate field trials, we are not requiring grain milling fraction studies or food additive tolerances for oat milling fractions. If the petitioner should propose a future use which results in detectable residues in the grain, processing studies and possibly food/feed additive tolerances will be needed for the milled fractions.
6. In the absence of detectable residues in animal feed items oat grain and straw, we are not requiring tolerances for meat, milk, poultry or eggs at this time. If the petitioner should propose a future use which results in detectable residues in animal feed items, tolerances may then be required for secondary residues in meat, milk, poultry, and eggs.
7. An International Residue Limit Status Sheet (Codex) is attached to our review. There are no Codex, Mexican, or Canadian tolerances for these chemicals on oats.
8. No Craven residue data were submitted or used in support of current action.
9. Apparently both the treated and control values for DPX-L5300 in the Robinson, KS 0.45 oz. a.i./A. trial were obtained from the same sample: barcode 52989. The petitioner should verify data transcription error and that the correct sample identification is barcode 52985.

### Recommendations

We recommend against the establishment of the proposed tolerances for residues of thifensulfuron methyl and tribenuron methyl in oat grain, each at 0.05 ppm, and in oat straw, each at 0.1 ppm. For a favorable recommendation, the petitioner should submit the results of analysis of thifensulfuron methyl by multiresidue methods. Also, the petitioner should

verify the data transcription error in the Robinson, KS trial; i.e., that the correct barcode is 52985 for the treated sample.

### DETAILED CONSIDERATIONS

#### Manufacture and Formulation

The plant regulating product Harmony® Extra DF is formulated as a granular material intended to be dissolved in water for application by ground equipment. The dual active formulated product contains 50% by weight of the active ingredient thifensulfuron methyl (aka DPX-M6316, Pinnacle®, Harmony®) and 25% by weight of the active ingredient tribenuron methyl (DPX-L5300, Express®).

#### Directions for Use

##### Harmony® Extra Herbicide DF:

##### Winter Oats:

Make application after the crop is in the 2-leaf stage, but before the flag leaf is visible.

##### Spring Oats:

Make applications after the crop is in the 3-5 leaf stage, but before jointing.

Do not use on variety "Oogle" as crop injury can occur.

##### Application Rates: Oat (Spring and Winter)

Use 0.3 to 0.4 ounce Harmony® Extra per acre for control of the weeds listed in WEEDS CONTROLLED table. If predominant weed in the field is one of these listed under partial control, always add a tank mix partner such as 2,4-D; MCPA; Buctril; or Banvel/Banvel SGF. Some of these tank mixtures are permitted in certain states only; refer to label instructions.

See label for specific use directions for specific weed pests.

Do not use less than 0.3 ounce of Harmony® Extra per acre.

Do not graze or feed forage or hay from treated area to livestock (Harvested straw may be used for bedding and/or feed).

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Do not apply to wheat, barley, or oat crops underseeded with another crop.

Aerial application: use at 2 to 5 gallons per acre. Do not use less than 3 GPA in ID, OR, UT, or WA. Refer to Special Local Need label for aerial application in the state of Washington.

Surfactants:

Always add a non-ionic surfactant of at least 80% active ingredient at 0.25% vol/vol (1 quart per 100 gallons of spray solution).

Use 0.06%-0.25% vol/vol. surfactant (1/2 - 2 pints per 100 gallons of spray solution) when applying Harmony® Extra in liquid nitrogen fertilizer.

Do not use Harmony® Extra plus malathion as crop injury will occur.

We note that at the maximum application rate of 0.4 oz. Harmony Extra/A., the dosage rate is 0.2 oz. a.i./A. for thifensulfuron methyl and 0.1 oz a.i./A. for tribenuron methyl.

Nature of the Residue

The nature of the DPX-M6316 residue in wheat and barley grain and straw has been previously discussed in the Harmony® registration standard. It was concluded that the nature of the residue was not adequately known for the purposes of the standard. The petitioner later responded and upon further review it was concluded that the nature of the residue in wheat and barley was adequate for the establishment of tolerances on these commodities. The metabolism of thifensulfuron methyl (DPX-M6316) in corn, wheat and barley is adequately known and the residue of concern is the parent compound per se. We conclude that the residue of concern in oat grain, straw, forage, and fodder is the parent compound.

The nature of the tribenuron methyl residues in wheat and barley has been previously discussed in PP7F3540, which see. We conclude that the residue of concern in oat grain, fodder, forage, and straw is the parent compound.

