sec-butyl (**3d**) and isobutyl derivatives (**3b**) exhibited similar toxic behavior to the imported fire ants in the prescreening test.

The *O,O*-dialkyl *O*-[*p*-(*N*-alkylcarbamoyl)phenyl] phosphorothionates exhibited uncommon delayed toxicity for organophosphorous compounds. Of the approximately 800 organophosphorous compounds that have been evaluated as possible imported fire ant toxicants, only 10 have exhibited delayed toxicity. All 10 are halogenated phosphorothionates (Banks et al., 1977). A comparison of the ester phosphorothionate derivatives (**4**) to the amide derivative (**3**) (Table III) indicates that the toxicities of the 0.1% solutions of the amides were only slightly more toxic than those of corresponding ester derivatives to the imported fire ant, but substitution of the amide group for a ester group greatly enhanced the delayed killing property of the phosphorothionates.

Phosphorothionates **3b** and **3e** exhibited delayed toxicity over almost a 10-fold concentration range while **3h** (R′ = Et; R = *i*-Bu) turned out to be one of the few known *class iv* (Banks et al., 1977) imported fire ant toxicants. Phosphorothionates **3e** and **3g** were chosen to undergo evaluation in the secondary screening tests against whole colonies of imported fire ants. This test should reveal any inherent difficulties in using these compounds as imported fire ant toxicants, such as lack of bait acceptance or poor distribution of the bait throughout the mound. In these tests the chemicals were offered to the ants in soybean oil impregnated on an extruded corn pellet carrier (5 g/colony) for 4 days, and a special laboratory diet was fed for the rest of the test. General observations on the status of the colony and mortality were recorded weekly. The test was continued until the queen, brood, and 90% or more of the workers were dead or until the colony recovered and returned tonormal (Williams et al., 1980). The results of this test are given in Table IV. Both baits were able to control the imported fire ant colonies at the 1% toxicant in soybean oil concentration. Toxicant **3g** baits were, as expected, considerably more toxic than those of **3e**. The former compound caused considerable ant mortality even at the 0.5% and 0.1% toxicant in soybean oil levels. The baits were acceptable to the imported fire ant, and no problems surfaced that would indicate any difficulty in the bait being distributed throughout the colony.

The data presented in this report provides evidence that *O,O*-dialkyl *O*-[*p*-(*N*-alkylcarbamoyl)phenyl phosphorothionates are a very promising new series of imported fire ant toxicants that may provide a viable alternative chemical method for controlling the imported fire ant.

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Degradation of the Toxicant AC 217,300 in Amdro Imported Fire Ant Bait under Field Conditions

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The rate of decomposition of AC 217,300 [tetrahydro-5,5-dimethyl-2(1*H*)-pyrimidinone [3-[4-(trifluoromethyl)phenyl]-1-[2-[4-(trifluoromethyl)phenyl]ethenyl]-2-propenylidene]hydrazone], the active component of Amdro fire ant bait, was determined under ambient summer climatic conditions. Samples analyzed by GLC showed rapid decomposition during daylight hours but no decomposition during evening hours. No thermal decomposition was detected in the absence of light; therefore, the decomposition was attributed to photolysis. Concurrent bait toxicity bioassays corroborated the results obtained from the chemical studies. Our results indicate that the time of application may influence the efficacy of Amdro fire ant bait.

The red imported fire ant (RIFA), *Solenopsis invicta*, Buren, infests large areas of nine Southeastern and Southern states and has been the subject of extensive control efforts since 1957 (Lofgren et al., 1975). From 1962 to 1978 mirex bait was the method of choice for control of RIFA; however, in 1978 the Environmental Protection Agency canceled the registration of mirex because it was a possible carcinogen. The main reason for the paucity

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Table I. Climatic Conditions for Selected Time Periods Expressed as the Mean and Standard Deviation for Readings Taken at 0, 24, 48, and 72 Hours after the Commencement of the Amdro Degradation Experiments

time (EST)	air temp, °C	tray temp, °C	relative humidity, %	light intensity, lx
10:00 a.m.	29.4 ± 1.0	34.9 ± 3.4	78.8 ± 1.5	834 ± 123
11:00 a.m.	30.7 ± 1.6	37.7 ± 3.7	75.3 ± 6.2	1063 ± 51
12:00 p.m.	32.2 ± 2.3	40.7 ± 7.9	65.8 ± 11.1	1139 ± 315
1:00 p.m.	32.2 ± 1.0	41.6 ± 6.6	68.3 ± 12.9	1216 ± 274
2:00 p.m.	33.6 ± 1.6	47.2 ± 1.5	58.8 ± 6.5	1389 ± 94
3:00 p.m.	35.2 ± 1.9	49.7 ± 5.4	55.3 ± 8.8	1313 ± 309
4:00 p.m.	32.9 ± 4.8	40.4 ± 9.4	66.0 ± 23.2	1146 ± 294
5:00 p.m.	31.6 ± 5.5	36.4 ± 7.8	69.8 ± 22.3	907 ± 403
10:00 p.m.[a]	26.8 ± 2.6	26.0 ± 2.3	81.0 ± 8.5	0

