Primary Evaluator	Danette Drew, Chemist Reregistration Branch 3 Health Effects Division	Date: 5/25/04
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This DER was originally prepared under contract by Dynamac Corporation (20440 Century Boulevard, Suite 100; Germantown, MD 20874; submitted 04/05/2004). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

46151701 de Weerd, J. (2003) Magnitude of Residue of Chlorpropham in Raw and Processed Potato Fractions after Post-Harvest Aerosol (165%) Application. Study Number: DCLGLP03-002. Unpublished study submitted by PIN/NIP, Inc. 88 p.

EXECUTIVE SUMMARY:

Pin/Nip, Inc. has submitted data depicting the magnitude of chlorpropham residues in/on processed potatoes after postharvest fumigation in a storage facility. At a commercial storage facility containing approximately 2,700,000 lb of potatoes, chlorpropham was applied through the ventilation system at a rate of 0.0275 lb ai/1,000 lb of potatoes. Treatment was made with a 9.709 lb/gal RTU formulation applied as an aerosol using standard aerosol generating equipment. The ventilation system moves air through the storage facility, pushing air beneath the potato pile, which then flows upward. Samples of whole potatoes were collected from the top, middle, and bottom portions of the storage facility at intervals of 10 days prior to treatment and 1, 15, 28, 62, and 91 days posttreatment. Using simulated commercial procedures, potato samples from each sampling interval were processed into chips, and potatoes from the 28-, 62-, and 91-day sampling intervals were processed into flakes.

Samples of potato peel, pulp, chips, and flakes were analyzed for residues of chlorpropham using an HPLC/UV method; residues in whole potatoes were calculated by summing the actual residues quantitated in the potato peel and pulp and dividing by the whole potato weight. The registrant reported the LOQ as 0.05 µg/mL of final extract volume; based on the varying weights of samples in the study, this corresponds to LOQs of 0.02-0.06 ppm for pulp, 0.15-0.43 ppm for peel, 0.06-0.18 ppm for chips, and 0.15 ppm for flakes. Adequate method recoveries were observed from whole potato samples fortified at 2 and 20 ppm and from chip and flake samples fortified at 0.5 and 2 ppm.

Although samples were apparently not stored frozen prior to analysis, all samples were extracted within 18 days of collection. Certain extracts were stored for extended periods (up to 19 days) prior to analysis; however, the extracts of concurrent fortification samples were subjected to the same extended storage conditions. Adequate recoveries were observed in these samples, indicating stability during storage; therefore, HED will not require supporting storage stability data for this study.

Residues of chlorpropham in/on whole potatoes collected from the top, middle, and bottom portions of the storage facility following fumigation treatment ranged 3.17-6.16 ppm, 5.28-11.23 ppm, and 6.69-13.30 ppm, respectively. The processing data indicate that residues of chlorpropham do not concentrate in chips or flakes ($\leq$0.1x processing factors) processed from potatoes bearing quantifiable residues of chlorpropham following postharvest fumigation treatment.

Based on the report from the processing facility, typically peel is collected, pressed through a fruit press, and the pressed peel blended with cut trimmings to generate wet peel samples. If the results for pressed and blended potato peel are used to represent "wet peel," the data indicate that residues concentrate in potato wet peel; the average processing factor was 7.2x.

The reported processing factors for chips and flakes do not exceed the theoretical concentration factors. According to Tables 2 and 3 of OPPTS 860.1520, the theoretical concentration factors are 4.7x for dried potatoes (flakes, granules) based on loss of water, and 4.0x for potato processed waste. The processing factor for potato peel exceeds the theoretical processing factor for processed potato waste.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the potato processing study data are classified as scientifically acceptable.

COMPLIANCE:

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Chlorpropham is a plant growth regulator used to inhibit sprout formation on stored potatoes. The Chlorpropham RED was issued 10/96, and the Report of FQPA Tolerance Reassessment Progress and Interim Risk Management Decision (TRED) for chlorpropham was issued 9/02. Chlorpropham is formulated as an emulsifiable concentrate (EC) or ready-to-use solution (RTU).

