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

JUN 26 1991

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Captan - Storage Stability Studies for the Captan Registration Standard and Follow-Up to Seed Treatment Residue Data; MRID No. 415576-01; Branch No. 6995; DP Barcode No. 155338

FROM: Christine L. Olinger, Chemist
Special Review Section I
Chemistry Branch II - Reregistration Support
Health Effects Division (H7509C)

A handwritten signature in cursive script, appearing to read "Christine Olinger".

THRU: Andrew Rathman, Section Head
Special Review Section I
Chemistry Branch II - Reregistration Support
Health Effects Division (H7509C)

TO: Carol Peterson
Reregistration Branch
Special Review and Reregistration Division (H7508C)

ICI Americas, Inc. has submitted a final report for captan storage stability studies in response to DEB comments (C. Olinger 10/6/89, 1/29/90, 7/30/90; L. Propst 12/19/89). The Residue Chemistry Chapter of the Registration Standard concluded that no data were available regarding the storage stability of residues of captan in/on plant or 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."

Residue data regarding seed treatment uses were required to be submitted by July 6, 1989 as outlined in the Data Call-In Notice (April 29, 1985) and the Special Review Position Document #4. The requirements as specified in the DCI are as follows:

"EPA requires residue data for captan and THPI for representative crops to support low level tolerances covering seed treatments. Residue data for crops grown from treated seed must be submitted for corn, soybeans, potatoes, rice or a small grain, and two of the vegetables having seed treatments."

Previous DEB reviews of seed treatment data have concluded the seed treatment magnitude of residue data are adequate. However the storage stability data which are required to support the residue studies were incomplete. Accordingly ICI Americas, as part of the Captan Task Force, has submitted a complete storage stability study in response to DEB comments.

Based on the Use Index information compiled for the 1985 Registration Standard, captan formulations are registered for use as slurry, dry, seed piece (potato), and/or planter box seed treatments at a variety of rates and formulations. The following commodities have registered uses of captan seed treatments (CBRS is not aware of any cancellation of any of these uses): alfalfa, barley, beans, beets, broccoli, Brussels sprouts, cabbage, cantaloupe, carrots, cauliflower, clover, collards, sweet corn, field corn, cotton, cucumber, eggplant, flax, grasses, kale, lentils, lespedeza, millet, muskmelons, mustard, oats, okra, onions, peanuts, peas, pepper, potato (seed piece), pumpkins, radishes, rape, rice, rutabagas, rye, safflower, sesame, sorghum, soybeans, spinach, squash, sugar beets, sunflower, Swiss chard, tomatoes, trefoil, turnips, watermelons, and wheat.

Conclusions

1. CBRS considers the seed treatment residue data requirements satisfied. No additional data are required.
2. Storage stability requirements with respect to seed treatment residue data have been satisfied. No additional data are required to support seed treatments.

Recommendations

CBRS considers the seed treatment residue data requirements from the Registration Standard satisfied. No further magnitude of residue or storage stability data are required to support seed treatments with captan.

Since the data requirements for seed treatments are satisfied tolerances must be proposed for all commodities for which there are registered seed treatments (if tolerances have not been previously established). CBRS has previously recommended for the establishment of the following **new** tolerances (C. Olinger 7/30/90) for captan and its metabolite tetrahydrophthalimide at a level of 0.1 ppm (the combined limits of determination) if proposed by the Captan Task Force: cotton, flax, lentils, okra, peanuts, radishes, rape, safflower, sesame, sugar beets, sunflowers, and Swiss chard. CBRS also previously recommended for a **reduction** in tolerances for captan and its metabolite tetrahydrophthalimide for the following commodities to 0.1 ppm from established levels if proposed by the Captan Task Force (C. Olinger 7/30/90): beets, broccoli, Brussels sprouts, cabbage, cantaloupe, carrots, cauliflower, collards, cotton, cucumber, eggplant, honeydew melon, kale, muskmelon, mustard greens, onion (dry bulb), onion (green), pea, pepper, pumpkin, rutabaga, soybean, spinach, squash, tomato, turnip, and watermelon. Interim tolerances have been established for beans and potatoes. CBRS can recommend for reduction of the tolerances for captan and its metabolite tetrahydrophthalimide to 0.1 ppm for beans and 0.5 ppm for potatoes (N. Gray 4/22/88). CBRS can now recommend that the Captan Task Force propose new tolerances, or reduce established tolerances, (to a level of 0.1 ppm, the combined limits of determination of both captan and THPI) for the following commodities: alfalfa, barley, clover, grasses, lespedeza, millet, oats, rice, rye, sorghum, trefoil, and wheat.

