

ESTIMATION OF EXPOSURE OF PERSONS IN
CALIFORNIA TO PESTICIDE PRODUCTS THAT
CONTAIN CAPTAN

By

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ABSTRACT

Captan (cis-N[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide) is a protectant-eradicator fungicide of low acute mammalian toxicity. Its major reported use in California is on almonds. Animal feeding studies indicate that it is metabolized and excreted rapidly, with more than half the test dose excreted within 24 hours of administration. The major metabolites (tetrahydrophthalimide oxidation products) are excreted primarily through urine, which permits human biomonitoring. Potential human exposure ranges from <20 mg/day (applicators) to greater than 1000 mg/day (mixer/loader). Human exposure monitoring and dermal penetration studies support an estimate of dermal absorption of 6 percent per 24 hours.

This report was prepared as Appendix B to the Department's risk assessment document for captan. Captan is in risk assessment for oncogenic effects noted in rodents.

APPENDIX B

California Department of Food and Agriculture Worker Health and Safety Branch

Human Exposure Assessment

CAPTAN

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GENERAL CHEMISTRY AND ACUTE TOXICITY

Captan (cis-N[(trichloromethyl) thio]-4-cyclohexene-1,2-dicarboximide) has a melting point of 175°C. It is an off-white powder that is insoluble in water and moderately soluble in organic solvents. It is used as a protectant-eradicator fungicide. In dry conditions it is stable but degrades rapidly in water or alkaline environments. In water (pH 7) captan has a half-life of 2.5 hours. It has a very low acute toxicity with an oral LD₅₀<rat> of 9000 mg/kg and a dermal LD₅₀<rabbit> of 7,500 mg/kg (1). Captan is a moderate eye irritant.

METABOLISM STUDIES

Captan metabolism has been studied in rats (2)(3)(4)(5), mice (5), goats (2)(6)(7), and cattle (8). In rats, urinary excretion accounts for 84 percent of administered oral dose. The rat studies have identified the following materials as major metabolites of captan (numbers are percentage of metabolite found in rat urine):

cis-1,2-dicarboximido-4-cyclohexene (THPI)	15 percent
cis-1-carboxy-2-carboxamido-4-cyclohexene (THPAM)	12 percent
hydroxylates of THPI: 5-OH-THPI	10 percent
3-OH-THPI	38 percent
4,5-diol	11 percent

These are all modifications of the tetrahydrophthalimide moiety of captan. THPI is further metabolized by hydroxylation and epoxidation.

The initial scission of the N-S bond also results in the formation of thiophosgene (9), a moderately toxic material. This bond breakage is accomplished by either hydrolysis or sulfite/thiosulfite radical reaction. Urine is the principal route of elimination (3)(4)(5) with lesser amounts in exhaled air (¹⁴C-trichloromethyl tagged)(3)(5) and feces. Exhalation is only important in the first 12 hours (up to 22 percent of ¹⁴C-tagged material eliminated). This indicates that the trichloromethyl group is very labile and is subject to further degradation. Excretory metabolites of the trichloromethylthio moiety include dithiobis(methane-sulfonic) acid, thiazolidine-thione carboxylic acid and thiophosgene. Studies in rats, mice and goats (6) indicated the following ranges of percent excretion:

Table One: Interspecies elimination of captan over time. Values are the sum of radioactivity (^{14}C labeled) detected in urine/feces/exhaled air.

TIME	PERCENT OF TOTAL DOSE ELIMINATED (all routes)		
	RAT	MOUSE	GOAT
12 hrs.	23	58.6	NS
24 hrs.	59.5	75.7	NS
48 hrs.	76.0 to 92	80.2	97
72 hrs.	80.4 to 88.6	81.9	NS
96 hrs.	81.5 to 96	84.7	NS

NS - Not studied

CDFA, WH&S, H. Fong, 1987

Captan does not accumulate in the body tissues. In general, more than 50 percent of the dose was excreted (all routes) within 24 hours in each test species.

DERMAL ABSORPTION

The use of aqueous vehicles presents several experimental problems related to captan's insolubility and instability in water. By using minimal amounts of aqueous carrier, researchers have attempted to reduce the significance of these factors for in vivo dermal absorption studies.

