formulation. At Redlands, the FW-293 applications resulted in as effective control as the standard dosage of demeton.

In experiments conducted in the San Joaquin Valley, FW-293 was more effective than either ovex or Chlorobenzilate in controlling the citrus flat mite (Table V). Ovex is not an effective treatment for this mite, but Chlorobenzilate has resulted in effective reduction in mite populations (*2*).

FW-293 was less effective than petroleum oil or Chlorobenzilate in the control of citrus bud mite (Table VI), but when a combination of FW-293 and Chlorobenzilate was used the treatment was more effective than Chlorobenzilate alone (Table VI).

In limited field trials, FW-293 resulted in good initial reduction of populations of the six-spotted mite, *Eotetranychus sexmaculatus* (Riley), the Yuma mite, *E. yumensis* (McG.), and the citrus rust mite, *Phyllocoptruta oleivora* (Ashm.). As reinfestations of these mites did not occur on the test plots before the groves required re-treatment for some other pest, data on the relative effectiveness of FW-293 with standard treatments are not available.

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PESTICIDE RESIDUES

Field Persistence of the Acaricide 4,4′-Dichloro-alpha-(trichloromethyl)-benzhydrol (FW-293) on and in Mature Lemons and Oranges

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Residues of the new acaricide, 4,4′-dichloro-α-(trichloromethyl)benzhydrol, or FW-293, were determined on and in lemons and oranges and in dried citrus cattle feed resulting from these fruits. The longevity of these residues is illustrated by the half-life values of 170 to 350 days for Valencia oranges and 120 to 150 days for lemons. Comparisons of the magnitudes of the residues obtained simultaneously by three methods indicate little if any metabolic or other degradation of FW-293 residues *in situ*. Negligible amounts of FW-293 were found in edible portions of the fruit. The peel retained approximately 30% of its FW-293 residues after being processed into dried citrus cattle feed.

THE COMPOUND, 4,4′-dichloro-α-(trichloromethyl)benzhydrol, or FW-293, is a general acaricide against several mites and is proving useful in the control of the citrus red mite, *Metatetranychus citri* (McG.) and the citrus flat mite, *Brevipalpus lewisi* McG., on lemons and oranges in California (*4*). The present paper is concerned with the magnitudes of persisting residues of this acaricide in lemons and navel oranges treated in the field with commercial formulations.

Two semispecific analytical methods suitable for determining the magnitudes of residues of FW-293 on and in citrus tissues have been discussed (*3,5*). The first method (chloroform method) determines chloroform released quantitatively from FW-293 treated with strong alkali; the second method (ketone method) determines the 4,4′-dichlorobenzophenone moiety of the parent molecule as liberated by mild alkaline treatment or as deposited in the fruit tissues by metabolic or other degradation *in situ*. Simultaneous scrutiny, by both analytical methods, of fruit samples collected at successive intervals after application, should therefore afford insight into degradative pathways of residues persisting within the treated fruits. For example, if the chloroform-type assays consistently diverged from the benzophenone-type assays with increasing posttreatment time, *in situ* degradation of the parent molecule would be proved.

On the other hand, if both types of assay conformed in decreasing the magnitudes of residues found, volatility or other losses of the entire parent molecule would be indicated. Finally, if both methods showed that the persisting residues were not decreasing with time, there could be little doubt that the parent deposits or residues were resisting mechanical dislodgment and metabolic, or other, degradation.

To supplement evaluations of these three possible types of residue behavior, a third analytical method was also employed. Determinations were made on parallel aliquots of the stripping solutions by means of the chloroform method and by the combustion total organic chloride method (*1*); additional key determinations were made by the more complicated ketone method on other parallel aliquots of the stripping solutions.

Data from all three methods agree in that they indicate that FW-293 residues on and in lemons and Valencia oranges deviate from the previously established (*1,2*) degradation and persistence behavior of other acaricide residues in citrus fruits. FW-293 residues persist without significant change for remarkably long periods after establishment as residues.

Materials and Methods

Mature Valencia orange trees were sprayed on June 28, 1955, with either 1.6 pounds of a 25% wettable-powder formulation of FW-293 per 100 gallons of water or with 1.6 pints of a 25% emulsifiable-concentrate formulation of FW-293 (2 pounds per gallon) per 100 gallons of water. Applications were made as conventional sprays, using a high-pressure reciprocating pump and manually operated spray guns. Final sprays were applied at the rate of approximately 1500 gallons per acre. Mature lemon trees were sprayed similarly using the same spray concentrations on December 12, 1955. Mature navel orange trees were similarly treated January 5, 1956.

