Table IV. Effectiveness of Lanolin as a Keeper during Tedion Nitration

	Tedion Added, γ							Tedion Added, γ					
	10	20	30	50	100[a]	200[a]	400[a]	5	10	20	20[b]	30	40
	No Lanolin							Lanolin, 75 Mg.					
Tedion recovered, γ	5.2	3.5	8.5	40.0	82.0	186	392	4.4	10.0	18.8	18.0	28.5	45.6
	5.3	7.0	10.8	39.6	82.0	188	403	5.0	10.6	16.9	20.0	30.0	44.0
	4.0	8.0	16.1	40.5	90.0	178	400		9.5	18.0	19.5		41.2
	5.0	4.0	11.6	41.6					10.5	17.0	18.0		39.6
	3.0	16.6	22.3	43.5					8.5	22.0	19.5		42.0
									9.6	19.8	20.0		41.2
									11.0	20.0	18.0		
									11.5	22.6	16.0		
										22.0	23.0		
										20.4	19.5		
Recovery, %	45	39	46	82	85	92	99	94	102	99	98	98	105

[a] 1/10 aliquots taken after extraction from alkali solution.
[b] 50 mg. of lanolin used.

Table V. Recovery as Function of Time Lapse between Addition of Potassium Hydroxide to Nitrated Tedion and Extraction with Chloroform

Added, γ	Time Lapse, Minutes	Recovery γ	Recovery %
20	0	19.7	
		20.5	100.5
20	5	19.7	
		19.7	98.5
20	15	12.5	
		15.0	67.5

Color Development. In preparation for the color development step, it is extremely important to eliminate chloroform from the sample prior to the addition of pyridine. Chloroform and pyridine react to give a red color very similar to the Tedion color according to the Fujiwara reaction (*2*). This reaction has recently been made the basis of an analytical method for the determination of Kelthane (*4*).

It is necessary to check each bottle of pyridine prior to use. Some samples will develop a red color in the presence of potassium hydroxide and should not be used.

Anhydrous pyridine will not develop a satisfactory color with nitrated Tedion; therefore water must be added to the pyridine. A maximum color per microgram of Tedion is obtained when the water content of the pyridine is approximately 4%.

The Tedion color reaches a maximum intensity about 2 minutes after the potassium hydroxide is added and remains stable for at least 30 minutes.

Interfering Pesticides. DDT interferes with the method and a correction must be made. TDE (DDD) also interferes, but not to the same extent. The miticide, 4-chlorodiphenyl sulfone (Sulfenone), reacts quantitatively by this method. Methoxychlor, ovex, Perthane, parathion, malathion, ziram, ethion, Thiodan, and Captan do not interfere.

Acknowledgment

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ACARICIDE RESIDUES

Persistence of Tedion Residues on Fruits

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TEDION WAS DISCOVERED in the laboratories of N. V. Philips-Roxane of the Netherlands. Tedion is very effective in the control of several species of mites, which include the citrus red mite, *Metatetranychus citri* (Mc G.), the European red mite, *Metatetranychus ulmi* (Koch), the Willamette mite, *Eotetranychus willamettei* (Mc G.), the Pacific mite, *Tetranychus pacificus* (Mc G.), the two-spotted mite, *Tetranychus telarius* (Linn), and the Atlantic mite, *Tetranychus atlanticus* (Mc G). In addition, Tedion shows promise for the control of clover mite, *Bryobia praetiosa* (Koch), and of the peach silver mite, *Vasates cornutus* (Banks).

A colorimetric microanalytical method is available for the determination of Tedion. This method is suitable for residue determinations and was used exclusively in obtaining the data given here. Data illustrating recoveries from four different fruit extracts by this method of analysis are to be published in another paper (*2*).

Materials and Methods

Apple, pear, peach, lemon, and orange trees bearing fruit were sprayed with either 1.0 or 3.0 pounds of 25% Tedion wettable powder per 100 gallons of water. The sprays were applied to the pears and peaches with air carrier-type orchard equipment using approximately 500 gallons of spray per acre. The oranges and lemons were sprayed with conventional high pressure spray machines using approximately 1000 gallons per acre. The apples were

The compound 2,4,5,4′-tetrachlorodiphenyl sulfone is a very effective acaricide against several species of mites. Data are given showing the magnitudes of Tedion spray surface residues found on apples, pears, peaches, lemons, and oranges. Time studies on these fruits indicate that Tedion residues diminish largely as a result of fruit growth and not by decomposition. Results illustrate the magnitudes of Tedion residues which may be expected on apples, pears, peaches, plums, and prunes when sprays are applied from 3 to 130 days before harvest time. Maximum residues found from sprays containing 1 pound of Tedion 25% wettable powder per 100 gallons of water on these fruits varied from 1.3 to 3.6 p.p.m.

sprayed to runoff by manually operated spray guns from a conventional high pressure spray rig. All sprays for the time studies were applied 32 days before the harvest of each crop.