Two in vivo dermal absorption studies using Captan 50WP spiked with ^{14}C -captan have been conducted using male Sprague-Dawley rats. The first study (10) used two dose rates of ^{14}C -carbonyl captan; 0.5 mg and 5.0 mg on non-occluded application sites measuring 103 cm^2 . Captan was applied in an aqueous suspension (0.2 ml). The study lasted eight hours with sacrifices at one, two, four, and eight hours. The researchers observed the following: Absorption appears to reach a maximum of 6.4 (SD 5.7) percent of the 0.5 mg dose (mean of data obtained at four and eight hour samples) and 9.0 (SD 6.6) percent of the 5.0 mg dose (mean of data obtained at two, four and eight hour samples). However, there were no significant differences in mean percent absorption between the two doses at any time. The maximum absorption rate appears to have occurred between hours 2 and 4. These values are based on the total of tagged material found in urine, feces, carcass and cagewash. Inspection of the data shows that some ^{14}C -captan was probably sloughed directly to the cage wash fraction. Most of the applied dose was still in/on the skin, even after eight hours. We concur with the researchers' suggestion that only the captan in suspension was appreciably absorbable while the dry material remaining after carrier evaporation was not available for absorption. The average percentages of absorbed ^{14}C -captan are given below. These data were apparently used by EPA to calculate an absorption rate of 1.3 percent per hour (9).

Table Two: Average percentage of ¹⁴C-captan dose absorbed by rats.

TIME (hour)	0.5 MG. DOSE		5.0 MG. DOSE	
	Avg. %	SD	Avg. %	SD
1	1.5	0.4	2.8	2.5
2	5.8	4.2	10.1	9.6
4	8.9	7.7	7.3	7.2
8	4.0	1.0	9.4	3.4

CDFA, WH&S, H. Fong, 1987

The second study (11) used a dose rate of 4.88 mg. on a non-occluded application site of 6.52 cm². ¹⁴C-Trichloromethyl-captan was administered as a propylene glycol suspension (0.1 ml). In the five day (120 hours) study (with no interim sacrifices), urine, feces and exhaled air were collected. The cumulative average absorption was 54 percent (range 33 percent to 76 percent) and absorption was assumed to be linear over the life of the study. A table of percent recovery of dose versus time in excreta was developed (Table Three). An average hourly absorption factor of 1.3 percent per hour was calculated by WH&S from 2.5 to 25 hours post-exposure. This time period corresponds to the fastest absorption rate, as the curve flattens out after 30 hours. The 12 and 24 hour absorption values would be 16 percent and 31 percent.

Table Three: Percent of dose recovered in urine, feces and CO₂

TIME (hours)	CUMULATIVE %				% per hour
	Urine	Feces	CO ₂	Total	
2.5	2.0	0.0	1.25	3.25	1.3
5	3.75	1.0	2.5	7.25	1.5
10	7.0	2.5	4.2	13.7	1.4
15	8.75	6.25	5.05	20.1	1.3
20	10.5	9.5	6.0	26.0	1.3
25	12.0	12.0	6.44	30.4	1.2
30	13.75	13.75	6.88	34.4	1.2
35	15.0	15.0	7.45	37.5	1.1
40	16.25	16.25	7.65	40.2	1.0
45	17.0	17.5	7.9	42.4	1.0

CDFA, WH&S, H. Fong, 1987

The Captan Task Force/ICI Americas completed an in vitro dermal absorption study, using both human and rat epidermis and technical grade captan or formulated 50WP (44). The epidermal membranes, after being judged fit for use, were stretched over a support screen which was suspended in contact with a receptor chamber filled with a receptor fluid consisting of slightly acidified (to inhibit captan degradation) ethanol. A donor chamber (well) was placed over the membrane and filled with the test solution. Six different applications were made to the two different species' skin. Technical captan was used at two different doses (200 mg/cm² and 0.04 mg/cm²); the 50 WP at 200 mg/cm²; two 1:70 aqueous spray solutions at either

10 or 100 ul/cm² (72 or 720 ug/cm², respectively); and one spray solution of a 3:1 mixture at 10 ul/cm². Test material was kept in contact with the skin membranes for 55 hours.