Nature of the Residue in Animals

In regards to thifensulfuron methyl, based upon the goat metabolism study with 2800 x feeding level exaggeration and upon the no detectable levels of thifensulfuron methyl residues in oat grain, oat forage or oat fodder and oat straw, (see below under Residue Data), we can conclude that the nature of the residue is adequately understood for the purposes of establishing the proposed tolerance on oat grain and oat straw. We conclude that metabolism studies in poultry are not needed at this time. However, if the petitioner should

propose a use which results in significant levels of residues of concern in poultry feed, poultry metabolism studies would be needed.

In regards to tribenuron methyl, we concluded that residues would not occur in animal feed items (DPX-L5300, R. W. Cook). We conclude that the nature of the residue is adequately understood for the purposes of establishing the proposed tolerance on oat grain and oat straw. We conclude that metabolism studies in poultry are not needed at this time. However, if the petitioner should propose a use which results in significant levels of residues of concern in poultry feed, poultry metabolism studies would be needed.

For both chemicals, the residue of concern is the parent compound.

#### Analytical Method MRID417934O1

##### Analysis of oat grain and straw.

The analytical method used by E. I. du Pont for obtaining residue data is a modification of a method previously submitted in regard to tribenuron methyl (Express, DPX-L5300). The method is titled "Analysis of DPX-L5300 in Wheat Grain and Wheat Straw by Liquid Chromatography" and bears the code number AMR-1242-88 (draft version dated 8/10/88) by L. H. Larochelle and L. J. Major. The method has been previously used for the analysis of tribenuron methyl and currently additional recovery/validation data are submitted for thifensulfuron methyl.

Basically, the method involves triple extraction of the chopped substrate by buffer/methanol, acidification and cleanup by HPLC followed by quantitation on another HPLC. A review of the modified method can be found in CBII-RS review of C. Stanton/C. Olinger (EPA Reg. No. 352-538, 6/17/91) amended use to extend application timing. In that review, it was concluded that the modified methods were sufficient for data collection purposes only. However, several questions were raised regarding the method, specifically concerning the stability of extracts and the dates of extraction, analysis, and concurrent fortifications.

The contract residue analysis laboratory Enviro-Test Laboratories, 9936 67th Avenue, Edmonton, Alberta T6E 0P5, Canada, further modified the analytical procedure for their laboratory. The modifications appear to be slight and are fully detailed in the current submission. The changes involve larger sample size, sample concentration, and concentration of HPLC eluting solvents.

Recovery data are presented for analysis of thifensulfuron methyl and tribenuron methyl at Enviro-Test Laboratories.

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## Recovery of Harmony® Extra in Oat Grain and Straw

Site	<u>Thifensulfuron methyl</u>		<u>Tribenuron methyl</u>	
	<u>Fortification</u>	<u>Recovery</u>	<u>Fortification</u>	<u>Recovery</u>
<u>Oat Grain</u>				
Danville, IA	--	--	0.011	76
Robinson, KS	0.024	100	0.010	95
St. Joseph, LA	0.048	104	0.040	75
Hollandale, MN	0.012	100	0.010	95
Oregon, MO	0.096	83	0.10	90
Cassville, NC	0.012	92	0.010	70
Crooks, SD	0.012	108	--	--
McKinney, TX	--	--	0.010	86
	Range		Range	
	0.012 - 0.096		0.010 - 0.040	
	Average → 98		Average → 84	
<u>Oat Straw</u>				
Madera, CA	0.024	75	0.020	80
Danville, IA	0.049	92	0.062	92
Robinson, KS	0.048	125	0.040	78
Oregon, MO	0.024	75	0.020	80
Cassville, NC	0.096	99	0.12	92
Crooks, SD	0.024	83	0.020	80
McKinney, TX	0.096	88	0.080	96
Arkansaw, WI	0.098	99	0.24	96
	Range		Range	
	0.024 - 0.098		0.020 - 0.24	
	Average → 92		Average → 87	

From Table VI and VII

The limit of detection and limit of quantitation are reported by the petitioner to be:

Limits of Detection and Quantitation for  
Thifensulfuron methyl and Tribenuron methyl

Chemical	Commodity	Detection	Quantitation
Tribenuron methyl	Grain	0.0053	0.01
Tribenuron methyl	Straw	0.009	0.018
Thifensulfuron methyl	Grain	0.0056	0.013
Thifensulfuron methyl	Straw	0.018	0.04

From Appendix XIII

We conclude that the method is adequate for the purposes of obtaining residue data.