Mature orange fruit samples for assay of residues were collected 1, 5, 11, 15, 24, 43, 78, and 103 days after treatment. Mature lemon fruit samples for assay were collected 0, 10, 17, 24, and 31 days after treatment. Eight fruits (two from

Table I. Persistence of FW-293 Residues in Peel of Field-Treated Valencia Oranges as Determined by Three Residue Methods

(Expressed in p.p.m.)

	1.6 Pints 25% Emulsifiable Concentrate/100 Gallons Water				Untreated Controls			1.6 Pounds 25% Wettable Power/100 Gallons Water				
	Washed Fruit[a]		Unwashed Fruit[a]					Washed Fruit[a]		Unwashed Fruit[a]		
Days Elapsed	Colorimetric method	Total-chloride method	Colorimetric method	Total-chloride method	Colorimetric method	Total-chloride method	Total-ketone method	Colorimetric method	Total-chloride method	Colorimetric method	Total-chloride method	Total-ketone method
1	3.1	5.0, 4.9	7.7, 7.0	10.9, 8.8	0.1	0.6, 0.4	0.0	1.0, 0.7	1.9, 2.0	5.4, 5.3	8.0, 8.0	6.2, 6.3
5	...	5.0, 6.5	5.6	7.7, 7.7	0.1	0.9, 1.0	...	...	2.2, 3.8	5.2	7.0, 7.6	...
11	6.5, 7.1	7.3, 5.3	7.4	9.6, 9.9	0.2	0.4, 0.7	...	2.0	5.6, 3.2	6.1, 6.2	7.4, 7.9	...
15	...	6.8, 7.0	5.6, 7.1	10.7, 9.9	0.0	1.4, 0.5	...	...	6.3	4.3, 6.2	7.4, 7.6	...
24	5.9	6.4	7.9, 7.4	8.4, 9.0	0.1	0.4, 0.4	0.0	4.1	6.1, 4.5	5.9, 5.8	6.7, 7.0	6.6, 6.8
43	6.7	8.0, 8.6	7.7	8.3, 7.5	0.0	0.3, 0.4	0.0	5.3	5.9, 5.8	3.1, 2.7	7.3, 6.9	6.1, 5.9
78	...	...	6.2	5.9, 7.3	0.0	1.0, 1.2	0.0	...	...	4.3, 4.9	6.8, 6.8	5.5, 5.5
103	...	...	7.5, 6.2	7.8, 7.5	0.1	1.3, 0.3	...	...	...	3.9, 3.1	5.2, 5.3	...

[a] Pulp (edible portion) analyses showed 0.00 to 0.15 p.p.m. by these methods after 1/2 to 76 days, with high value at 21 days. All values are corrected for recovery (colorimetric, 99%; total chloride, 98%; total ketone, 84%) and are based upon weight of peel only (mature Valencia oranges have 18.7 ± 6.3 wt. % peel from 297 measurements).

each quadrant) were picked from each of four trees in each plot, and the resulting fruit was processed as a unit. The two replicates for each treatment were processed separately.

The unwashed fruits were peeled and 1-pound subsamples of the minced peel were processed with petroleum ether in the manner previously described (*1*), except for certain duplicated orange samples which were washed manually with detergent solution before peeling to evaluate ease of removal of deposits and extrasurface residues.

Lemon fruits were harvested 39 days after treatment and navel orange fruits were harvested 35 days after treatment for processing to simulate dried citrus cattle feed. The fruits were juiced, the juice was discarded, and the remaining rag was ground in a food grinder, sprinkled with hydrated lime at the rate of 4 grams per kg. of rag, mixed to disperse the lime, and allowed to stand for 30 to 60 minutes. Initially, the pH of the mixture was between 12 and 14, but it decreased to a final pH between 5 and 7 after standing with lime. This aged mixture was then pressed in a Carver press at about 500 pounds per square inch to remove liquids; the resulting solids were spread to a depth of about 3/4 inch and dried in a forced-draft oven at 50° C. for from 12 to 16 hours, at which time the water content was between 8 and 12%. Pound lots of the dried product were equilibrated with petroleum ether in the usual manner (*1*) to afford final stripping solutions.

Aliquots of the stripping solutions were assayed by combustion techniques for total chloride (*1*), by chloroform evolution from alkali for unchanged FW-293 (*5*), and by alkaline hydrolysis and chromic anhydride oxidation for total ketone (*3*).