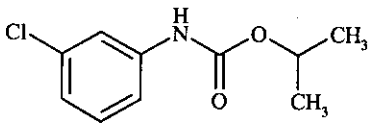
TABLE A.1. Chlorpropham Nomenclature.	
Compound	
Common name	chlorpropham
Company experimental name	N/A
IUPAC name	isopropyl 3-chlorocarbanilate
CAS name	1-methylethyl (3-chlorophenyl)carbamate
CAS registry number	101-21-3
End-use product (EP)	9.709 lb/gal RTU (Pin Nip 98.6% Chlorpropham, Aerosol Grade - Potato Sprout Inhibitor; EPA Reg. No. 65726-3) 2 lb/gal EC (Pin Nip 2 EC, Emulsifiable Concentrate - Potato Sprout Inhibitor; EPA Reg. No. 72790-1)

TABLE A.2. Physicochemical Properties of Technical Grade Chlorpropham.		
Parameter	Value	Reference
Melting point/range	38-40 °C	Chlorpropham RED, 10/96
pH	5.62-5.66	Chlorpropham RED, 10/96
Density	1.17 g/cm^3	Chlorpropham RED, 10/96
Water solubility	89 ppm (25 °C)	Chlorpropham RED, 10/96
Solvent solubility	soluble in ethyl and isopropyl alcohols, ketones, and aromatic solvents	Chlorpropham RED, 10/96
Vapor pressure	2.46 x 10^{-2} Pa at 25 °C	Chlorpropham RED, 10/96
Dissociation constant, pK_a	13.8 in 19% ethanol/water (v/v) at 20 °C	Chlorpropham RED, 10/96
Octanol/water partition coefficient, Log(K_{OW})	3.47 at 25 °C	Chlorpropham RED, 10/96
UV/visible absorption spectrum	not available	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

TABLE B.1. Study Use Pattern on Potato				
Location (City, State, Year)	Application			
	EP [1]	Method; Timing	Single/Total Rate (lb ai/1,000 lb of potatoes)	Tank Mix Adjuvants
Commercial storage facility in Osgood, ID; 2003	9.709 lb/gal RTU	Postharvest via thermal aerosol fogger connected to the ventilation system [2]	0.0275	None

[1] EP = End-use Product.
[2] The ventilation system was closed to the outside during treatment and for 24 hours after treatment; fresh air ventilation was resumed 24 hours after treatment.

Storage facility temperatures were maintained at standard commercial temperatures ranging 4.5-8 °C.

B.2. Processing Procedures

Two samples of potatoes, one for the RAC sample and one for processing into chips, were collected from the top, middle, and bottom of the potato pile 10 days prior to treatment (control) and at 1, 15, 28, 62, and 91 days posttreatment. Each sample consisted of 10 potatoes. Samples were shipped within 24-48 hours of collection to DiChlor Research Laboratory (Meridian, ID) for processing and residue analysis. An additional bulk sample of potatoes (~13.5 kg) was collected at three sampling intervals during the storage period (28, 62, and 91 days posttreatment) and shipped within 24-48 hours of collection to Englar Food Laboratories, Inc. (Moses Lake, WA) for processing into flakes. At the analytical laboratory, samples were stored in mechanically cooled storage bins.

At DiChlor, whole potatoes for processing into chips were rinsed with water, blotted dry, peeled, and sliced in a food-slicer. Potato slices were rinsed again in water and fried in vegetable oil at 176 °C.

At the Englar processing facility, samples were stored refrigerated (7.5 °C) and processed into flakes within 7-10 days of collection using simulated commercial procedures. Briefly, potatoes were first tub washed with water to simulate flume washing. Washed potatoes were then peeled using a steam peeler, scrubbed, and the peel was hydraulically pressed, if necessary, to increase solids content. The potatoes were then cut into slabs 1.0- to 1.5-cm using a food cutter/slicer, spray washed with cold water to remove free starch, pre-cooked at 70-77 °C, and cooled to 32 °C. Precooked potatoes were then steam-cooked at 94-100 °C and mashed using a meat grinder. Food additives were added, and the wet mash was dried through a drum dryer. The resulting large flakes were fed through a hammermill for uniform milling of the flakes. Processed flake samples were frozen and shipped overnight to DiChlor for residue analysis.