The results indicated that human skin was 3 to 100-fold less permeable than rat skin to captan. The dose of 720 ug/cm² is very close to the dose used in the second in vivo rat study: 748 ug/cm². The mean absorbed dose in vitro for rat skin was 1.04 ug/cm²/hr and for human skin it was 0.285 ug/cm²/hr (based on captan values + 2 x THPI). Setting up a rat:human ratio using the previously cited 24 hour rat in vivo absorption value of 31 percent, the following equation can be generated by WH&S:

	<u>IN VITRO</u>		<u>IN VIVO</u>
HUMAN	0.285 ug/cm ² /hour	=	X %
RAT	1.04 ug/cm ² /hour		31 %

CDFA, WH&S, R. Krieger, 1989

Solving for X yields an absorption in 24 hours for a human of 8.5 percent. This value assumes that the in vivo to in vitro relationship for captan in rats is equal to that for humans. WH&S calculated ([flux x time] ÷ dose) in vitro rat and human dermal penetration percentages at the 720 ug/cm² dose. These were 8 percent for rat and 2 percent for man, over the course of the exposure period. These percentages underestimate actual in vivo percentages of absorption, but the relative rates of absorption between species is consistent.

Two studies of human worker exposure (43)(45) also provided data for human dermal absorption estimations. The strawberry harvester study (43) urinalysis results showed that very little THPI was excreted. The median THPI output was 0.005 ppm, with a range of <0.005 to 0.014 ppm. By comparing the average urine data (0.1 mg/day THPI = 0.2 mg/day captan penetrated exposure) to the amounts found by dermal dosimetry (~10 mg/day), an estimate of the daily dermal penetration was derived.

$$0.1 \text{ mg/day(urine)} \div 10 \text{ mg/day(dermal dosimeter)} = 1 \text{ percent}$$

Factors such as the interception of the potential dermal dose by the dosimeters (making the captan unavailable for urinary excretion), rounding and averaging errors, using the relatively minor metabolite THPI as the marker, and the unverified assumption that dermal dosage will be excreted the same as an oral dosage, will tend to increase this value. One percent can be assumed to be the lower limit of absorption.

The other worker exposure study (45) has not been published and is presently available only in memorandum form. It was also a strawberry harvester study. Unlike the earlier study (43), the dermal exposure was independently characterized using total-body dosimeters with and without urinary monitoring. The following study period used minimal dermal dosimetry to allow maximal dermal exposure/penetration but still measure dermal exposure. During this study period, urinary output of THPI was measured. Comparing

dermal dosimeter results with THPI output, an absorption factor of 5.8 percent was estimated. However, many of the same caveats as applied to the the earlier study also apply to this one.

The variability of the dermal absorption results (31 percent rat in vivo; 8.5 percent in vitro human extrapolation; 1 and 5.8 percent "in vivo" man, 2 percent man and 8 percent rat in vitro) does not allow an exact derivation of a dermal absorption rate. But eliminating both extremes and giving greater weight to the human data for the remaining values, a dermal absorption rate of 6.0 percent per 24 hours (0.25 percent/hour) was used by WH&S to estimate absorbed dose for regulatory purposes.

WORKER EXPOSURE

Several captan exposure studies have been conducted with workers. There are seven mixer/loader/applicator (M/L/A) studies (12,13,14,15,16,17,18); two harvester exposure compilations (9)(19), five harvester studies (35,36,37,38,43), two seed treatment worker exposure studies (20)(21), a retrospective worker cohort study (22), and the EPA estimated mixer/loader/applicator exposure data base (9). All exposures are potential dermal exposures (dosimeter data) unless otherwise noted.

Mixer/Loader/Applicators (M/L/A)

The first M/L/A study reviewed (12) used Orthocide 83 (wetttable powder) through an air-blast sprayer. This formulation, containing 83 percent a.i. is not available in California. The application rate was 1.34 lb/Ac (1.11 lb/Ac of a.i.). Mixer/Loader (M/L) total potential dermal exposure ranged from 124.5 mg/day to 351 mg/day, averaging 244 mg/day. The applicator (APPL) exposure varied from 88.0 mg/day to 656.7 mg/day, averaging 408.7 mg/day. Inhalation exposure was insignificant, with a study maximum of 0.53 mg/day for one of the M/L replicates. Hand exposure amounted to more than half of the total exposure for both M/L and APPL. Cloth gloves were used as the hand exposure collection media.