Results

Valencia Oranges. Residue values for FW-293 on and in Valencia oranges,

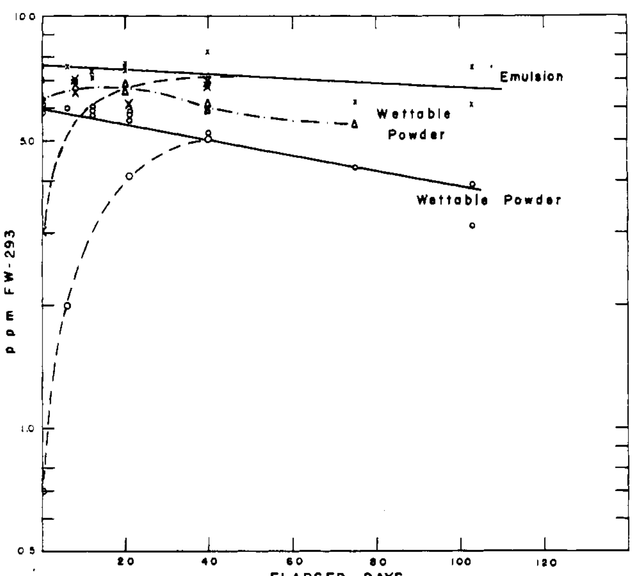

Figure 1. Persistence of FW-293 residues on and in Valencia orange peel, based upon weight of peel only (see Table I, footnote a) as determined by chloroform colorimetric method

--- Washed fruit
-.- Total-ketone method
All values are corrected for background (0.0 to 0.1 p.p.m.) and for recovery (99% for chloroform method, 84% for total-ketone method)

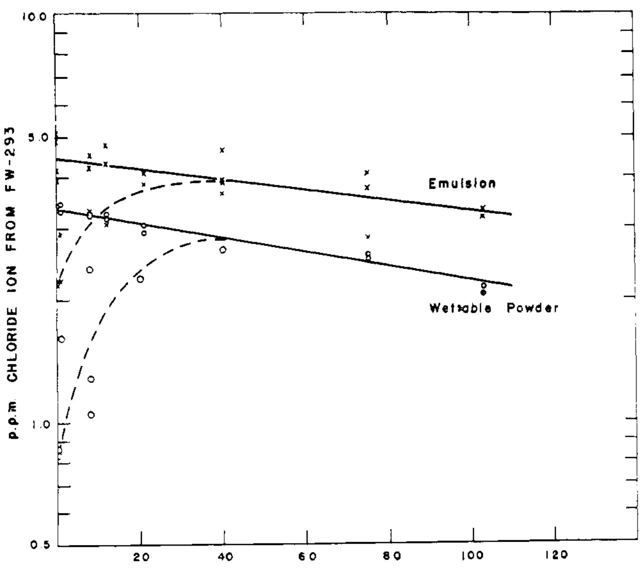

Figure 2. Persistence of FW-293 residues on and in Valencia orange peel, based upon weight of peel only (see Table I, footnote a) as determined by the total-chlorine method

--- Washed fruit
All values are corrected for background (0.4 to 1.3 p.p.m.) and recovery (98%). To convert to p.p.m. FW-293, multiply each chloride value by 2.09

by the three previously mentioned methods of analysis, are presented in Table I and in Figures 1 and 2. Values for pulp (edible portion) analyses are also presented in Table I.

Lemons. Residue values for FW-293 on and in lemons, by the colorimetric method and combustion chloride method are collated in Table II and graphically represented in Figures 3 and 4. Values for pulp (edible portion) analyses are also presented in Table II.

Dried Citrus Cattle Feed. Values for FW-293 residue remaining after processing field-treated lemon peel and navel orange peel into dried citrus cattle feed are presented in Table III.

Discussion

These data demonstrate the longevity of residues of FW-293 on and in citrus fruits, as emphasized by the half-life values (*1,2*) listed in Table IV. Previous residue studies for numerous insecticides and acaricides on and in citrus peel have shown half-life values in the range of 7 to 60 days (*1,2*), whereas half-life values for FW-293 on and in citrus peel are between 120 and 350 days.

Residue evaluations with Valencia oranges included a series in which the fruits were washed in a detergent solution prior to being peeled and processed so as to obtain information as to possible ease of removal of deposits and extrasurface residues. Comparison of these data with the data from unwashed fruit (see Figures 1 and 2) shows that FW-293 penetrates into the oily and waxy portions of the peel rather slowly. Thus, it

Table II. Persistence of FW-293 Residues in Peel of Field-Treated Lemons as Determined by Two Residue Methods

(Expressed in p.p.m.)