B.3. Analytical Methodology

Potato peel and pulp, and processed chip and flake samples were analyzed for residues of chlorpropham using an HPLC/UV method. Residues in whole potatoes were calculated by summing the actual residues quantitated in the potato peel and pulp and dividing by the whole potato weight. For a complete description of the method, refer to the method validation study (DER for MRID 46151702). A brief description of the method follows.

Whole potatoes were first washed with water to remove soil and debris, then peeled. Peel, pulp, chip, and flake samples were blended with a reagent grade alcohol (90-91% ethanol denatured with 5% isopropyl alcohol and 4-5% methanol; 100% or 80% in water), warmed to 50 °C for 30 minutes in a water bath, and shaken for 20 minutes at ambient temperatures. The extract was filtered for HPLC analysis. The reported limit of quantitation (LOQ) was 0.05 µg/mL of final extract volume (10x the noise level), and the limit of detection (LOD) was set at 3x the noise level (no actual value was specified). Based on the weights and extraction volumes reported for the samples in this study, the LOQ of 0.05 µg/mL corresponds to 0.15-0.43 ppm for peel, 0.02-0.06 ppm for pulp, 0.06-0.18 ppm for chips, and 0.15 ppm for flakes.

Untreated potato samples (collected prior to fumigation treatment) were spiked with chlorpropham for concurrent method recoveries by trickling a chlorpropham solution onto the outer peel of the whole potato. After spiking the whole potato was separated into peel and pulp for analysis, and chlorpropham recoveries from whole potato were calculated from the residues in the peel and pulp, based on weight. Concurrent method fortifications were made directly to chips and flakes for analysis. Besides concurrent method validation, chlorpropham verification standards ranging 1-40 µg/mL were analyzed after every 10 samples to confirm the accuracy of the method. The average deviation from the expected concentration of chlorpropham in the verification standards ranged 0.9-7.8%.

C. RESULTS AND DISCUSSION

Whole potatoes were collected from the top, middle, and bottom portions of the storage facility at intervals of 1, 15, 28, 62, and 91 days following postharvest fumigation with chlorpropham at a rate of 0.0275 lb ai/1,000 lb of potatoes, applied through the ventilation system.

Sample storage intervals are summarized in Table C.2; the registrant stated that samples were stored in mechanically cooled storage bins but did not report the storage temperatures. Although samples were apparently not stored frozen prior to analysis, whole potato samples were extracted within 5 days of collection, chip samples were extracted within 18 days of collection, and flake samples were extracted within 14 days of collection. [We note that the registrant did not provide the dates of processing for chips or flakes. Storage intervals for chips were calculated from the date of whole potato collection. For flakes samples, it was assumed that samples were processed 2 days prior to arrival at the analytical laboratory; i.e., that samples were shipped from the processing facility the day after processing.] Certain extracts were stored for extended periods (up to 19 days) prior to analysis; however, the extracts of concurrent fortification samples were subjected to the same extended storage conditions. Adequate recoveries were observed in these samples, indicating stability during storage; therefore, HED will not require supporting storage stability data for this study.

Concurrent recovery data from the potato processing study are presented in Table C.1. Samples of potato peel, pulp, chip, and flake samples were analyzed for residues of chlorpropham using an HPLC/UV method; residues in whole potatoes were calculated by summing the actual residues in the potato peel and pulp and dividing by the whole potato weight. The LOQ ranged 0.02-0.06 ppm for pulp, 0.15-0.43 ppm for peel, and 0.06-0.18 ppm for chips and was 0.15 ppm for flakes. Adequate method recoveries were observed from whole potato samples fortified at 2 and 20 ppm and from chip and flake samples fortified at 0.5 and 2 ppm. Apparent residues of chlorpropham were 0.05-0.07 ppm in/on the "control" whole tuber samples (0.20-0.40 ppm in/on peel and 0.02-0.03 ppm in/on pulp) collected 10 days prior to treatment and 0.06-0.07 ppm in chips processed from untreated potato tubers; flakes were not processed from untreated potatoes. The petitioner did not address the residues in the control samples, but did note that the storage facility had previously been used to store chlorpropham-treated potatoes. Because the residue in the treated samples were significantly higher than in the control samples, residues in the control samples are not of concern for this study.