A second M/L/A study (16) used Captan 50WP at 6 lb/Ac (3 lb/Ac of a.i.). Two rates of application were employed; 20 gallon/Ac and 100 gallon/Ac. Air-blast equipment was used for the applications. The M/L was exposed to 1496 mg/day, of which 1224 mg was by way of hand exposure (82%). Hand washings were done with an ethanol solution. The applicators were exposed to 20.4 mg/day, 50 percent on the hands and 50 percent on the remaining body. Once again inhalation exposure was negligible.

The third M/L/A study (15) with Captan 50WP at 2 lb/Ac (1 lb/Ac of a.i.) combined patch data from the tractor driver, the applicator and the mixer/loader. A single orifice hand-wand was used. The data was not presented in a way to separate out job-task exposure, though the authors concluded that the differences between the mean patch values of the applicator and the tractor driver were not statistically significant (252 ug vs. 300 ug). The average patch residue was 2.66 ug/cm². This equals 6.96 mg on the unprotected body, assuming exposure to the head, neck and hands (area=2,618 cm²). The sampling period was four hours, so daily exposure was 13.9 mg/day. The number of dermal dosimeters used per worker (three on body) and the data presentation in this study is inadequate for a meaningful assessment of the dermal exposure. These data will not be used for exposure

assessment.

A Florida study (18) of two types of greenhouse application methods using Captan 50 WP found different levels of exposure to the tractor driver/applicator that were method dependent. The "Span" application resulted in total exposure of 2 mg/day while the "Boom" application exposure was 23 mg/day. The greatest exposure was to the total body (92 percent for boom sprayers, 63 percent for span sprayers).

A Minnesota study (14) looked at several applications of Captan 50WP to apples. There were 10 situations in which conditions of application rate, dilution rate, air-blast manufacturer, level of personal protection, and personnel involved were varied. Each applicator also functioned as his own mixer/loader. Dermal body exposure was measured using Durham and Wolfe dosimeters. Hand exposure was measured using EtOH washes. The lowest exposure occurred to a worker who wore no gloves but did wash his hands after every mix/load operation. He also used a closed cab to apply 3 lb/Ac (1.5 lb/Ac a.i.). His exposure was 2.1 mg/day. All the other applicators used open cab tractors. The highest exposure (67.5 mg/day) was for a worker who washed his hands and used gloves. The mean exposure of open cab M/L/A's was 22.2 mg/day. Inhalation exposure ranged from 0.003 mg/day to 0.09 mg/day. The maximum inhalation exposure is only 0.4 percent of the average dermal exposure. In seven out of 10 cases in this study, hand exposure accounted for more than 50 percent of the dermal load (range 50 percent to 95 percent). The average percent of hand exposure was 56.7 percent. The worker with the highest percentage of dermal exposure on the hands (95 percent) wore rubber gloves but did not wash after each mix/load operation. Of workers who wore gloves and did wash, their average hand exposure was 45.4 percent of the total dermal dose.

The next two studies were not used for exposure assessment calculations since they did not contain sufficient information for worker exposure calculations.

The M/L/A air monitoring study from Oudbier (13) used an unidentified formulation of captan and an unspecified rate of application. The Durham and Wolfe method of inhalation exposure measurement with respirators equipped with gauze pads was used. A secondary method using impingers yielded suspect results. There was no captan detected in the ethylene glycol media, even though companion gauze pads showed relatively high levels of residue. The media may have degraded the captan before it could be analyzed. No dermal exposure measurements were made. The highest inhalation exposure to a mixer/loader was 2.11 mg/day; the highest applicator was 0.15 mg/day. The mixer/loader value is an extrapolation from a total of 31 minutes of exposure, the applicator from almost three hours (170 minutes).

An applicator study on chrysanthemums (17) using Captan 50WP was done to compare captan penetration of cotton/polyester blend (Cot-Poly) clothing to GORE-TEX fabric. Contaminated control samples reduced the value of the study. This study also did not fully address worker exposure since hand exposure was not monitored. The study demonstrated that under light spray contact conditions, Cot-Poly and GORE-TEX provided similar levels of protection (1.45 percent penetration of captan through the test fabric). Under laboratory conditions of multiple exposures resulting in the wetting

of the fabric, Cot-Poly had 14 percent penetration while GORE-TEX had little change in percent penetration. Maximum inhalation exposure, using Durham and Wolfe's respirator method, was only 50.2 ug/day.