[a] Results for 0, 24, and 48 h times only.

of insecticides registered for control of RIFA with toxic baits is the need for toxicants to exhibit delayed action. this property is needed so that foraging ants have time to distribute the bait to other colony members before they are killed (Stringer et al., 1964). U.S. Department of Agriculture scientists have screened over 6700 chemicals in an effort to identify those toxicants that have the required delayed activity (Banks et al., 1977 and references cited therein; unpublished data).

A promising substitute for mirex was reported recently when a new class of insecticides, the amidinohydrazones, was discovered by American Cyanamid Co. (Lovell, 1979). Williams et al. (1980) reported that in laboratory bioassays AC 217,300 [tetrahydro-5,5-dimethyl-2(1*H*)-pyrimidinone [3-[4-(trifluoromethyl)phenyl]-1-[2-[4-(triflouromethyl)-phenyl]ethenyl]-2-propenylidene]hydrazone] was effective as a RIFA bait toxicant. Subsequently, Banks et al. (1981) and Harlan et al. (1981) demonstrated control of RIFA in small- and large-scale field trials with baits containing AC 217,300. The compound has also been found to be effective against the big-headed ant, *Pheidole megacephala* (Su et al., 1980). AC 217,300 was conditionally registered by EPA in Aug 1980 for control of RIFA in pastureland and nonagricultural areas, and the commercial bait is marketed under the trade name Amdro.

Information regarding the stability of bait formulated AC 217,300 under field conditions would be important in regard to both its efficacy and its environmental acceptability. We report here results of tests designed to determine the rate and environmental factors involved in the degradation of AC 217,300 formulated bait exposed to natural summer climatic conditions in Florida.

MATERIALS AND METHODS

Commerically available Amdro was obtained from the American Cyanamid Co. The bait consisted of 0.88% AC 217,300 dissolved in once-refined soybean oil–cosolvent and impregnated onto pregel defatted corn grits (30% by weight). The bait was spread in a monolayer on the surface of three green 40 × 52 cm trays. Another sample of the bait formulation was refrigerated and used when required as a standard. The trays were placed outdoors in an unobstructed area at 10:00 a.m. (EST) on June 9, 1981. Hourly measurements of climatic conditions were made the first four test days from 10:00 a.m. to 5:00 p.m.; an additional reading was made at 10:00 p.m. on the first 3 days. Temperature readings were made with an Electromedics (Englewood, CO) M-99 digital thermometer, and the relative humidity was measured with a Pinco Instruments (Southampton, PA) D-430 pocket sling psychrometer. A Weston Model 756 illumination meter was used to measure the light intensity.

Three samples of Amdro bait were collected from each tray after 12, 24, 36, 48, 60, 72, and 144 h and evaluated for toxicity in a primary screening bioassay described by Williams et al. (1980). A single sample of the standard and an untreated check were evaluated with each of the sample groups. Samples obtained at the same time intervals were prepared for gas–liquid chromatography (GLC) by tightly packing 1.0 g of bait into a small chromatography column (14 × 0.5 cm). Approximately 9.5 mL of methylene chloride (CH_2Cl_2) was passed through the column into a 10-mL volumetric flask and diluted with CH_2Cl_2 to the mark. This solution was analyzed on a Varian gas chromatograph, Model 3700, fitted with a flame ionization detector. A 1.8 m × 2 mm i.d. glass column was packed with 3% OV-101 on 120–140-mesh Gas-Chrom Q. An analytical sample of AC 217,300 supplied by American Cyanamid Co. was used to precondition the column and to qualitatively identify the toxicant from Amdro bait samples (retention time ca. 13 min, oven temperature programmed from 200 to 250 °C at 5 °C/min, N_2 carrier gas at 25 mL/min). The GLC data were quantitatively analyzed with a Varian Vista 401 data processor. In another set of experiments three trays of Amdro were placed in an oven at 52 °C in the absence of light, and samples were taken at 0, 48, 96, and 144 h. Chemical analyses were carried out as described above.