SRRD is advised that recommendations for new/modified tolerances are based on the use information from the 1985 Registration Standard. According to E. Wilson of the Registration Division (personal communication, 6/19/91), he is not aware of any new seed treatment uses approved since then. A LUIS report is due to be issued for captan August 1, 1991. CBRS would appreciate receiving any information SRRD has regarding approval or cancellation of any seed treatment uses since 1985, so the recommendations regarding new/modified tolerances may be reconsidered if necessary.

Detailed Considerations

Deficiencies from the 7/30/90 memorandum of C. Olinger are restated below.

Conclusion 2 (7/30/90 C. Olinger)

"Additional storage stability data have been presented for corn grain and several other commodities. In the absence of detailed study information, DEB cannot provide conclusions regarding the storage stability of captan and THPI on corn grain."

Conclusion 3 (7/30/90 C. Olinger)

"DEB reserves judgement on translation of storage stability of other RAC's to wheat grain until the final storage stability studies are reviewed."

In response to these comments ICI Americas Inc. has submitted the final report for captan storage stability studies (MRID No. 415576-01). Interim results have been previously reviewed by DEB (L. Propst 12/19/89).

In study 2 field treated cherries and tomatoes bearing detectable residues of captan were placed into frozen storage and analyzed for residues of captan and its primary metabolite, tetrahydrophthalimide (THPI) periodically. Several other commodities purchased from local markets or distributors were fortified with both captan and THPI. Commodities were generally chopped or macerated prior to fortification. Two crops were fortified separately with captan and THPI. Prepared samples (chopped, macerated, etc.) were placed into frozen storage and analyzed periodically for residues of captan and THPI.

In study 3 commodities were fortified separately with captan and THPI. Comparisons between method of preparation (e.g. chopped vs. whole commodity) were done as well. Samples were placed into frozen storage and analyzed periodically for residues of captan and THPI.

Analytical Method

Chevron Method RM-1K-2 was used for collection of residue data. Prepared samples are acidified immediately after maceration and extracted with ethyl acetate. The extract is dried with sodium sulfate, filtered, partitioned with dilute phosphoric acid, dried again with sodium sulfate, and evaporated to dryness. The residue is reconstituted with dichloromethane and cleaned up on a nuchar-silica column. Prior to the column clean-up extracts from oily crops are partitioned with acetonitrile/hexane and occasionally, gel permeation chromatography clean-up. The final eluate from the nuchar-silica column is evaporated to dryness and reconstituted with an appropriate solvent for analysis by gas chromatography with element specific detection. For the analysis of captan an electrolytic conductivity detector in the chlorine mode or an electron capture detector was used. A nitrogen-phosphorus detector or an electrolytic conductivity detector in nitrogen mode was used for the determination of THPI. The limit of determination for each analyte is 0.05 ppm.

Results of Storage Stability Studies

Interim results have shown rapid degradation of captan in some

matrices, particularly if the commodity was extensively processed prior to fortification. THPI has shown greater stability and results have shown virtually all of the captan degrades to THPI. Therefore most of the captan-fortified samples were also analyzed for THPI. Since the molecular weight of captan is twice that of THPI the concentration of THPI is doubled to determine the captan equivalent concentration in the commodity. CBRS has reservations about this approach, but will accept it for these studies.

Concurrent fortifications were conducted for all commodities in studies 2 and 3. Results of recoveries are summarized in the following table for all commodities.

Study No.	Analyte	Spiking Levels, ppm	Range of Recoveries, %	Average Recovery, %	Standard Deviation	No. of Determinations
2	Captan	0.05 - 20	72 - 119	92	12	48
	THPI	0.05 - 1.0	52 - 128	91	16	47
3	Captan	0.5	68 - 113	91	10	151
	THPI	0.5	68 - 118	86	6	150

A summary of results from studies 2 and 3 is presented in the following Tables 1 through 4. From these results it is apparent that the stability is somewhat dependent upon the extent of sample preparation prior to storage. According to the registrant the samples (from magnitude of residue studies) were placed into frozen storage unprocessed. The maximum acceptable storage period for each commodity is presented in Tables 5 (study 2) and 6 (study 3).