Harvesters

Harvester exposure has been reported in seven documents. One report (9) has a compilation of strawberry harvester exposure. There was no information concerning the captan formulation used nor the application rate. The following table outlines the worker exposure values, in progression of days post-application (9):

Table Four: Mean strawberry harvester exposure to captan foliar residues as compared to the time after application.

<u>DAYS POST APP.</u>	<u>MG/DAY (8 HOUR)</u>
3	139
3	132
3	57
4	312
10	52
23	38
48	47

CDFA, WH&S, H. Fong, 1987

This study also reported weeders' exposure as 753 mg/day. However, another report (23) amplified the weeders' exposure results and showed that this value is based on anomalous conditions. The weeders were young children whose dermal dosimeter results showed exceedingly high values on the head-neck and chest patches but low hand exposure values. Since they were working as weeders, the highest potential exposure areas should be the bare hands, forearms and legs. The results suggest that the children may have engaged in unusual work practices (throwing contaminated material, assuming a prone position on contaminated soil, etc.). This high value of 753 mg/day should not be used for assessment of adult worker exposure but is an indication that children's exposures may be unacceptably high. This study was conducted outside California.

A picker study (19) was done on apple harvesters in an orchard which had been treated with Captan 50WP at 6 lb/Ac (3 lb/Ac a.i.). Dermal dosimeters and air monitoring (quartz fiber filters) were utilized. The following table shows the levels of exposure compared to the days post-application:

Table Five: Mean apple harvester exposure to foliar captan residues as compared to days after application. Comparative data on foliar residue is also given.

<u>DAYS POST APP.</u>	<u>MG/DAY</u>		<u>FOLIAR RESIDUE (PPM)</u>
	<u>DERMAL</u>	<u>AIR</u>	
1	97.4	0.48	128
3	84.6	0.73	85
7	77.8	0.43	37
14	48.0	0.51	39

CDFa, WH&S, H. Fong, 1987

Inhalation exposure was one percent or less. The greatest exposure per area occurred on the hands, averaging 5 mg/day.

Four other harvester exposure studies were submitted by the Captan Task Force (lead company: ICI Americas, Inc). Four crops were studied (peaches, tomatoes, strawberries and grapes) under similar sampling conditions. All worker exposure was monitored using exterior dosimeters, handwashes and air sampling. Applications were done at maximum label rates and high frequencies of application for each of the crops. These conditions are not representative of normal agricultural use practices in California. When other data, using more representative rate and application frequencies is available, that data will be used for calculation of Lifetime Average Daily Dosage. The average daily actual dermal exposure (not potential) to workers in each crop was calculated by WH&S for harvesters. For peaches, exposure was 171.0 mg/day; for tomatoes exposure was 194.9 mg/day ; for strawberries exposure was 90.9 mg/day ; for grapes exposure was 168.5 mg/day. A major amount of the exposure for the grape harvesters was on the legs. The inhalation component was insignificant in all studies.

Two other harvester studies were conducted by the Department of Food and Agriculture (CDFa)(43)(45). In both studies, strawberry harvesters were monitored using full-body dermal dosimetry, allowing for measurement of actual dermal exposure (not potential). In the earlier study (43), one group of workers was asked to wear rubber gloves, the others did not. Handwashes were taken from both groups to ascertain the protective value of glove use. The total-body monitoring was done four hours for one day of the three day monitoring period. This may have reduced potentially measurable urinary metabolites ~20 percent. Handwash monitoring was done for the full seven hour work periods. Urine monitoring for the metabolite THPI was also performed, collecting total urines for the duration of the study. Creatinine levels were measured for indication of compliance.

The dermal dosimetry data indicated that hand exposure was a major contributor to the worker exposure values, with 34 to 52 percent of the total exposure occurring on the hands. The use of gloves reduced mean total exposure more than 70 percent. Total exposure for ungloved workers over the two days of dermal monitoring was 21.8 (Day 1) and 42.6 (Day 2), for an average exposure of 32 mg/day. The gloved workers' exposure over that same period was 4.6 (Day 1) and 12.4 (Day 2) for an average exposure of 8.5

mg/day. This data will be used in lieu of the ICI strawberry harvester exposure for calculation of L.A.D.D.