	1.6 Pints 25% Emulsifiable Concentrate/100 Gallons Water		Untreated Controls		1.6 Pounds 25% Wettable Powder/100 Gallons Water	
Days Elapsed	Colorimetric method[a]	Total-chloride method[a]	Colorimetric method	Total-chloride method	Colorimetric method[a]	Total-chloride method[a]
0	15.7, 13.2	15.3, 13.7	0.2	0.6	...	6.5, 8.0
10	13.7, 10.7	13.9, 10.9	0.1	1.7, 1.8	5.7, 7.7	5.7, 6.8
17	13.7, 11.8	14.0, 12.4	0.1	0.7	5.4, 7.6	6.1
24	12.4, 10.6	12.7, 10.8	0.2	0.6	5.4, 6.8	5.7
31	10.7, 9.7	12.2, 11.9	0.1	1.3	3.8, 5.5	6.1

[a] Pulp (edible portion) analyses at 10 days showed 0.00–0.05 p.p.m. by both methods. All values are corrected for recovery (colorimetric, 99%; total chloride, 98%) and are based upon weight of peel only (mature lemons have 30.0 ± 8.5 wt. % of peel from 632 measurements).

Table III. FW-293 Residues in Dried Citrus Cattle Feed by Colorimetric Method

(Expressed in p.p.m.)

Treatment	Lemons[a,b]	Navel Oranges[a,c]
1.6 pints 25% emulsifiable concentrate/-100 gallons water	14.4, 11.3, 10.5, 11.2	13.9, 15.2, 16.8, 16.0
1.6 pounds 25% wettable powder/100 gallons water	7.3, 8.0, 7.6, 7.3	8.1, 8.8, 9.6, 9.6
Untreated[d]	0.2, 0.3	0.1, 0.1

[a] All values are corrected for recovery (navel oranges, 81%; lemons, 92%).
[b] Harvested 39 days after field treatment.
[c] Harvested 35 days after field treatment.
[d] Untreated subsamples fortified with 6.3 p.p.m. of FW-293 afforded recoveries of 88 to 96% with orange feed and of 79 to 82% with lemon feed.

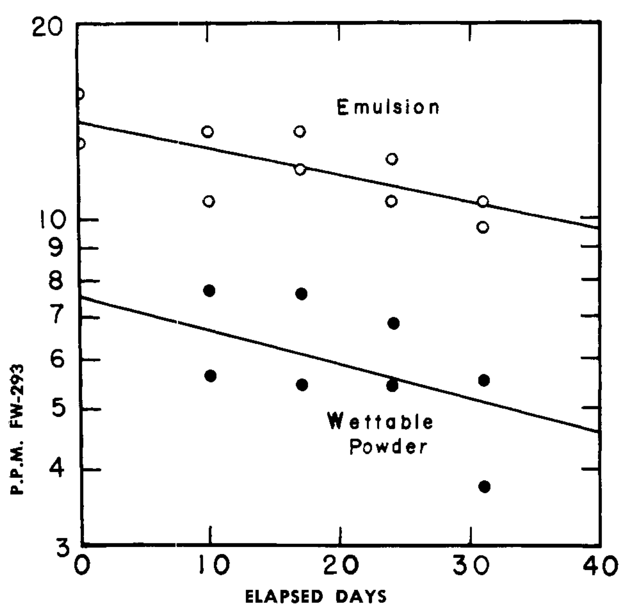

Figure 3. Persistence of FW-293 residues on and in lemon peel, based upon weight of peel only (see Table II, footnote a), by the chloroform colorimetric method

All values are corrected for background (0.0 to 0.2 p.p.m.) and for recovery (99%)