Although the stability of captan per se is poor, since it degrades to THPI which exhibits much greater stability CBRS will consider these data acceptable. CBRS will accept translation of corn grain storage stability to wheat grain. There are no outstanding data requirements with regard to seed treatments.

Tolerance Considerations

Since the data requirements for seed treatments are satisfied tolerances must be proposed for all commodities for which there are registered seed treatments (if tolerances have not been previously established). CBRS has previously recommended for the establishment of the following new tolerances (C. Olinger 7/30/90) for captan and its metabolite tetrahydrophthalimide at a level of 0.1 ppm (the combined limits of determination) if proposed by the Captan Task Force: cotton, flax, lentils, okra, peanuts, radishes, rape, safflower, sesame, sugar beets, sunflowers, and Swiss chard. CBRS also previously recommended for a reduction in tolerances for captan and its metabolite tetrahydrophthalimide for the following commodities to 0.1 ppm from established levels if proposed by the

Captan Task Force (C. Olinger 7/30/90): beets, broccoli, Brussels sprouts, cabbage, cantaloupe, carrots, cauliflower, collards, cotton, cucumber, eggplant, honeydew melon, kale, muskmelon, mustard greens, onion (dry bulb), onion (green), pea, pepper, pumpkin, rutabaga, soybean, spinach, squash, tomato, turnip, and watermelon. Interim tolerances have been established for beans and potatoes. CBRS can recommend for reduction of the tolerances for captan and its metabolite tetrahydrophthalimide to 0.1 ppm for beans and 0.5 ppm for potatoes (N. Gray 4/22/88). CBRS can now recommend that the Captan Task Force propose new tolerances, or reduce established tolerances (to a level of 0.1 ppm, the combined limits of determination of captan and THPI), for the following commodities: alfalfa, barley, clover, grasses, lespedeza, millet, oats, rice, rye, sorghum, trefoil, and wheat.

SRRD is advised that recommendations for new/modified tolerances are based on the use information from the 1985 Registration Standard. According to E. Wilson of the Registration Division (personal communication, 6/19/91), he is not aware of any new seed treatment uses approved since then. A LUIS report is due to be issued for captan August 1, 1991. CBRS would appreciate any information SRRD has regarding approval or cancellation of any seed treatment uses since 1985, so the recommendations regarding new/modified tolerances may be reconsidered if necessary.

cc: CLOlinger (CBRS), Circulate, Reg. Std. File, RF, SF,
RDSchmitt, W. Smith (CBRS), J. Miller (RD; PM-23), C. Furlow
(PIB/FOD)

H7509C:CBRS:CLOlinger:clo:CM#2:Rm 803C:557-1406: 6/21/91

RDI: ARRathman: 6/24/91 EZager: 6/24/91

Table 1. (continued)

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Commodity	Interval (Months)	Captain Recovery, ppm ¹	Captain Recovery, %	THPI Recovery, ppm	Total Recovery, ppm ²	Total Recovery, % ³
Corn Grain	Initial Fortification	0.5	NA	0.5	1.5	NA
	0	0.382	76	0.442	1.267	84
	1	0.460	92	0.460	1.379	92
	3	0.080	16	0.409	0.898	60
	6	0.029	6	0.453	0.934	62
Soybean Grain	Initial Fortification	0.48	NA	0.24	0.96	NA
	0	0.287	60	0.243	0.773	81
	1	0.210	44	0.207	0.623	65
	3	0.142	30	0.323	0.787	82
	6	0.116	24	0.212	0.540	56
	15	0.041	9	0.102	0.245	26

¹Average of two or more determinations unless otherwise specified.²Total residue concentration expressed as captain.³Based on amount added at fortification.⁴NA = not applicable.