#### Multiresidue Methods:

Tribenuron methyl (DPX-L5300) has undergone testing by multiresidue methods. Multiresidue method I, II, III, and IV will not detect tribenuron methyl residues (PP7F3740, 4/21/89, R. W. Cook). Thifensulfuron methyl has not undergone testing by multiresidue methods. The petitioner should submit the results of analysis of thifensulfuron methyl by multiresidue methods.

#### Storage Stability

We have previously concluded that residues of thifensulfuron methyl and tribenuron methyl are stable under frozen storage conditions for intervals at least as long as those intervals encountered herein. (see PPOF3872, R. W. Cook and PP7F3540, 4/26/88, R. W. Cook). Residues of thifensulfuron methyl were stable up to 24 months in corn matrices and up to 42 months in wheat and barley. Residues of tribenuron methyl were stable in wheat grain and straw under frozen conditions for intervals up to 21 months. We conclude that previously submitted available stability data indicate that residues of thifensulfuron methyl and tribenuron methyl are adequately stable for the intervals encountered in this submission.

#### Residue Data MRID41793401

The study of residues of thifensulfuron methyl and tribenuron methyl in oat grain, forage and fodder and oat straw has been submitted by the petitioner in Du Pont Study No. AMR-1281-88 "Magnitude of Residues of Harmony® Extra Herbicide in Oats When Applied as a Single Late Season Application", by Richard A. Guinivan and Ruthe J. Hay. 12/13/90.

Two laboratories were involved in either preparation of the samples for analysis or the analysis itself: Du Pont Agricultural Products Department, Research and Development Division Experimental Station, Wilmington Delaware, 19898 and Enviro-Test Laboratories, 9936 67th Avenue, Edmonton, Alberta T6E 0P5, Canada. Sample preparation was conducted at DuPont Laboratories and the residue analysis was conducted at Enviro-Test Laboratories. Residue field trials were conducted in 10 states. Each trial used dosage rates of 1x and 2x, except in Crooks, SD, where examination of the application records showed that miscalculation resulted in 16x (oz. a.i./A.) and 32x (14.4 oz. a.i./A.) application rates. Residue data from SD is submitted for review, but the residue levels are not included in average values for the different trials. The time interval from last application to sampling ranged from 39 to 57 days.

We note that both the treated and control values for DPX-L5300 in the Robinson, KS 0.45 oz. a.i./A. trial were obtained from the same sample: barcode 52989. We presume this

is a data transcription error and the correct sample identification is barcode 52985. The petitioner should verify correction.

Residues of thifensulfuron methyl and tribenuron methyl in oat grain from oats treated at 1x and 2x were below the quantitation level of 0.013 ppm and 0.01 ppm respectively and also below the reported detection level of 0.005 ppm.

Except as discussed below, residues of thifensulfuron methyl and tribenuron methyl in oat straw were below the quantitation level of 0.018 ppm and 0.04 ppm respectively and also below reported detection level of 0.009 ppm and 0.018 ppm, respectively, in oat straw from oats treated at 0.45 a.i./A. and 0.90 a.i./A.

The exception occurred at the Madera, CA, residue trial site, where thifensulfuron methyl residues were found at 0.041 ppm (0.064 ppm; no peak in duplicate analysis) and 0.3 ppm (0.32 ppm; 0.27 ppm) and tribenuron methyl residues were 0.029 ppm (0.021 ppm; 0.036 ppm), from 0.90 oz. a.i./A. While the Madera, CA, site received very little rainfall (0.3 in.) and no irrigation during the trial and while the residue level of 0.3 ppm thifensulfuron methyl resulted from 2x application, the data demonstrate that the decline and/or disappearance of residues of both thifensulfuron methyl and tribenuron methyl are dependent upon local weather conditions. While the 1x application rate showed less than the proposed 0.1 ppm tolerance in oat straw, we are concerned that 2x application rate showed 0.3 ppm or 3x the proposed tolerance residue of 0.1 ppm in oat straw. If the petitioner intends to increase the application rate in the future, as sometimes occurs, this Madera, CA, residue data indicate that overtolerance situations could occur.

Residues of thifensulfuron methyl and tribenuron methyl  
in oat straw at Madera, CA.

