A STUDY OF FOLIAR RESIDUES FOLLOWING APPLICATION OF SUPRACIDE TO ORANGE TREES

RIVERSIDE COUNTY JUNE 1975
KERN COUNTY JULY 1975

Keith T. Maddy
Agricultural Chemicals & Feed
1220 N Street
Sacramento, CA 95814

PERSONNEL

California Department of Food and Agriculture, Division of Inspection Services, and Chemistry Laboratory Services:

Keith T. Maddy	Staff Toxicologist
Jerry W. Alexander	Agricultural Chemist
A. Scott Fredrickson	Agricultural Chemist
Terry Jackson	Agricultural Chemist
Charles S. Kahn	Agricultural Inspector
Gary W. Sprock	Agricultural Inspector

Riverside County Agricultural Commissioner's Office:

Wallace C. Manning	Deputy County Agricultural Commissioner
Charles J. Collins	County Agricultural Inspector

Kern County Agricultural Commissioner's Office:

Jesse E. Bridges	Deputy County Agricultural Commissioner

In California citriculture scalicides are usually applied for the first time each season at petal fall (April - May for California navel oranges). Applications are then made throughout the summer as necessary. Once fruit has developed beyond an oil sensitive stage (August for California navel oranges) scalicides applied in conjunction with spray oils are particularly effective and widely used. Amounts of major scalicides applied for control of scale and other pests on oranges through September in 1975 were:

Pesticide	Pounds	Acreage treated
Guthion	27,620	14,330
Malathion	71,520	17,670
Parathion	119,650	43,410
Sevin	80,780	7,560
Supracide*	24,470	10,000

* Registered for use on citrus in California August 1974.

Supracide 2E, Ciba Geigy, contains two pounds of the organophosphate methidathion, per gallon of emulsifiable concentrate. In addition to the use on citrus, it is also registered for use on alfalfa, cotton and tobacco. From the standpoint of human safety, supracide, with acute oral and dermal LD_{50} values (rats) of 25-48 and 375 mg/kg respectively, shows promise as a less toxic substitute for more dangerous scalicides such as parathion.

On the basis of limited data, the California Department of Food and Agriculture has set a temporary 30-day worker reentry interval for Supracide 2E applied to citrus. To aid in establishing a permanent reentry interval, residue studies were carried out in two orange groves during the Summer of 1975. One of the groves was located in Riverside County and the other in Kern County. These groves are designated 1 and 2 for convenience.

METHODS AND MATERIALS

The Applications

Grove	Location	Date	Applicator	Dilution	Gallons/ Acre	Methidathion/ Acre
1	Riverside	6/3/75	Lamar Bros. Pest Control	2 pts/100 gal	500	2.5 lbs.
2	Edison	7/15/75	Foothill Spray Co.	1 pt/100 gal	1875	4.7 lbs.

Sampling Procedures

Foliage samples consisted of 100 leaf discs gathered with either a 2.5 or 1.8 centimeter diameter leaf punch and 10 x 4.5 centimeter wide mouth sample bottles. Twenty-five trees were selected and marked in each grove and four leaf discs were taken per tree for each sample.

In grove 1, where there was sufficient space between trees to allow passage across rows, the trees were sampled at 90° intervals around the tree as diagramed in Figure 1. The trees of grove 2 were grown together so as not to permit passage across the rows, the trees were sampled at 0°, 45°, 90° and 135°. This procedure is depicted in Figure 2. Sampling locations were constant throughout all sampling intervals. Three identical samples were collected at each interval. All trees sampled were no less than four trees from the edge of the grove.

Samples were placed in ice upon leaving the grove and immediately transported to the laboratory for chemical extraction normally completed the same day.

Analytical Procedures

Two samples of each triplicate set taken at each sampling interval were analyzed for dislodgeable and penetrated residue; the third for total residue.

The procedure used for the extraction of dislodgeable, penetrated and total Supracide residues from leaf discs is described in an attachment.

Ethyl acetate was the organic solvent used in all extractions.

Analysis of the samples was by gas chromatography.