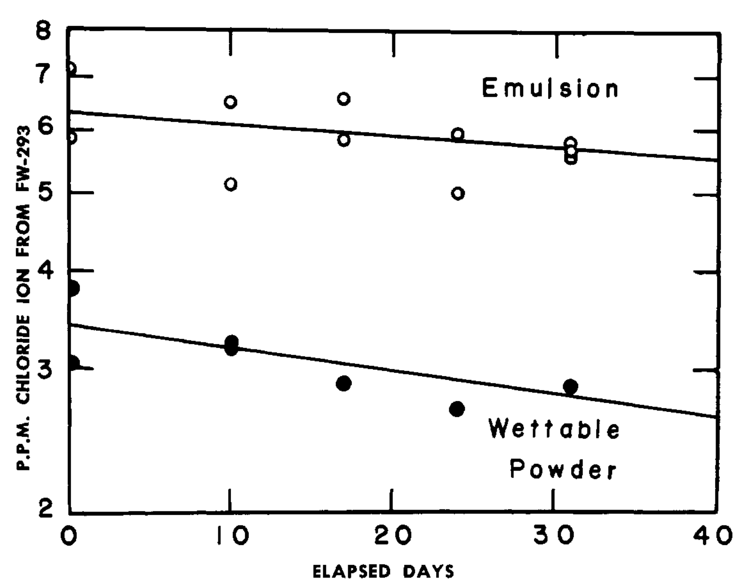

Figure 4. Persistence of FW-293 residues on and in lemon peel, based upon weight of peel only (see Table II, footnote a), by the total-chloride method

All values are corrected for background (0.6 to 1.8 p.p.m.) and for recovery (98%). To convert to p.p.m. FW-293, multiply each chloride value by 2.09

Table IV. Half-Life Values in Days for Residues of FW-293 in Peel of Field-Treated Citrus Fruits as Determined by Three Analytical Methods

Treatment	Colorimetric Method	Total Chloride Method	Total Ketone Method
Valencia Oranges			
1.6 pints 25% emulsifiable concentrate/100 gallons of water	320	350	...
1.6 pounds 25% wettable powder/100 gallons of water	200	170	220
Lemons			
1.6 pints 25% emulsifiable concentrate/100 gallons of water	150	150	...
1.6 pounds 25% wettable powder/100 gallons of water	120	140	...

appears that the residues of FW-293 from both emulsifiable concentrates and wettable powders on fruit harvested prior to 40 days after treatment may be reduced by a washing procedure.

From comparisons of the half-life values listed in Table IV of residue values accrued by the three analytical methods of gradient specificity, no appreciable residue metabolism or other degradation of the compound FW-293 is evident. Also, there is no evidence of appreciable physical losses through vaporization or dislodgment (*1*) of the acaricide. FW-293 is remarkably stable as a residue on citrus fruit. This stability is further evidenced by the magnitudes of the residues remaining after the peel has been processed into dried citrus cattle feed (Table III). Citrus peel loses about 70% of its weight during this processing; simultaneously it loses less than 70% of the FW-293 residue as established by the chloroform method. As this manufacturing operation favors chemical loss of analytical identity of the residue from the lime treatment, and for mechanical losses by solubility in the discarded press-oil emulsion and by volatilization during the forced-air drying, the magnitudes of these losses are low.

Acknowledgment

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FUMIGANT ADSORPTION BY SOILS

Adsorption of 1,2-Dibromo-3-Chloropropane Vapor by Soils

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The isothermal adsorption of 1,2-dibromo-3-chloropropane vapor by various dry soils was studied and the Brunauer, Emmett, and Teller equation applied to the data. The adsorption capacity of a dry organic soil was relatively low when compared with most mineral soils. Surface area measurements of the soils indicated that vapor adsorption was limited to the external surface of the clay fraction. The adsorption data reduced to unit surface showed that the adsorptive capacity of a dry soil is a function of the external surface area and the predominant clay mineral in the system. Kaolinitic and illitic soils adsorbed more fumigant, per unit surface, at higher P/P_0 values, but slightly less at lower P/P_0 values than montmorillonitic soils.

Because of its promising nonphytotoxic properties, 1,2-dibromo-3-chloropropane is being utilized as a soil fumigant. The over-all effectiveness of dibromochloropropane as a fumigant will depend upon the ability of its vapor to diffuse through the soil. Thus, any factor that influences vapor diffusion will affect the efficiency of dibromochloropropane's fumigant action.

This study was initiated to observe the adsorptive capacities of seven soils for dibromochloropropane and to apply the Brunauer, Emmett, and Teller (BET) equation (*2*) to the experimental data.

Materials and Method

Adsorption isotherm data were obtained by passing a stream of fumigant vapor of known relative pressure through a soil sample. The sample was housed in an adsorption chamber that could be removed from the system and weighed. When the weight remained constant with time, the state of equilibrium was assumed to exist between the vapor stream and soil sample. The amount adsorbed was regarded as the weight difference of the soil sample prior to and after exposure to the fumigant. The apparatus used has been described (*8*).

The soils were ground to pass through a 60-mesh screen and were dried for 15 hours at 105° C. in air prior to adsorption measurements.

The predominant clay mineral in each soil was determined by x-ray diffraction and differential thermal analyses.