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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Captan - Storage Stability Studies for the Captan Registration Standard

DEB No. 4204
MRID No. 407523-01

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Background

The Residue Chemistry Chapter of the Captan Registration Standard, published August 15, 1985, concluded that no data were available regarding the storage stability of residues of captan in or on plant commodities or in animal commodities. The following data were requested:

> The storage intervals and conditions of storage of samples used to support all established tolerances for residues must be submitted. These data must be accompanied by data depicting the percent decline in residues at the times and under the conditions specified. On receipt of these data, the adequacy of the aforementioned tolerances will be reevaluated.
>
> All residue data requested in this Registration Standard must be accompanied

by data regarding storage length and conditions of storage of samples analyzed. These data must be accompanied by data depicting the stability of residues under the conditions and for the time intervals specified.

This Submission

ICI Americas, Inc. has submitted three studies intended to evaluate the stability of captan residues after storage for up to 2 years under controlled conditions in various raw agricultural commodities (RACs) in which initial captan and tetrahydrophthalimide (THPI) residue levels have been determined. THPI is a principal plant metabolite and also a degradation product of captan. Study 1 is complete. Interim results are given for studies 2 and 3.

Analytical Method

The analytical method used to quantitate captan and THPI residues is entitled "Determination of Captan and THPI Residues in Crops." This method is designated Method RM-IK-2 by its supplier, Chevron Chemical Company. Briefly, samples are macerated, immediately acidified with phosphoric acid, then extracted three times with ethyl acetate. The extracts are combined, dried with sodium sulfate, filtered, washed three times with dilute phosphoric acid, then filtered through sodium sulfate and evaporated to dryness. The residue is dissolved in dichloromethane and passed through a nuchar-silica column to remove interfering coextractives; the residue from oily crops first passes through a standard acetonitrile-hexane partition step and is further cleaned up by gel permeation chromatography prior to the nuchar-silica cleanup. The final eluate is evaporated to dryness, and the residue is redissolved in a measured volume of solvent prior to analysis by gas chromatography.

Captan and THPI are each quantitated by gas chromatography using element-selective detection. For captan, a Coulson electrolytic conductivity detector operated in the chlorine-selective mode or an electron-capture detector may be used. For THPI, a Coulson detector operated in the nitrogen-selective mode, or a nitrogen-phosphorous detector may be used. This method is intended for determinations of captan and THPI at levels greater than 0.05 ppm.

Total residue concentrations expressed as captan were calculated from the GC determinations of captan and THPI by adding twice the concentration of THPI to that of captan. This procedure was followed because a given amount of THPI

requires as precursor twice this amount of captan, on a weight/weight basis. One gram of captan produces, upon decomposition or metabolism, almost exactly 0.5 g of THPI.

Study 1

Field treated commodities were macerated, analyzed for initial residue levels of captan and THPI, and stored in the dark at -20 ± 10 °C in glass bottles with polyethylene-lined lids. At intervals of 3, 6, and 14 months, the samples were chosen randomly from storage and reanalyzed. At each withdrawal two untreated samples were removed. The following table presents the results of this study.

Sample	Interval (Months)	Captan ppm	THPI ppm	Total ppm*	Total Recovery %
Apple	Initial	2.65	0.095	2.84	-
	3	2.75	0.11	2.97	105
	6	2.8	0.12	3.04	107
	14	2.9	0.13	3.16	111
Cucumber	Initial	1.05	0.12	1.29	-
	3	0.43	0.22	0.87	67
	6	0.55	0.28	1.11	86
	14	0.39	0.34	1.07	83
Lettuce	Initial	13.0	0.22	13.4	-
	3	8.80	0.43	9.66	72
	6	8.07	0.72	9.51	71
	14	7.37	0.58	8.53	63
Spinach	Initial	32.0	2.65	37.3	-
	3	34.4	9.91	54.2	145
	6	29.9	7.56	45.0	121
	14	31.6	11.5	54.6	146
Strawberry	Initial	8.65	0.24	9.13	-
	3	6.67	0.36	7.39	81
	6	6.40	0.41	7.22	79
	14	6.40	0.50	7.40	81

*Expressed as captan.