The instruments used were Varian 2700 and Varian 2100 gas chromatographs under the following conditions:

Varian 2700

Flame photometric detector @ 250° C
Detector gas flow rates: H_2 - 100 ml/min
Air - 80 ml/min

Column - 6' x 2 mm I.D. of 3% OV-101 on 100/120 mesh Chromosorb W-HP @ 200° C

Carrier gas - N_2 40 ml/min.
Injector temperature - 230° C
Retention time - Methidathion 4 min.

Varian 2100

Flame photometric detector
Detector gas flow rates: H_2 - 100 ml/min
Air - 80 ml/min

Column - 5.25' x 2 mm I.D. of 3% OV-101 (carbowax vapor - deposition treated on 100/120 mesh Chromosorb W-HP @ 185° C

Carrier gas - N_2 at 40 ml/min
Injector temperature - 230° C
Retention time - Methidathion 5.5 min.

Results and Discussion

Dislodgeable, penetrated, and total residue values are given in Table 1. Dislodgeable residue degradation is illustrated in Figure 3.

The maximum level of methidathion residue permitted on oranges for human consumption is 2 ppm. It appears that the dislodgeable residues on citrus foliage will decrease to this level in about 20 days when applied at 20-24 pints per acre as a dilute spray. Use at the maximum permissible rate of 40 pints per acre or as a low volume spray may extend this period considerably. The magnitude of the extension must, however, be determined by future studies at the higher rates.

The present temporary reentry interval appears adequate to protect citrus workers engaging in substantial contact with foliage and should be retained until further studies are completed.

TABLE 1. METHIDATHION RESIDUE

Application No. 1 -- 2.5 lbs. methidathion/500 gallons/acre.

Days Post Application	Dislodgeable Residue ppm	Dislodgeable Residue ug/cm^2	Penetrated Residue ppm	Total Residue ppm
1	40.2	1.34	8.4	56.0
	46.3	1.56	5.8	
2	32.1	1.05	15.5	37.0
	26.9	0.90	14.4	
7	4.4	0.17	7.3	9.8
	10.1	0.64	12.0	
14	1.7	0.06	5.1	6.7
	2.1	0.07	4.6	

Application No. 2 -- 4.7 lbs. methidathion/1875 gallons/acre

Days Post Application	Dislodgeable Residue ppm	Dislodgeable Residue ug/cm^2	Penetrated Residue ppm	Total Residue ppm
1	45.1	1.46	10.9	51.7
	39.9	1.25	15.1	
3	18.6	0.58	10.1	28.6
	17.9	0.54	17.8	
10	10.9	0.35	14.1	18.2
	8.8	0.25	9.1	
15	2.7	0.08	7.7	14.7
	5.0	0.16	12.6	

TABLE 2. DAILY TEMPERATURE AND PRECIPITATION OBSERVATIONS MADE BY RIVERSIDE CIT. EXPERIMENTAL STATION RIVERSIDE COUNTY, CALIFORNIA

	Temperatures (°F) 24 hours ending at 8:00 a.m.		Precipitation (Inches) 24 hour amounts observation time 8:00 a.m.
Date	Max	Min	
5/26	86	54	
27	77	56	
28	87	58	
29	96	56	
30	91	56	
31	87	55	
5/01	87	55	
02	85	53	T
03	83	56	T
04	74	56	
05	76	53	
06	84	55	
07	87	52	
08	82	54	
09	80	53	
10	87	56	
11	89	53	
12	97	57	
13	86	59	
14	85	57	
15	85	55	
16	85	59	T
17	71	58	T
18	70	55	.03
19	66	53	
20	68	55	
		TOTAL	.03

TABLE 3. DAILY TEMPERATURE AND PRECIPITATION
OBSERVATIONS MADE BY THE NATIONAL WEATHER SERVICE AT BAKERSFIELD AIRPORT
KERN COUNTY, CALIFORNIA