Compound	0.45 oz. a.i./A.	0.90 oz. a.i./A.
Thifensulfuron methyl	Average 0.041 ppm	Average 0.3 ppm
	Duplicates: (0.064 ppm; no peak)	Duplicates: (0.32 ppm; 0.27 ppm)
Tribenuron methyl	<0.018 ppm (Detection Limit) <0.04 (Quantitation Limit)	0.029 ppm  Duplicates: (0.021 ppm; 0.036 ppm),

We conclude that residues of thifensulfuron methyl are not likely to exceed the proposed tolerances of 0.05 ppm in oats grain and 0.10 ppm in oat straw, when used in a single application at no more than 0.45 oz Harmony Extra (equivalent to 0.22 oz. a.i. thifensulfuron methyl/A.) with a preharvest interval of 30 days prior to harvest of oat grain or straw. We conclude that residues of tribenuron methyl are not likely to exceed the proposed tolerance of 0.05 ppm in oat grain and 0.10 ppm in oat straw, when used in a single application of 0.45 oz. Harmony Extra (equivalent to 0.11 oz. a.i. tribenuron methyl/A.) with a minimum preharvest interval of 30 days prior to harvest of oat grain or straw.

#### Processed Commodities:

In the absence of detectable residues of thifensulfuron methyl in oat grain from either 1x or 2x application rate, and considering the 16x and 32x residue data from the Crooks, SD, misapplication trial which also showed no detectable residues in oat grain, we are not requiring oat grain milling fraction data at this time for thifensulfuron methyl. During our considerations of tribenuron methyl (PP7F3540, 4/21/89) in regards to wheat and barley and in compliance with current Branch guidance, residue data from exaggerated rate field trials showing no detectable residue of tribenuron methyl were sufficient in lieu of processing studies; we extend that conclusion herein to the current commodity oat grain milling fractions.

#### Meat, Milk, Poultry, and Eggs

The animal feed items of concern herein are oat grain, hay, straw, forage and hulls. Oat grain constitutes up to 20% of the beef diet, 50% of the dairy cattle diet, 25% of the poultry diet and 80% of the swine diet. Oat hulls constitute up to 5% of the beef cattle diet. Oat forage constitutes up to 20% in beef cattle and 40% in dairy cattle and is not used in poultry or swine diets. Oat straw may constitute 10% of the cattle diet (both beef and dairy).

As in the previous petition (PP6F3431) for Harmony®, in the light of the goat metabolism study showing 'minimal' transfer of thifensulfuron methyl (DPX-M6316) residues to meat and milk at 2800x feeding levels and in the absence of detectable residues in animal feed items oat grain, oat forage, oat fodder and oat straw, we are not requiring tolerances for residues of thifensulfuron methyl in meat, milk, poultry or eggs at this time. If the petitioner should propose a future use which results in detectable residues in animal feed items, tolerances may then be required for secondary residues in meat, milk, poultry, and eggs.

Similarly, in the absence of detectable residues of tribenuron methyl (DPX-L5300) in oat grain, oat forage, oat fodder, and oat straw, we are not requiring tolerances for residues of tribenuron methyl in meat, milk, poultry or eggs at this time. If the petitioner should

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propose a future use which results in detectable residues in animal feed items, tolerances may then be required for secondary residues in meat, milk, poultry, and eggs.

Other Considerations

International Residue Limits

An International Residue Limit Status Sheet (Codex) is attached to our review. There are no Codex, Mexican, or Canadian tolerances for these chemicals on oats.

Attachment: IRLS (Codex)

cc:PM25, Cook, PP0F3961, PP0F3962 ,RF,Circ(7),PIB/FOD(Furrow)  
H7509C:CBTS:RCook:rc:x77484:Rm810H:5/18/92  
RDI:R.S.Quick:5/15/92:R.Loranger:5/15/92

*F. News 2/5/92*

INTERNATIONAL RESIDUE LIMIT STATUS

Cemical: thifensulfuron methyl & tribenuron methyl  
 Harmony (DPX-M6316) Express (DPX-L5300)

Codex No:

Codex Status:

Proposed U. S. Tolerance

No Codex Proposal Step 6 or Above

Petition No: PP1F3961  
 PP1F3962

Residue (if Step 8):

CB Reviewer: R. W. Cook

Residue (if Step 8):

Residue: Parent compound per se  
 according to 180.439 and 180.???

Crop(s)	Limit (mg/kg)	Crop(s)	Limit (mg/kg)
		Thifensulfuron methyl	
		Oat Grain	0.05 ppm
		Oat Straw	0.10 ppm
		Tribenuron methyl	
		Oat Grain	0.05 ppm
		Oat Straw	0.10 ppm

Canadian limits:

Mexican Limits

No Canadian limit

No Mexican limit

Residue

Residue

Crop(s)	Limit (mg/kg)	Crop(s)	Limit (mg/kg)

Notes:

Page 1 of 1.  
 Form Revised 9/90



13544



R100533

**Chemical:** Thifensulfuron; Tribenuron

**PC Code:** 128845; 128887

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