Study 2

In this study, cherry and tomato samples were from captan-treated crops, while samples of almonds, apple juice, corn grain, potato tubers, soybeans, beet tops, and soybean forage were commercially obtained from local markets or

producers. The cherry and tomato samples were macerated, analyzed for captan and THPI, then stored. The remaining commodities were macerated and divided into several portions that were fortified with both captan and THPI ranging from 0.2 to 0.5 ppm, then stored. (The only exceptions were beet tops and soybean forage, for which separate samples were fortified with either captan or THPI). The interim results of that study are presented in the following table.

RAC	Interval (Months)	Captan Recov. ppm	THPI Recov. ppm	Total Recov. ppm	Total Recov. %
Almond					
(Fortification, ppm)		0.5	0.5	1.5	
	0	0.38	0.44	1.25	83
	1	< 0.05	0.64	1.28	85
	3	< 0.05	0.36	0.72	48
	6	< 0.05	0.42	0.84	56
Apple Juice					
(Fortification, ppm)		0.48	0.24	0.96	
	0	0.41	0.24	0.89	93
	1	0.41	0.26	0.94	98
	3	0.58	0.15	0.88	91
	6	0.48	0.15	0.77	80
	15	0.31	0.28	0.87	91
Cherry					
Field Treated Samples					
Initial Concentration	0	20.8	0.26	21.3	
	1	24.8	0.30	25.4	120
	3	18.9	0.35	19.6	92
	6	12.4	0.36	13.2	62
	12	15.9	0.30	16.5	78
Corn Grain					
(Fortification, ppm)		0.5	0.5	1.5	
	0	0.38	0.44	1.27	84
	1	0.46	0.46	1.38	92
	3	0.08	0.41	0.90	60
	6	0.03	0.45	0.93	62
Potato Tubers					
(Fortification, ppm)		0.48	0.24	0.96	
	0	0.47	0.17	0.81	84
	1	0.32	0.14	0.60	63
	3	0.25	0.23	0.71	74
	6	0.27	0.24	0.76	78
	15	0.14	0.25	0.64	67

RAC	Interval (Months)	Captan Recov. ppm	THPI Recov. ppm	Total Recov. ppm	Total Recov. %
Soybean Grain (Fortification, ppm)		0.48	0.24	0.96	
	0	0.29	0.24	0.77	81
	1	0.21	0.21	0.62	65
	3	0.14	0.32	0.79	82
	6	0.12	0.21	0.54	56
	15	0.04	0.10	0.25	26
Tomato Field-treated Samples Initial Concentration		0.88	0.09	1.06	
	1	0.40	0.22	0.83	79
	3	0.30	0.25	0.80	75
	6	0.28	0.35	0.98	93
	12	0.14	0.34	0.81	77
	20	0.15	0.30	0.74	70

RAC	Interval (Months)	Captan Recov. ppm	THPI Recov. ppm	Captan Recov. %	THPI Recov. %
Beet Tops (Fortification, ppm)		0.48	0.48		
	0	0.55	0.69	115	143
	1	0.10	0.24	22	50
	3	0.19	0.32	40	67
	6	0.13	0.35	27	73
	15	< 0.05	0.31	0	73
Soybean Forage (Fortification, ppm)		0.52	0.52		
	0	0.38	0.44	73	85
	1	0.38	0.39	73	75
	3	0.35	0.40	67	77
	6	0.22	0.22	42	42
	15	0.36	0.38	69	74

In this study, a total of 47 separate captan fortifications were made at levels between 0.48 and 20 ppm. Captan recoveries ranged between 72 and 119 percent.

In the 47 fortifications made with THPI at levels from 0.24 to 1 ppm, recoveries ranged between 52 and 125 percent.

Study 3

In this study, the stability of captan and THPI in RACs were evaluated independently. The samples were ground by machine only enough to allow for representative subsampling prior to fortification. In two cases, corn and almonds, whole samples were also analyzed. Because machine grinding of spinach resulted in finely macerated material, coarsely hand-chopped spinach was also tested. The following table presents the interim results of that study.