	Temperatures (°F) 24 hours ending at 8:00 a.m.		Precipitation (Inches) 24 hour amounts observation time 8:00 a.m.
Date	Max	Min	
7/15/75	90	68	
16	91	69	
17	94	71	
18	94	73	
19	95	69	
20	97	72	
21	98	71	
22	101	75	
23	104	76	
24	106	76	
25	108	78	
26	110	81	
27	109	83	
28	103	78	
29	94	72	
30	93	66	
31	91	66	
		TOTAL	0

FIGURE 1

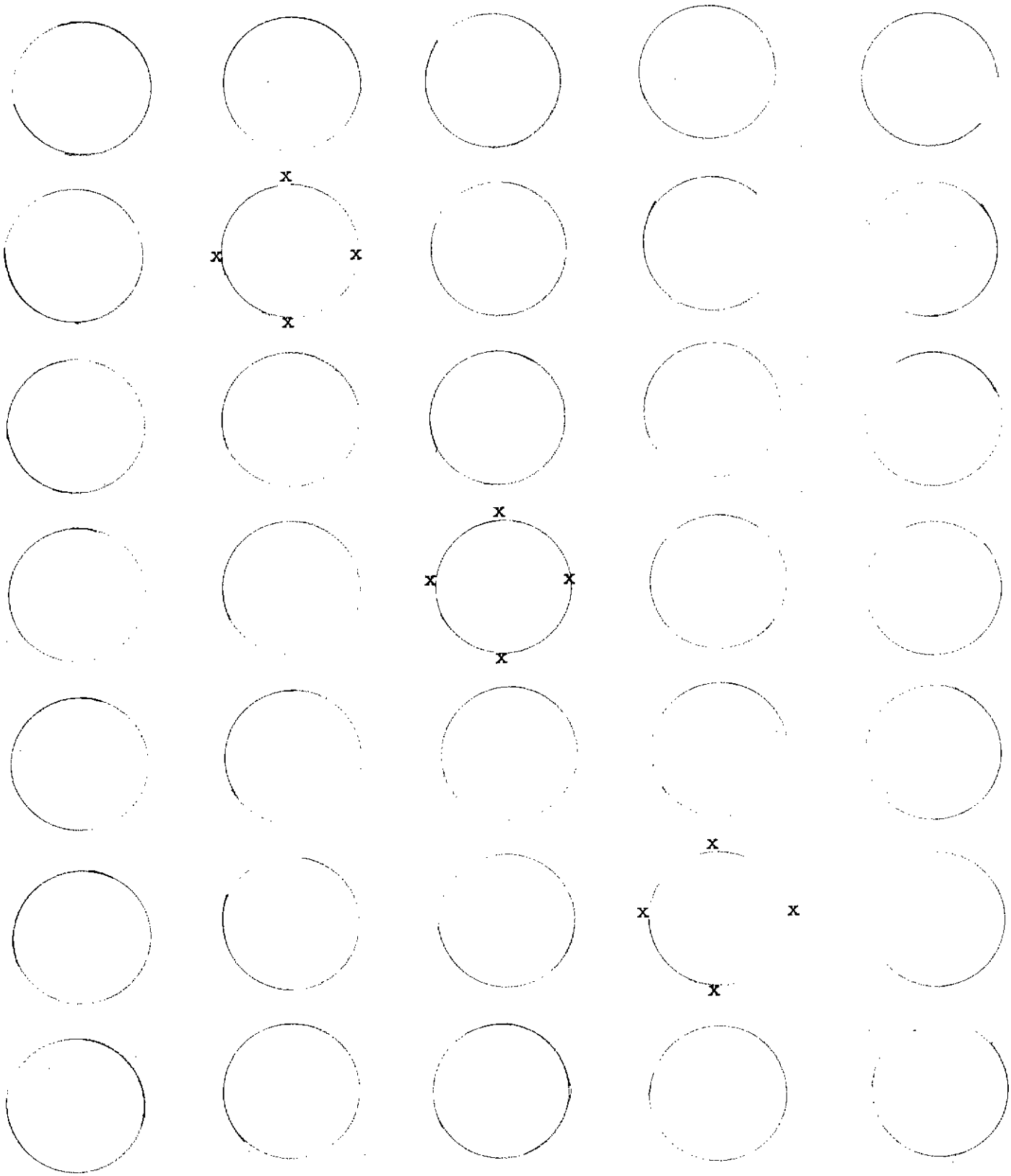


FIGURE 2

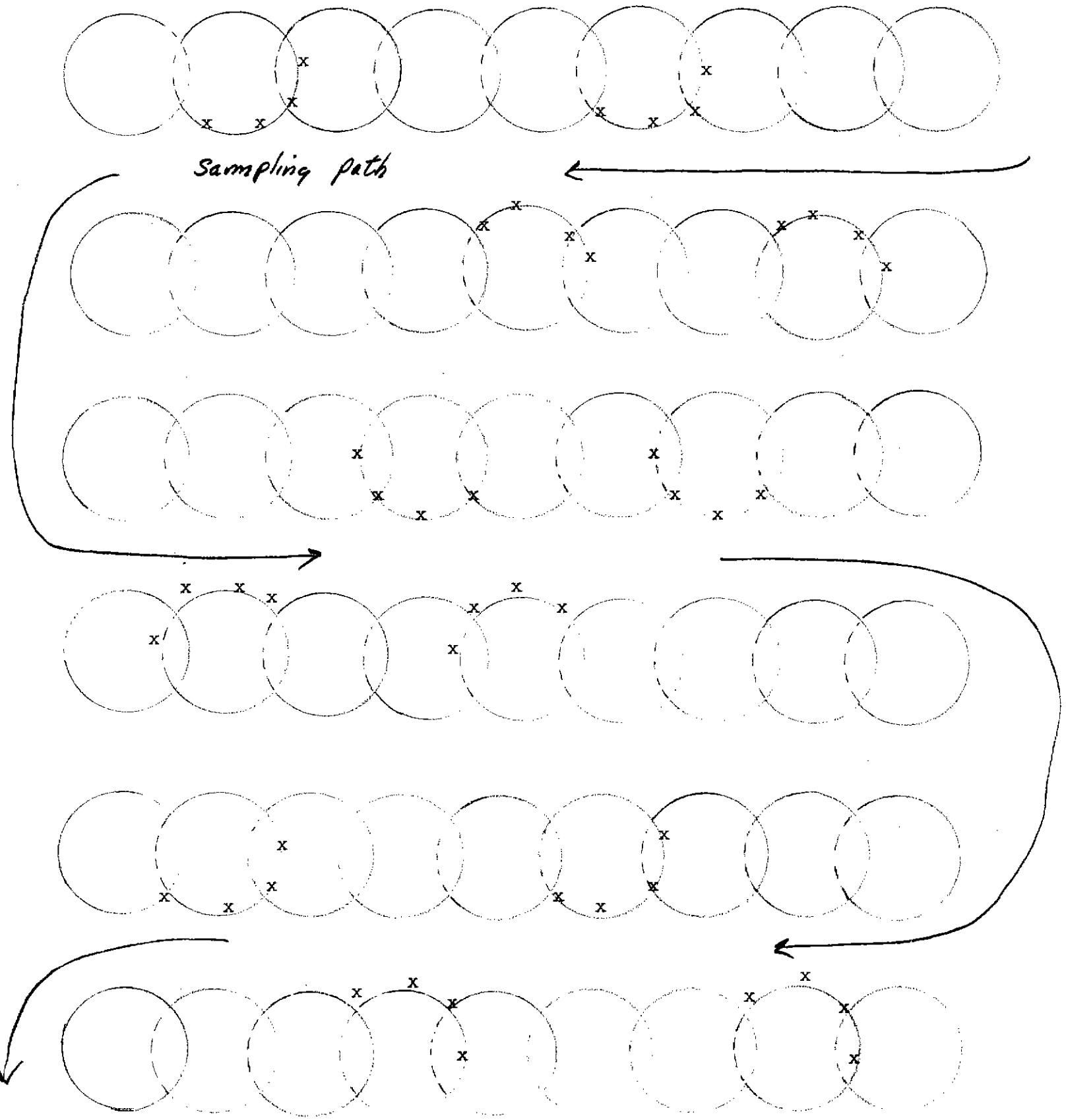
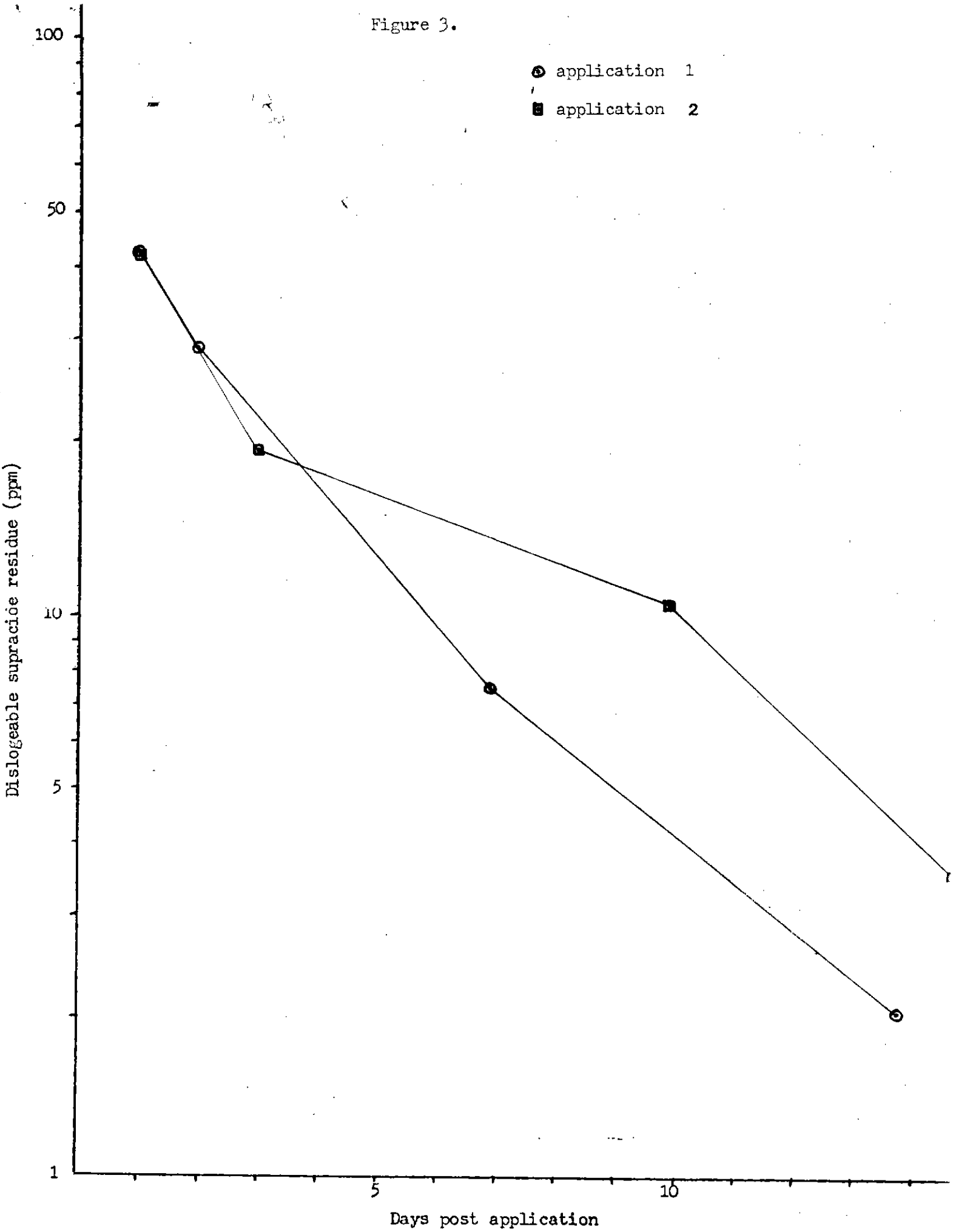