To obtain harvest samples from normal treatments, apple, pear, peach, and plum trees, and grapevines were treated, at various times during the fruit growing season for mite control studies, with 1 pound of Tedion 25% wettable powder per 100 gallons.

Fruit samples for the residue analyses (Table I) were taken at random from sprayed trees at 0, 2, 4, 8, 16, and 32 days after treatment. A second time study was made on mature navel oranges over a longer period (Table IV) where samples were taken at 0, 8, 24, 42, 55, and 100 days after Tedion was applied to the fruit. A collection of harvest samples (Table V) was randomized in the same manner as the time study sampling. In each case, the number of fruit was regulated to give a 2000-gram sample for analysis. All samples were field collected and unwashed.

Each sample was placed in a $2^1/_2$-gallon glass jar with 500 ml. of U.S.P. chloroform and turned end over end in a tumbling machine for 5 minutes. The stripping solution was then filtered and aliquots were taken for analysis in the manner described by Fahey, Cassil, and Rusk (*1*).

Discussion of Results

Tedion surface residues found in the 32-day time studies on apples, pears, peaches, oranges, and lemons are shown in Table I. When the results are expressed in terms of parts per million as they are in this table, there is an apparent and significant reduction in the residues with time on all fruits except on lemons. This decrease in residues is largely a result of fruit growth during the 32 days of the tests. The lemons did not show any significant increase in weight during the period of this study. There is a significant difference in the amounts of surface residues found on different crops, probably due to the variation in texture of the fruit surfaces. For example, the pubescent surface of the peach will retain more initial deposit upon spraying than will the waxy surface of an apple or pear.

Table I. Tedion Surface Residue Time Study on Five Different Fruits

Days after Treatment	Application Rate, Pounds 25% Wettable Powder/ 100 Gallons	Tedion, P.P.M.				
		Apples	Pears	Peaches	Lemons	Oranges
0	1	1.2	1.4	2.4	3.3	1.8
2	1	1.5	1.7	2.3	3.6	1.5
4	1	1.3	1.1	2.3	3.3	1.3
8	1	1.0	1.9	2.5	3.0	1.6
16	1	1.0	0.9	1.3	2.4	1.2
32	1	0.4	0.5	0.6	2.6	0.4
0	3	4.2	3.4	7.0	6.1	2.5
2	3	4.0	2.3	5.7	6.1	2.1
4	3	3.2	2.5	6.6	5.9	4.0
8	3	4.3	3.4	6.8	5.1	3.3
16	3	2.4	1.9	4.1	7.6	2.0
32	3	1.7	0.9	2.0	6.5	1.1

Table II. Results (from Table I) Expressed in Micrograms of Tedion per Fruit to Remove Fruit Growth Factor

Days after Treatment	Application Rate, Pounds 25% Wettable Powder/ 100 Gallons	Tedion, γ per Fruit			
		Pears	Peaches	Oranges	Lemons
0	1	80	81	132	228
2	1	121	77	108	276
4	1	76	82	86	236
8	1	140	98	136	207
16	1	82	74	92	192
32	1	67	85	42	200
Average		94	83	99	223
0	3	189	233	190	393
2	3	153	197	131	487
4	3	179	236	273	437
8	3	242	289	280	393
16	3	181	213	152	584
32	3	112	267	110	565
Average		176	239	189	477

Residues in terms of Tedion per individual fruit are presented for pears, peaches, oranges, and lemons (Table II). Presentation in this manner eliminates the apparent decrease of residue caused by fruit growth. It is evident from Table II that a considerable variation in spray deposition occurs from the spraying operation in the field. Consequently, there is a large variation in residues on the fruit taken at random from the tree. It is well recognized by people working on spray residues that sampling errors of 25% and larger are frequently encountered.

Although the data in Table II appear to show some decrease in Tedion residues due to other causes than fruit growth, such a conclusion can best be reached by the use of a recognized statistical method, "analysis of variance" (*3*). The analysis of variance on the data in Table II is presented in Table III. This analysis shows highly significant differences between the amounts of residue deposited on different crops, but no significant differences between days when the samples were taken for chemical analysis. Thus it may be concluded from the data available in this time study (Table II) that there was no measurable reduction in Tedion

Table III. Analysis of Variance Summary Showing Significance of Results in Table II

Source of Variance	Degrees of Freedom	Sum. of Squares		F Value		Required F Value at 5%
		1-lb. rate	3-lb. rate	1-lb. rate	3-lb. rate	
Total	23	93,426	429,882	..	..	..
Between crops	3	78,084	353,614	48.2[a]	26.5[a]	3.29
Between days	5	7,240	9,685	2.68	0.44	2.90
Remainder	15	8,102	66,583	..	..	..