Table II. Daytime Climatic Conditions during the First 4 Days of the Amdro Degradation Experiment

day[a]	air temp, °C	tray temp, °C	relative humidity, %	light intensity, lx
1	33.0 ± 2.2	40.7 ± 8.8	69.1 ± 10.2	994.6 ± 252
2	34.2 ± 2.8	43.9 ± 6.8	59.5 ± 10.7	1292 ± 267
3	30.7 ± 3.5	41.7 ± 8.2	71.0 ± 21.2	1032 ± 349
4	30.7 ± 2.1	38.8 ± 5.0	71.1 ± 9.1	1163 ± 231

[a] All results are reported as the mean and standard deviation for eight hourly readings from 10:00 a.m. to 5:00 p.m. (EST).

RESULTS AND DISCUSSION

The climatic conditions were typical of summer weather in north central Florida where late afternoon thundershowers are almost a daily occurrence. Mean hourly weather conditions are shown in Table I. The mean daytime temperature in the tray ranged from 5 to 15 °C higher than the mean air temperature. Although this would appear to be an artificially high temperature, the surrounding ground temperatures were always within a few degrees of the tray temperature. The relative humidity measurements indicated an early morning moisture "burn-off" followed by a buildup of humidity in the late afternoon. The large standard deviations in relative humidity between 3:00 and 5:00 p.m. were associated with late afternoon rains. The light intensity peaked at 2:00 p.m. and then declined with cloud formation in late afternoon. Evening climatic conditions (Table I) recorded at 10:00 p.m. were as expected. The tray temperatures were in some instances more than 20 °C cooler than daytime temperatures, and the light intensity was nil. The mean daytime climatic conditions (Table II) showed daily

Table III. Toxicity of Bait Formulated Amdro after Exposure to Daily Ambient Conditions for Several Days

time and material tested	% mortality after indicated days[a]						
	1	2	3	6	8	10	14
0 h							
standard	65	90	100				
check	0	0	0	2	2	3	5
12 h							
sample	49 ± 8	82 ± 6	89 ± 9	94 ± 3	98 ± 2	99 ± 1	99 ± 1
standard	80	98	100				
check	0	0	0	0	0	0	0
24 h							
sample	45 ± 12	74 ± 3	90 ± 9	91 ± 9	99 ± 1	100	
standard	83	100					
check	0	0	0	0	2	3	3
36 h							
sample	10 ± 10	30 ± 17	41 ± 18	49 ± 18	53 ± 15	58 ± 17	68 ± 11
standard	92	98	100				
check	0	0	2	3	5	5	8
48 h							
sample	1 ± 2	16 ± 6	41 ± 4	49 ± 8	56 ± 5	59 ± 6	68 ± 9
standard	82	100					
check	0	0	3	5	7	10	10
60 h							
sample	5 ± 5	16 ± 10	23 ± 14	31 ± 21	36 ± 22	40 ± 24	44 ± 22
standard	98	100					
check	3	8	8	8	8	8	8
72 h							
sample	0 ± 0	3 ± 0	6 ± 3	11 ± 3	15 ± 4	17 ± 5	27 ± 5
standard	100						
check	0	3	3	3	3	3	3
144 h							
sample	1 ± 1	17 ± 6	21 ± 6	31 ± 4	38 ± 9	41 ± 9	46 ± 10
standard	85	100					
check	0	0	0	23	33	33	37

[a] Standard and check are single tests for each time period. Sample percents are the mean and standard deviation for three replicates.

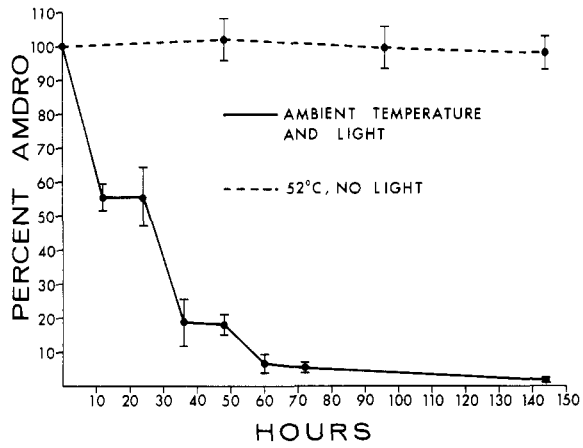

Figure 1. Effects of ambient field temperature and light on the decomposition of AC 217,300 in Amdro bait and the effects of heat alone on the decomposition.