The other strawberry harvester study conducted by CDFA (45) used total-body dermal doismeters, handwipes and handwashes. The report has not been written, but preliminary data was available. This data showed that the average harvester dermal exposure was 35.12 mg/day/person. The upper-body accounted for 91 percent of the exposure (31.96 mg); the lower-body for 5.6 percent (1.97 mg) and the hands had only 3 percent of the exposure (1.19 mg). This study, being incomplete, is not used in the LADD table (Table Seven).

Seed Treatment

Two studies in seed-treatment facilities were conducted. Stauffer measured airborne levels of captan at two seed-corn treatment plants (20). The highest time weighted average (TWA) found was 0.6 mg/m³ for seed baggers. Stauffer also conducted a survey of their Calhio manufacturing plant. The job task titled "Dumper" received the highest average TWA of 8.0 mg/m³. All other jobs measured at the plant were below the American Conference of Governmental Industrial Hygienists' Threshold Limit Value^R of 5 mg/m³. This level is also the Cal/OSHA Permissible Exposure Limit.

A seed potato study (21) followed the seed crop from treatment to planting. The material used was captan five percent protectant dust, applied at 1.5 lb. (1.2 oz. of a.i.) of dust per 100 lb. of potato cuttings. The dusting hoppers were filled from 50 lb. bags. Dust exposure varied by work task. The task of "hopper filler" resulted in the highest exposure, since this worker also had to reach into the treatment drum to retrieve rocks. This high exposure was during treatment of an especially rock-laden batch of potatoes. The hopper filler's total dermal exposure was 120 mg/day, of which 61 mg was from hand exposure. Inhalation exposure was 13.6 mg/day. A more representative exposure value was 65 mg/day, of which 37 percent was from hands and 7.5 percent from inhalation exposure. All other worker categories had exposure averaging 4 mg/day.

Home and Garden Uses

Most registered products are dusts that are difficult to work with without considerable inhalation and dermal exposure. Only a few products are liquid formulations.

A typical person might use home and garden type products five times a year. If label directions were followed, excessive exposure should not occur. However, the experience of CDFA has been that a substantial number of users in the home and garden category do not follow the label and thus significant exposure does occur even though the number of days of exposure per year is low. Also the person who operates a part-time neighborhood gardening business could be exposed to considerable amounts of captan.

Actual exposure data to persons for home and garden uses was not provided by registrants. We estimate an extreme case exposure for home, garden and turf use by a person to be up to 500 mg per person per day for three days a week, six months a year.

Painter Exposures

The extreme case exposure of a painter is estimated by WH&S to be up to 6 grams of paint on the skin per day. If a paint contained one-tenth of one percent of the active ingredient, then dermal exposure could be 6 mg per day, three days per week, three months per year.

Workers Incorporating Captan Into Products Such As Adhesives, Plastics, Bedding and Pillows

The extreme case exposures in this group could be the person who incorporates the 90 percent captan formulation into adhesives for about 40 days a year with 200 mg of dermal exposure per day (8000 mg per year).

Treating Skin of Animals

Attempting to dust animals often results in the person doing the dusting receiving considerable personal exposure. In a damp climate, with continuing fungal problems in an animal's haircoat, 200 mg of dermal exposure of captan from treating just one horse may be expected. According to practicing veterinary doctors, weekly treatments could occur (33). If more animals were treated, by persons who treat large number of animals in veterinary hospitals and ranches, this rate of annual exposure could be up to 20,000 milligrams per year.

EPA Exposure Estimates

A final document of worker exposure was provided by the EPA (9). The estimated exposure database, based on surrogate data, supplied the following information:

Table Six: Estimated worker exposure to captan, from EPA estimated exposure table.