[a] Highly significant.

Table IV. Tedion Surface Residues on Mature Navel Oranges

(These fruit did not increase in size during this study)

Days after Treatment	Tedion 25% Wettable Powder			
	1 Lb./100 Gal.		3 Lb./100 Gal.	
	Sample 1, p.p.m.	Sample 2, p.p.m.	Sample 1, p.p.m.	Sample 2, p.p.m.
0	1.2 ± 0.1	1.2 ± 0.0	3.3 ± 0.2	3.3 ± 0.1
8	0.9 ± 0.1	1.2 ± 0.1	3.2 ± 0.3	3.2 ± 0.4
24	1.0 ± 0.2	1.0 ± 0.1	2.6 ± 0.4	2.2 ± 0.1
42	0.8 ± 0.1	1.0 ± 0.0	2.5 ± 0.1	2.7 ± 0.1
55	1.1 ± 0.0	..	3.1 ± 0.1	..
100	0.7 ± 0.0	..	2.6 ± 0.1	..
Av.	0.95	1.1	2.9	2.9

Table V. Magnitudes of Tedion Residues Found between Last Application and Harvest

(Tedion applied at rate of 1 lb. of 25% wettable powder per 100 gallons)

Apples		Pears		Peaches		Plums	
Days after spray	Tedion, p.p.m.	Days after spray	Tedion, p.p.m.	Days after spray	Tedion, p.p.m.	Days after spray	Tedion, p.p.m.
27	1.4	12	2.1	7	2.9	3	1.3
32	1.1	27	1.2	19	1.7	6	0.8
35	2.3	28	2.6	19	0.9	9	0.8
47	0.5	28	2.1	26	1.4	18	0.6
51	0.7	30	0.8	28	0.5	19	0.8
60	0.7	32	0.7	30	0.4	19	0.2
76	0.6	51	0.4	32	0.8	27	0.8
98	0.1	63	0.5	41	0.6	27	0.8
120	0.6	63	0.3	41	0.5	35	0.2
130	0.2	102	0.1	..	..	35	0.3

residues except that caused by fruit growth. These data indicate that Tedion is very stable when exposed in spray residue form on tree fruits under high summer temperatures and that its vapor pressure must be low at temperatures from 75° to 100° F., the range in which these studies were conducted.

A second time study of Tedion surface residues on navel oranges is given in Table IV. In this case, the residues were followed over a period of 100 days. The results are expressed only in terms of parts per million because the oranges were mature when sprayed and records did not show any increase in fruit weight during the 100-day study. The data show no significant decrease in Tedion residues over the 100-day period, indicating again that Tedion is very stable when exposed to weathering. The plus and minus values shown in this table are standard deviations calculated from three to eight replicate chemical analyses of a single strip solution, thus showing the precision of the colorimetric method employed in this study.

Additional data showing the magnitude of Tedion residues found on random samples of apples, pears, peaches, and plums from 39 different orchards under different climatic conditions are given in Table V. This is not a true time study, because no two samples came from the same orchard. It does illustrate the magnitude of Tedion residues to be expected on mature fruit when picked at the indicated interval after the last spray. In these studies 25% Tedion wettable powder at 1 pound per 100 gallons was applied to the indicated crops.

To date only two samples of grapes have been analyzed. These samples contained 0.5 and 0.6 p.p.m. of Tedion at 77 and 100 days, respectively, after a spray of 6 pounds of 25% Tedion wettable powder per acre was applied to the grapevines.

Biological performance data obtained on both citrus and deciduous trees show that Tedion has a long residual value against several species of mites over periods of 3 to 9 months. The chemical residue data presented here appear to be in accordance with the biological observations.

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INSECTICIDE RESIDUES

Residue Determination of Sevin (1-Naphthyl *N*-Methylcarbamate) in Wine by Cholinesterase Inhibition and Paper Chromatography

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THE RECENTLY DEVELOPED insecticide, Sevin (1-naphthyl *N*-methylcarbamate) (Union Carbide Chemicals Co.) has found use in the control of the grape leaf folder (*10*). It was necessary, therefore, to develop a sensitive method for residue analysis of Sevin in wine made from grapes which had been sprayed with a formulated mixture of Sevin and sulfur. Two available methods are based on the hydrolysis of Sevin to 1-naphthol and the subsequent color development with aminoantipyrine or *p*-nitrobenzenediazonium fluoborate by diazotization (*2, 8*). An enzymatic