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Table 2. Results of Storage Stability Study 2 for those Commodities Bearing Field-Treated Detectable Residues

Commodity	Interval (Months)	Captan Recovery, ppm ¹	Captan Recovery, %	THPI Recovery, ppm	Total Recovery, ppm ²	Total Recovery, % ³
Cherries	Initial Concentration	20.8	NA ⁴	0.256	21.31	NA
	1	24.8	119	0.299	25.4	120
	3	18.9	91	0.346	19.63	92
	6	12.4	60	0.362	13.16	62
	12	15.9	76	0.301	16.5	78
Tomatoes	Initial Concentration	0.880	NA	0.089	1.058	NA
	1	0.404	46	0.215	0.834	79
	3	0.300	34	0.248	0.795	75
	6	0.283	32	0.348	0.979	93
	12	0.136	15	0.338	0.812	77
	20	0.147	17	0.298	0.743	70

¹Average of two or more determinations unless otherwise specified.²Total residue concentration expressed as captan.³Based on initial total residue.⁴NA = not applicable.

Table 4. Results for Study 3 Storage Stability

Commodity	Interval, months	Fortified with 0.5 ppm Captan						THPI Fortified	
		Captan ppm ¹	Captan % Recovery	THPI ppm	Total ppm ²	Total % Recovery	THPI ppm	THPI % Recovery	
Almond Nuts, whole	0	0.406	81	NA ³	NA	NA	0.444	89	
	1	0.266	53	NA	NA	NA	0.359	72	
	2	0.422	84	ND ⁴	0.422	84	NA	NA	
	3	0.382	76	ND	0.382	76	0.307	62	
	6	0.328	66	0.016	0.344	69	0.353	71	
	9	0.364	73	ND	0.364	73	0.450	90	
	0	0.504	101	NA	NA	NA	0.384	77	
	1	0.207	41	NA	NA	NA	0.381	76	
	2	0.33	66	0.065	0.46	92	NA	NA	
Apples	0	0.519	104	NA	NA	NA	0.417	83	
	1	0.41	82	NA	NA	NA	0.436	87	
	3	0.388	78	NA	NA	NA	0.400	80	
	6	0.382	76	NA	NA	NA	0.360	72	
	9.5	0.434	87	NA	NA	NA	0.487	97	
	0	0.47	94	NA	NA	NA	0.426	85	
Applesauce	1	0.401	80	NA	NA	NA	0.371	71	
	3	0.369	74	NA	NA	NA	0.363	73	
	6	0.370	74	NA	NA	NA	0.417	83	
	9.5	0.348	70	NA	NA	NA	0.380	76	

Table 4. (continued)

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Commodity	Interval, months	Fortified with 0.5 ppm Captan						THPI Fortified	
		Captan ppm ¹	Captan % Recovery	THPI ppm	Total ppm ²	Total % Recovery	THPI ppm	THPI % Recovery	
Corn Grain, whole	0	0.403	81	NA	NA	NA	0.460	92	
	1	0.130	26	NA	NA	NA	0.348	70	
	2	0.152	30	0.203	0.558	112	NA	NA	
	3	0.128	26	0.156	0.284	57	0.456	91	
	3.5	0.139	28	0.172	0.311	62	0.401	80	
	8	0.186	37	0.148	0.334	67	0.402	80	
	12	0.046	9	0.417	0.463	93	0.458	92	
	0	0.441	88	NA	NA	NA	0.402	80	
	1	0.053	11	NA	NA	NA	0.360	72	
Grape Pomace, Dry	0	0.406	81	NA	NA	NA	0.421	84	
	1	0.347	69	NA	NA	NA	0.361	72	
	3	0.408	82	NA	NA	NA	0.431	86	
	6	0.376	75	NA	NA	NA	0.378	76	
	9+	0.374	75	NA	NA	NA	0.408	82	
	0	0.458	92	NA	NA	NA	0.446	89	
Potato Tubers	1	0.366	73	NA	NA	NA	0.397	79	
	3	0.366	73	NA	NA	NA	0.372	74	
	6	0.372	74	NA	NA	NA	0.354	71	
	9.5	0.338	68	NA	NA	NA	0.356	71	
	0	0.338	68	NA	NA	NA	0.356	71	

Table 4. (continued)