<u>JOB</u>	<u>CROP</u>	<u>APP. DEVICE</u>	<u>DERMAL*</u>	<u>INHALATION*</u>	<u>TOTAL*</u>
M/L	Apples	NA	1440	48	1488
M/L	Grapes	NA	1440	48	1488
M/L	Peaches	NA	1440	48	1488
M/L	Almonds	NA	6400	26	6426
APPL	Apples	Air-blast	240	neg.	240
APPL	Grapes	Boom-rig	192	neg.	192
APPL	Peaches	Air-blast	320	neg.	320
APPL	Almonds	Aerial	18	neg.	18
APPL	Strawbs	Boom-rig	192	neg.	192
APPL	HOMEOWNER		14	neg.	14

* expressed in mg/day

NA = Not Applicable

neg. = negligible (~0.5 mg/day)

CDFA, WH&S, H. Fong, 1987

The following table is a compendium of selected worker exposure with estimates of absorbed dose (Daily Exposure x Dermal Absorption); daily absorbed dosage per kilogram (AADD: Annual Average Daily Dosage = [Absorbed Dose ÷ Weight] x [Days Exposed ÷ 365 Days/Year]); and Lifetime Average Daily Dosage (LADD: (AADD x Career Period) ÷ 70 Year Lifetime). The primary criterion for inclusion in this table is that the data is based on actual captan exposure data. The surrogate EPA estimations of exposure were not included because actual exposure studies of sufficient quality were available.

Table Seven: Compilation of exposure study data grouped by job task. Dermal absorption calculated at 6.0% per 24 hours exposed time. Weight is assumed as 70 kg for M/L/A, 54.8 kg for all others. Career period is assumed as 40 years (50 for home/garden) and average lifetime is 70 years. AADD: Annual Average Daily Dosage, LADD: Lifetime Average Daily Dosage. Days/Year are estimated number of 8 hour days of potential exposure.

Job Task	Daily Exp. mg/8hrs.	Days Year	Absorb. Dosage mg/day	AADD ug/kg/day	LADD ug/kg/d/70y	Ref.
MIXER/LOADER						
Mix/load	244	60	14.65	34.5	19.8	12
Mix/load	1496	60	89.75	210.8	120.5	16
APPLICATORS						
Blast	409	60	24.55	57.8	33.0	12
Blast	2	60	0.13	0.5	0.3	14
Blast	68	60	4.08	9.5	5.5	14
Blast	22	60	1.33	3.0	1.8	16
Blast	19	60	1.15	2.8	1.5	16
Boom	23	100	1.38	5.5	3.3	18
Span	2	100	0.13	0.5	0.3	18
Seed, Hi	134	60	8.05	19.0	10.8	21
Seed, Lo	11	60	0.65	1.5	0.8	21
HARVESTERS						
Strawbs, EPA	111	120	6.65	40.0	22.8	9
Strawbs, CDFA	32	120	1.93	11.5	6.5	43
Apple, Day 1	97	60	5.83	17.5	10.0	19
Apple, Day 14	48	60	2.88	8.5	4.8	19
Grape, ICI	169	80	10.15	40.5	23.3	38
Tomato, ICI	195	60	11.78	35.0	20.0	41
Peach, ICI	171	60	10.25	30.8	17.5	39
OTHER						
Home and Garden	500	18	30.00	27.0	19.3	
Painter	6	36	0.36	0.7	0.4	
AnimalCare	2000	60	120.00	360.0	205.8	

CDFA, WH&S, H. Fong, 1989

PLANT RESIDUE

Captan's foliar and fruit residue has been examined in several crops including grapes (24)(40), strawberries (25,26,34,42,43), almonds (27)(28), peaches (15,29,39), apples (15,30,31) and tomatoes (41). It was discovered that fruit slowly absorbs and degrades captan (30). Wet foliar conditions appear to decrease the half-life of captan on apple leaves (31). In wet conditions the half-life is approximately 3.5 to 7 days; in dry conditions the half-life is retarded up to 20 days on apples. On strawberry foliage, under conditions of repeated applications, captan degrades slowly. Half-lives of captan ranged from two to 20 days. Higher temperatures seemed to significantly accelerate degradation ($T_{1/2} = <3$ days when mean temp $\sim 20^{\circ}\text{C}$). The study mean $T_{1/2}$ was seven days. Leaf residue levels ranged from 2 ug/cm^2 (two days post-application) to $<0.1 \text{ ug/cm}^2$. (34) Recovery from fortified samples was 50 percent, possibly reflecting captan's instability in aqueous systems.

One set of studies (39,40,41,42) was conducted by the Captan Task Force on four different crops (peaches, grapes, tomatoes, strawberries) using the same protocol in each study. This was done in conjunction with the previously reported worker exposure studies performed by the Captan Task Force (35,36,37,38). The following table lists the residue levels at selected time intervals and the WH&S calculated half-lives for these studies. The registrant had reported equivalent half-life values except in the case of grapes (see * in table). The degradation curve shows an extreme biphasic profile and WH&S calculations were on only the second, slower phase of the curve. The registrant had integrated both parts of the curve and arrived at a half-life of 16 day. For assessment of potential residue exposures to field workers, the slower half-life is more appropriate.