		Fortified With 0.05 ppm Captan					Fortified With 0.05 ppm THPI	
		Captan ppm	Captan rec.	THPI ppm	Total ppm	Total rec.	THPI ppm	THPI rec.
	(Months)							
Almond Nuts, Coarsely Ground	0	0.5	101%	a	a	a	0.38	77%
	1	0.21	41%	a	a	a	0.38	76%
	2	0.33	66%	.07	.46	92%	a	a
Almond Nuts, Whole	0	0.41	81%	a	a	a	0.44	89%
	1	0.27	53%	a	a	a	0.36	72%
	2	0.42	84%	< 0.05	.42	84%	a	a
Apples	0	0.52	78%	a	a	a	0.42	83%
	1	0.41	82%	a	a	a	0.44	87%
	3	0.39	78%	a	a	a	0.40	80%
Apple Sauce	0	0.47	94%	a	a	a	0.43	85%
	1	0.40	80%	a	a	a	0.37	74%
	3	0.37	74%	a	a	a	0.36	73%
Corn Grain, Coarsely Ground	0	0.44	88%	a	a	a	0.40	80%
	1	0.05	11%	a	a	a	0.36	72%
Corn Grain, Whole	0	0.40	81%	a	a	a	0.46	92%
	1	0.13	26%	a	a	a	0.35	70%
	2	0.15	30%	0.20	0.56	112%	a	a
Dry Grape Pomace	0	0.41	81%	a	a	a	0.42	84%
	1	0.35	69%	a	a	a	0.36	72%
	3	0.41	82%	a	a	a	0.43	86%
Raisin	0	0.46	93%	a	a	a	0.39	79%
	1	0.36	71%	a	a	a	0.44	87%
	3	0.37	73%	a	a	a	0.53	107%

		Fortified With 0.05 ppm Captan					Fortified With 0.05 ppm THPI	
	(Months)	Captan ppm	Captan rec.	THPI ppm	Total ppm	Total rec.	THPI ppm	THPI rec.
Potato Tubers	0	0.46	92%	a	a	a	0.45	89%
	1	0.37	73%	a	a	a	0.40	79%
	3	0.37	73%	a	a	a	0.37	74%
Spinach, Finely Chopped	0	0.49	99%	a	a	a	0.43	85%
	1	0.15	30%	a	a	a	0.37	73%
Spinach, Chopped Coarsely	0	0.48	95%	a	a	a	0.44	88%
	1	0.056	11%	a	a	a	0.39	79%
	2	0.12	24%	0.10	0.32	63%	a	a
	3	0.14	28%	0.16	0.45	90%	0.47	95%
Tomato Sauce	0	0.42	84%	a	a	a	0.41	82%
	1	0.51	102%	a	a	a	0.38	77%
	3	0.44	87%	a	a	a	0.53	106%
Tomato	0	0.46	92%	a	a	a	0.37	75%
	1	0.38	76%	a	a	a	0.42	84%
	3	0.38	75%	a	a	a	0.46	92%
Tomato Dry Pomace	0	0.43	87%	a	a	a	0.43	85%
	1	0.42	84%	a	a	a	0.38	76%
	3	0.38	76%	a	a	a	0.40	80%

[a]Not analyzed.

In the above study, 80 fortifications using 0.5 ppm captan were made. Recoveries ranged between 68 and 109 percent. A total of 79 fortifications were made with 0.5 ppm THPI. Recoveries ranged between 70 and 118 percent.

DEB's Conclusions and Recommendations

The above studies indicate that residues of captan, per se, are unstable in most crops which have been macerated prior to storage. However, in those cases where captan degrades, it generates an equivalent amount of THPI. Therefore, the stability of captan is a function of the stability of THPI.

The registrant has calculated the total residue concentration expressed as captan by taking the levels of

captan and THPI determined by GC and adding twice the concentration of THPI to that of captan. It should be noted that we have some reservations as to the validity of this approach; however, on this basis, DEB concludes from the data submitted that the total residue concentrations expressed as captan are stable in the following RACs for the intervals specified:

Almonds	1 month
Apples	14 months
Apple Juice	15 months
Apple Sauce	3 months
Cherries	12 months
Corn Grain	1 month
Cucumber	14 months
Lettuce	6 months
Potatoes	6 months
Soybean Grain	3 months
Soybean Forage	15 months
Tomatoes	12 months
Strawberries	14 months
Spinach	3 months
Tomato Sauce	3 months
Dry Tomato Pomace	3 months
Dry Grape Pomace	3 months
Raisin	3 months
Beet Tops	Data Inconclusive

Final conclusions concerning the storage stability of total residues expressed as captan in the various RACs will be made at the time the final results are submitted for Study 2 and Study 3.

cc: Reading File, Circulation, Subject File, Captan Reg. Std. File, Reviewer, PMSD/ISB, Branch Chief
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