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Commodity	Interval, months	Fortified with 0.5 ppm Captan						THPI Fortified	
		Captan ppm ¹	Captan % Recovery	THPI ppm	Total ppm ²	Total % Recovery	THPI ppm	THPI % Recovery	
Raisin	0	0.464	92	NA	NA	NA	0.394	79	
	1	0.357	71	NA	NA	NA	0.437	87	
	3	0.366	73	NA	NA	NA	0.533	107	
	6	0.422	85	NA	NA	NA	0.485	97	
	10	0.364	73	NA	NA	NA	0.406	81	
	0	0.475	95	NA	NA	NA	0.438	88	
Spinach, coarsely chopped by hand	1	0.055	11	NA	NA	NA	0.393	79	
	2	0.121	24	0.097	0.315	63	NA	NA	
	3	0.14	28	0.155	0.450	90	0.474	95	
	9	0.057	11	0.274	0.331	66	0.359	71	
	12	0.031	6	0.358	0.389	78	0.469	94	
	0	0.493	99	NA	NA	NA	0.425	85	
Spinach, finely chopped	1	0.149	30	NA	NA	NA	0.367	73	
	0	0.483	97	ND	0.480	96	0.471	94	
Sugar Beet Tops	1	0.428	86	ND	0.461	92	0.353	70	
	3	0.456	91	0.097	0.554	111	0.419	84	
	6	0.424	85	0.155	0.424	85	0.373	75	
	12	0.334	67	0.274	0.439	88	0.332	66	
	0	0.461	92	NA	NA	NA	0.373	75	
	1	0.378	76	NA	NA	NA	0.422	84	
Tomato, whole fruit	3	0.376	75	NA	NA	NA	0.462	92	
	6	0.380	76	NA	NA	NA	0.427	85	
	9.5	0.396	79	NA	NA	NA	0.418	84	
	0	0.461	92	NA	NA	NA	0.373	75	

Table 4. (continued)

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Commodity	Interval, months	Fortified with 0.5 ppm Captan						THPI Fortified	
		Captan ppm ¹	Captan % Recovery	THPI ppm	Total ppm ²	Total % Recovery	THPI ppm	THPI % Recovery	
Tomato, dry pomace	0	0.433	87	NA	NA	NA	0.426	85	
	1	0.418	84	NA	NA	NA	0.381	76	
	3	0.378	76	NA	NA	NA	0.400	80	
	6	0.364	73	NA	NA	NA	0.392	78	
	9	0.378	76	NA	NA	NA	0.379	76	
Tomato Sauce	0	0.418	84	NA	NA	NA	0.411	82	
	1	0.508	102	NA	NA	NA	0.384	77	
	3	0.435	87	NA	NA	NA	0.529	106	
	6	0.422	84	NA	NA	NA	0.457	91	
	9.5	0.358	72	NA	NA	NA	0.394	79	
Wheat Forage	0	0.412	82	ND	0.414	83	0.386	77	
	1	0.386	77	0.146	0.532	106	0.459	92	
	3	0.366	73	0.080	0.446	89	0.387	77	
	6	0.097	19	0.350	0.447	89	0.544	109	
	12	0.043	9	0.183	0.226	45	0.351	70	

¹Average of two or more determinations.²Expressed as captan equivalents.³NA = not analyzed for THPI.⁴ND = not detected.

Table 5. Summary of Maximum Storage Stabilities from Study 2.

Commodity	Maximum Length of Storage, Captan (months)	Maximum Length of Storage, Captan + THPI (months)
Almonds, ground	0	1
Apple Juice	6	15
Beet Tops	0	12
Cherries	3	15
Corn Grain, ground	1	1
Potato tubers	0	6
Soybean Forage	1	15
Soybean Grain	0	3
Tomatoes	0	20

Table 6. Summary of Maximum Storage Stabilities from Study 3.

Commodity	Maximum Length of Storage, Captan (months)	Maximum Length of Storage, Captan + THPI (months)
Almonds, whole	9	9
Almonds, coarsely ground	0	2
Apples	9.5	9.5
Applesauce	9.5	9.5
Corn Grain, whole	0	12
Corn Grain, coarsely ground	0	1
Grape Pomace, Dry	9	9
Potato tubers	9.5	9.5
Raisins	10	10
Spinach, coarsely chopped	10	10
Spinach, finely chopped	0	1
Sugar Beet Tops	12	12
Tomato, whole fruit	9.5	9.5
Tomato, dry pomace	9	9
Tomato Sauce	9.5	9.5
Wheat Forage	3	12