Residue data from the potato processing study are reported in Table C.3. Residues of chlorpropham in/on whole potatoes collected from the top, middle, and bottom portions of the storage facility following fumigation treatment ranged 3.17-6.16 ppm, 5.28-11.23 ppm, and 6.69-13.30 ppm, respectively. The processing data indicate that residues of chlorpropham do not concentrate in chips or flakes ($\leq$0.1x processing factors) processed from potatoes bearing quantifiable residues of chlorpropham following postharvest fumigation treatment.

Samples of potato wet peel were not collected during the processing portion of the study. Based on the report from the processing facility (Englar), typically peel is collected, pressed through a fruit press, and the pressed peel is blended with cut trimmings to generate wet peel samples. Using the results for pressed, blended potato peel to represent "wet peel," the data indicate that residues concentrate in potato wet peel; the average processing factor was 7.2x.

The reported processing factors for chips and flakes do not exceed the theoretical concentration factors. According to Tables 2 and 3 of OPPTS 860.1520, the theoretical concentration factors are 4.7x for dried potatoes (flakes, granules) based on loss of water, and 4.0x for potato processed waste. The processing factor for potato peel exceeds the theoretical processing factor for processed potato waste.

The fortification levels used for concurrent method validation in this study (2 and 20 ppm for whole potatoes, 0.5 and 2 ppm for chips and flakes) bracketed the calculated residues in whole potatoes, but did not bracket the observed residues in chips and flakes. Several chip and flakes samples bore reported residues below 0.5 ppm. In addition, actual residues quantitated in pulp ranged <LOQ-0.72 ppm, and residues in peel ranged 17.7-122 ppm. Based on the analytical data included in the submission, the fortification procedures used resulted in residues of <LOQ-0.35 ppm in pulp and 9.7-239 ppm in peel. Therefore, HED will not require additional validation data for peel and pulp to support this study. For chip and flake samples, if the LOQ for these samples is considered to be 0.5 ppm (the lower limit of validation), the overall conclusions of the study, that residues do not concentrate in chips and flakes, do not change.

The registrant should note for future submissions that HED prefers validation data for each commodity as analyzed and that fortification levels should bracket the observed residue levels in each commodity. In addition, untreated samples should be generated for each commodity.

TABLE C.1 Summary of Concurrent Recoveries of Chlorpropham from Potato Fractions.

Matrix	Spiking level (ppm)	Sample size	Recoveries (%) [1]	Mean recovery ± SD
Potato, tuber [2]	2	30	73-116	96 ± 8
	20	30	80-104	
Potato, chips	0.5	30	71-115; 122, 128	95 ± 11
	2	30	83-110	
Potato, flakes	0.5	15	69; 75-99	90 ± 13
	2	15	82-118	

[1] Recoveries outside the 70-120% range are listed separately. Residues in fortified samples were corrected for average residues in the control samples collected 10 days prior to treatment: 0.05 ppm in/on whole tubers and 0.07 ppm in chips. For flake samples, residues in fortified samples were corrected for average residues in unfortified, treated samples.
[2] Whole potatoes were fortified and then separated into peel and pulp for separate analyses; residues in the whole potato tuber were calculated by the registrant by summing the actual residues in the peel and pulp (in µg) and dividing by the whole potato weight (in g).

TABLE C.2. Summary of Freezer Storage Conditions

Potato Matrix	Storage Temp.	Actual Storage Duration	Limit of Demonstrated Storage Stability
Potato RAC	"Cool"; temperatures not specified	1-5 days	None provided.
Potato chips		6-18 days	None provided.
Potato flakes		6-14 days	None provided.
Potato peel and pulp extracts	4 °C	0-19 days	None provided.
Potato chip extracts		0-15 days	None provided.
Potato flake extracts		0-1 days	None provided.