Figure 3.


application 1
application 2
100
50
10
5
1
Dislogeable supracide residue (ppm)
5
10
Days post application

Supracide® 2E

Insecticide-Miticide

SAMPLE LABEL

For control of certain insects of alfalfa, cotton and tobacco

Supracide 2E contains 2 lbs. active ingredient per gallon.

Danger:

Keep out of reach of children. Causes eye damage and skin irritation. Do not get in eyes, on skin, or on clothing. Wear goggles or face shield and rubber gloves when mixing. Avoid contamination of food and feed.

In case of skin contact, wash with plenty of water. In case of eye contact, flush with water for 15 minutes.

Harmful or fatal if swallowed. Do not breathe spray mist (prolonged or repeated inhalation of mist may be harmful). Wear an approved respirator during prolonged use.

Keep out of reach of domestic animals.

Not for use or storage in or around the home.

Note to Physician:
Atropine is antidotal. Do not induce vomiting.

Active Ingredients:	**92.1%**
O,O-dimethyl phosphorodithioate, S-ester with 4- (mercaptomethyl) -2-methoxy-Δ^2-1, 3, 4-thiiadiazolin-5-one	24.4%
Aromatic petroleum derivative solvent	6.8%
Xylene	60.9%
Inert Ingredients:	**7.9%**
Total:	**100.0%**

Fish and Wildlife Caution:
This product is toxic to fish, birds, and other wildlife. Keep out of any body of water. Do not apply where runoff is likely to occur. Do not apply when the weather conditions favor drift from areas treated. Do not contaminate water by cleaning of equipment, or disposal of wastes. Apply this product only as specified on this label.

Do not reuse container. Destroy it by perforating or crushing and burying in a safe place. Do not use, pour, spill or store near heat or open flame.

Store at temperature above 32°F.

EPA Reg. No. 100-501

DIRECTIONS FOR USE AND CONDITIONS OF SALE AND WARRANTY

IMPORTANT: Read the entire **Directions For Use** and the **Conditions Of Sale And Warranty** before using this product.

Conditions Of Sale And Warranty

The Directions For Use of this product reflect the opinion of experts based on field use and tests. The directions are believed to be reliable and should be followed carefully. However, it is impossible to eliminate all risks inherently associated with use of this product. Crop injury, ineffectiveness or other unintended consequences may result because of such factors as weather conditions, presence of other materials, or the manner of use or application all of which are beyond the control of CIBA-GEIGY or the Seller. All such risks shall be assumed by the Buyer.

CIBA-GEIGY warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the **Directions For Use**, subject to the inherent risks referred to above. **CIBA-GEIGY makes no other express or implied warranty of Fitness or Merchantability or any other express or implied warranty.** In no case shall CIBA-GEIGY or the Seller be liable for consequential, special or indirect damages resulting from the use or handling of this product. CIBA-GEIGY and the Seller offer this product, and the Buyer and user accept it, subject to the foregoing **Conditions Of Sale And Warranty** which may be varied only by agreement in writing signed by a duly authorized representative of CIBA-GEIGY.

11/72 CGA 130-141

CIBA–GEIGY

Supracide® 2E

General Information

Supracide 2E is an emulsifiable solution which when diluted with water according to the Directions for Use given below will control certain insect pests and mites on agricultural crops.

Do not enter treated fields the same day of application. Wear adequate clothing during the preparation of spray mixture, during application and when entering treated fields. Wash thoroughly before eating and at the end of each day's operation. Change clothing daily.

Directions for Use

Alfalfa (pure stands or stands containing clover or grass)

Alfalfa weevil, aphids, leafhoppers*, lygus bugs*: Apply 2-4 pts. per acre in a minimum of 10 gals. of water for ground applications or apply in a minimum of 2 gals. of water for aerial applications. Applications for alfalfa weevil control should be made to standing alfalfa when 20-30% of the growing tips show feeding damage. Stubble applications should be made immediately following a cutting. In the southern states, use 3-4 pts. per acre. For the other insects on alfalfa, apply when insects first appear. Make no more than one stubble application and no more than one foliage application per alfalfa cutting.

*Pacific and Intermountain States.

Note: 1) To avoid injury to pollinating insects, do not apply during bloom. 2) Do not apply within 10 days of harvesting or feeding to livestock.