Table Eight: Reported mean foliar levels of captan on four different crops. Values expressed in ug/cm^2 .

Time Post Application	MEAN FOLIAR CAPTAN RESIDUE			
	<u>Peach</u>	<u>Grape</u>	<u>Tomato</u>	<u>Strawberry</u>
0 Days	23.67	18.9	24.97	11.0
1 Day	25.40	20.3	23.07	8.3
3 Days	-Not Available-		35.10	8.1
5 Days	23.37	6.7	18.60	4.9
7 Days	23.94	5.4	13.14	5.4
14 Days	16.36	2.6	24.77	3.2
21 Days	15.01	3.3	-Not Available-	
Half-Life (days):	43	43*	32	10

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Using both the residue data at the time of allowed worker reentry from Table Eight and the corresponding harvester exposure data from Table Seven, harvester transfer coefficients can be derived by WH&S. These coefficients are:

Grapes: 15,633 cm²/hr
 Peaches: 3,292 cm²/hr
 Strawberries: 2,333 cm²/hr
 Tomatoes: 1,644 cm²/hr

Once again, it must be stressed that the rates/application frequencies used were much higher than found in common agricultural practice

REPORTED USAGE

The major uses of captan, as reported by the 1987 Pesticide Use Report from CDFA's Pesticide Use Enforcement Branch, are as follows:

Table Nine: Major crop uses of captan during 1987

<u>CROP</u>	<u>#APP</u>	<u>LB. APP</u>	<u>ACRES</u>	<u>PERCENT OF TOTAL APPLIED</u>
Almonds	409	129,560	34,978	37
Grapes	606	109,495	57,904	30
Prunes	208	44,204	13,031	13
Strawberries	600	37,111	22,935	11
Peaches	<u>89</u>	<u>9,741</u>	<u>2,620</u>	<u>3</u>
SUBTOTAL	1,912	330,111	131,468	94
All other	619	22,954	not avail.	6

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In California, 761,246 pounds of captan were reported sold, as per the CDFA "Pounds of Chemical Active Ingredient Reported Sold in 1987" (46). In 1987, there were 124 products registered in California, including dust and dust combinations (sulfur and/or DCNA) 50 percent of all products, wettable powders (WP) 19 percent, emulsifiable concentrates, primarily seed treatment, six percent and liquids, two percent. The dusts range from five percent to 75 percent a.i. The commercial agriculture use wettable powder is usually in a 50 percent concentration. Sixteen home-use materials are available, in dust, spray and WP formulations. Some contain other pesticides and are designed for broad-spectrum control. Included in some of these formulations are lindane, malathion, methoxychlor, carbaryl, zineb, PCNB, phosmet, and diazinon. The highest concentration of captan a.i. is found in Chevron Captan Technical with 92 percent. This manufacturing formulation is to be used in the manufacture of agricultural-use captan. Vancide 89 is a formulation made for incorporation into non-agricultural uses (plastics, soaps, other industrial materials) for which worker exposure studies are lacking.

WORKER ILLNESSES

From 1982 to 1988, there have been 66 captan related worker illness/injuries reported and classified by WH&S. The yearly average has been 9.6. Skin injuries (dermatitis) accounted for 67 percent, eye (including eye/skin) injuries 27 percent, and suspected systemic illness 6 percent. In the years 1983 through 1985, there was a marked increase in reported skin injuries, then in 1986 to 1988 the number drops down to historic levels. There have been no deaths reported from captan use.

Table Ten: Number of worker illness/injuries associated with captan exposure, from 1982 to 1988.

<u>YEAR</u>	<u>SYSTEMIC</u>	<u>EYE INJURY</u>	<u>DERMATITIS</u>	<u>TOTAL</u>
1982	0	4	3	7
1983	2	5	7	14
1984	0	2	10	12
1985	0	5	17	22
1986	1	0	2	3
1987	1	2	3	6
1988	0	0	2	2
TOTAL	4	17	44	66

CDFA, WH&S, Fong, 1989

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