TABLE C.3. Residue Data from Potato Processing Study with Chlorpropham.

RAC	Processed Commodity	Total Rate (lb ai/1,000 lb of potatoes)	PTI (days)	Top Sampling		Middle Sampling		Bottom Sampling	
				Residues (ppm)[1]	Processing Factor	Residues (ppm) [1]	Processing Factor	Residues (ppm) [1]	Processing Factor
Potato	Whole tuber (RAC)	0.0275	1	3.17	--	5.28	--	6.69	--
	Peel			23.80	7.5x	38.11	7.2x	49.96	7.5x
	Pulp			0.08	--	0.44	--	0.16	--
	Chips			<LOQ	<0.1x	<LOQ	<0.1	<LOQ	<0.1x
	Flakes			NS [2]	--	NS	--	NS	--
Potato	Whole tuber (RAC)	0.0275	15	4.60	--	8.45	--	13.30	--
	Peel			35.29	7.7x	62.41	7.4x	94.21	7.1x
	Pulp			<LOQ	--	<LOQ	--	0.05	--
	Chips			0.44	0.1x	0.61	0.1x	0.60	<0.1x
	Flakes			NS	--	NS	--	NS	--

TABLE C.3. Residue Data from Potato Processing Study with Chlorpropham.

RAC	Processed Commodity	Total Rate (lb ai/1,000 lb of potatoes)	PTI (days)	Top Sampling		Middle Sampling		Bottom Sampling	
				Residues (ppm)[1]	Processing Factor	Residues (ppm) [1]	Processing Factor	Residues (ppm) [1]	Processing Factor
Potato	Whole tuber (RAC)	0.0275	28	5.79	--	7.97	--	11.52	--
	Peel			42.92	7.4x	60.14	7.5x	85.21	7.4x
	Pulp			0.04	--	<LOQ	--	0.04	--
	Chips			0.41	0.1x	0.52	0.1x	0.51	<0.1x
	Flakes			0.16	<0.1x	0.14	<0.1x	0.22	<0.1x
Potato	Whole tuber (RAC)	0.0275	62	5.59	--	11.23	--	11.32	--
	Peel			36.94	6.6x	77.92	6.9x	77.54	6.8x
	Pulp			0.19	--	0.21	--	0.17	--
	Chips			0.53	0.1x	0.61	0.1x	0.62	0.1x
	Flakes			<LOQ	<0.1x	<LOQ	<0.1x	<LOQ	<0.1x
Potato	Whole tuber (RAC)	0.0275	91	6.16	--	10.00	--	10.83	--
	Peel			46.97	7.6x	68.41	6.8x	73.94	6.8x
	Pulp			<LOQ	--	0.21	--	0.25	--
	Chips			0.48	0.1x	0.52	0.1x	0.56	0.1x
	Flakes			0.33	0.1x	0.65	0.1x	0.82	0.1x

[1] The average residue, as reported by the petitioner, of 10 replicate samples from the single sample collected is presented and was used for calculating the processing factor. The LOQ ranged 0.02-0.06 ppm for pulp, 0.15-0.43 ppm for peel, and 0.06-0.18 ppm for chips, depending on sample weight, and was 0.15 ppm for flakes. Residues in whole potato tubers were calculated by the registrant by summing the actual residues in the peel and pulp (in µg) and dividing by the whole potato weight (in g). A value of half the LOQ (0.025 µg/mL) was used in these calculations and calculations of averages when residues were <LOQ.
[2] NS = Not sampled for processing of flakes.

D. CONCLUSION

The potato processing data indicate that the residues of chlorpropham do not appear to concentrate in potato chips and flakes ($\leq$0.1x processing factors) processed from potatoes treated with a postharvest fumigation application. Chlorpropham residues do concentrate in potato peel (average processing factor of 7.2x). The method used for sample analysis was determined to be adequate for the purposes of this study.

E. REFERENCES

None

F. DOCUMENT TRACKING

RDI: C. Eiden (5/26/04)
Petition Number(s): Not applicable
DP Barcode(s): D297631
PC Code: 018301

cc: Anthony Britton (SRRD), Michael Goodis (SRRD)

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