Cotton

Spider mites, boll weevil, bollworm: Primarily for spider mite control. Apply 4 pts. per acre in a minimum of 10 gals. of water when mite foliar feeding symptoms are present (feeding symptoms are red and yellow speckling of the leaves). Repeat applications can be made if necessary at 5-7 day intervals. If boll weevil and bollworms are present at time of application for spider mites, they will be controlled.

Note: 1) Do not make more than 3 applications per year. 2) Do not apply after the bolls begin to open, or within 60 days of harvest. 3) Do not graze treated cotton plants or feed gin waste to livestock.

Tobacco

Make applications at the rates listed below in a minimum of 25 gals. of water per acre when insects appear. Apply 1-3 repeat applications on a 7-14 day interval as needed. Do not apply in mixture with other pesticides or within 3 days of tobacco harvest.

Flea beetles, Hornworms: Apply 2-3 pts. per acre.

Budworms: Apply 4 pts. per acre.

Agricultural Division
CIBA-GEIGY Corporation
Ardsley, New York 10502

Agricultural Division
CIBA-GEIGY Corporation
P. O. Box 11422
Greensboro, North Carolina 27409
Telephone 919 292 7100

CIBA-GEIGY

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PRODUCT BULLETIN

SUPRACIDE® 2E INSECTICIDE
ORANGES AND GRAPEFRUIT
CALIFORNIA ONLY

GENERAL INFORMATION

Supracide 2E is an emulsifiable solution which when diluted with water according to the Directions for Use given below, will control insect pests on agricultural crops.

NOTE: The California Department of Agriculture has set a temporary 30-day reentry interval for Supracide on grapefruit and oranges. Thirty days must lapse between the time of application and the time a worker may enter the field to engage in any activity requiring substantial contact with treated foliage. The 30-day interval is considered temporary until a more definitive reentry study can be conducted under California conditions and guidelines.

This should remain in effect in 1975 until reentry data is presented and evaluated that might indicate a change

Keith F. Mar

Wear adequate protective clothing during the preparation of spray mixture, during application, and when entering treated fields. In case of skin contact, wash thoroughly with soap and water. Wash thoroughly before eating and at the end of each day's operation. Change clothing daily.

Do not reuse empty container. Dispose of in accordance with state and local regulations. Refer to Supracide 2E label for additional precautions and warnings.

DIRECTIONS FOR USE

Oranges and Grapefruit (California Only)

Make applications at the rates listed below in postbloom and/or summer sprays. Allow at least 45 days between applications. Severe infestations may require treatment at both times. Use the low rate for light infestations, and the high rate for moderate to heavy infestations. Thorough coverage is essential for good scale control.

California Red - Control of this pest may require two applications per year, preferably at postbloom and during the summer of 1-2 pts./100 gals. of dilute spray. Thorough coverage of trunks and limbs is essential for scale control.

* Do not apply more than 40 pts. per acre. The minimum amount of Supracide 2E applied per acre is dependent on the number of trees per acre and on tree height. Example: Mature trees of normal foliation require at least the height (in feet) of the tree plus 5 gals. of water for adequate coverage. Eighty trees per acre, 20 ft. tall require 80 x 25 = 2,000 gals. of dilute spray per acre.

Note: Do not graze treated areas. Do not apply more than two times per growing season. Do not apply within 14 days of harvesting.

Supracide®, trademark of CIBA-GEIGY for methidathion.
U. S. Patent Nos. 2,230,230 and 3,240,668

Tolerances: Grapefruit, Lemons, Oranges — 2 p.p.m.

CIBA-GEIGY Corporation
Agricultural Division
Greensboro, North Carolina 27409

LABELING ACCEPTABLE
STATE OF CALIFORNIA
DEPARTMENT OF FOOD AND AGRICULTURE
AGRICULTURAL CHEMICALS AND FEED
Date 8-6-74 Reviewer Stommel
Reg. No. 100-504-AA
ACCEPTANCE OF THIS LABEL DOES
NOT CONSTITUTE REGISTRATION.

August 6, 1974