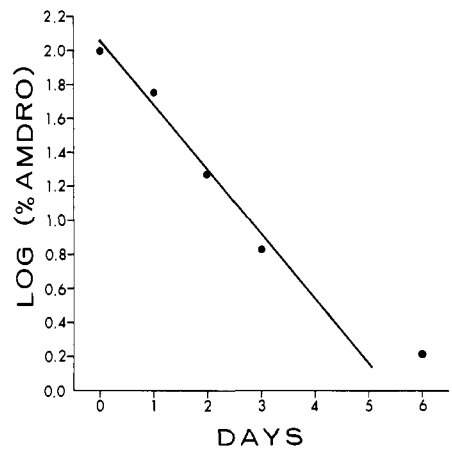

Figure 2. First-order rate plot of the daytime decomposition data from Figure 1.

fluctuations in all of the parameters measured, however, the differences were not significant.

The graph showing the percent AC 217,300 remaining in the bait (Figure 1) was characterized by a stepwise decrease through 60 h. It is obvious that decomposition of AC 217,300 occurred during daylight hours and essentially stopped during the nighttime hours. The major differences between the two time periods were the light intensity and the tray temperature. To determine the effect of heat on Amdro, we monitored the decomposition of AC 217,300 at 52 °C in the absence of light. The results (Figure 1) clearly showed that it is stable to heat and, therefore, must be very unstable in light. If the 12-h periods of little or no decomposition are ignored and the photoperiods brought together, a plot of the log of the decomposition (concentration = percent AC 217,300) vs. time gives a straight line (Figure 2). This is expected for a pseudo-first-order light-dependent decomposition process.

The rapid stepwise decomposition of AC 217,300 is evident also in the bioassay data shown in Table III. The data suggest that the bait would be ineffective for RIFA control after 12–30 h of exposure to sunlight. The high mortality found in the 144-h sample simply reflects a high check mortality for the particular bioassay trial.

Our studies have shown that AC 217,300 decomposes very rapidly when exposed to sunlight. Because almost half is lost in the first 12 h of daylight exposure, it may be more efficacious during hot weather to treat areas for fire ant control as close to dusk as possible. This would ensure that the maximum amount of AC 217,300 would

be available in the Amdro bait at a time when foraging activity was reaching its peak after the hot daytime malaise. In addition, our data indicate that the toxicant is air and heat stable; therefore, storage for long periods of time should not be detrimental. This paper was not aimed at residue analysis or to determine breakdown products; however, we can say that AC 217,300 will decompose rapidly under normal environmental conditions.

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Reaction of Trichlorfon with Diazomethane

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The reaction between trichlorfon and diazomethane was reinvestigated. Methyl trichlorfon was the initial reaction product that under the influence of excess diazomethane was transformed into (2,2-dichloro-1-methoxyethenyl)phosphonic acid dimethyl ester. A mechanism for this reaction is suggested. In addition, application of this method is explored for the estimation of trichlorfon and desmethyltrichlorfon in samples by gas chromatography.

Trichlorfon, (2,2,2-trichloro-1-hydroxyethyl)phosphonic acid dimethyl ester, has been on the market for over 25 years. Various derivatization techniques including acylation (Anderson et al., 1966), methylation with diazomethane (Zitko and Sergeant, 1977; Akhtar, 1982), decomposition at the injector block (El-Refai and Giuffrida, 1965; Anderson et al., 1966; Pieper and Richmond, 1976), alkaline conversion (Zitko and Sergeant, 1977), and trisilylation (Sergeant and Zitko, 1979; Akhtar, 1982) have been explored as a means of identification and estimation of trichlorfon in water and biological samples.

The reaction between trichlorfon and diazomethane had been reported to yield a complex mixture (Zitko and Sergeant, 1977; Akhtar, 1982) that was not considered suitable for quantitative estimation of trichlorfon by gas chromatography. However, the methylation reaction had not been thoroughly investigated as a means of an analytical method. In this report the methylation reaction has been reinvestigated to see if the methylation technique can be an effective analytical method for estimation of trichlorfon and desmethyltrichlorfon by gas chromatography.

EXPERIMENTAL SECTION

Chemicals. Glass-distilled, pesticide-grade solvents were used as received. Diazomethane was prepared by the action of 50% KOH on *N*-nitroso-*N*-methylurea in ether (Schultz et al., 1971). **Caution:** Both nitrosomethylurea and diazomethane are highly toxic chemicals. Special care must be taken in handling these chemicals. Trichlorfon (I) and desmethyltrichlorfon (IV) were available from a previous study (Akhtar, 1982).

Reaction of Trichlorfon with Diazomethane. An aliquot (100 μL, 102.5 μg) of trichlorfon in acetone solution was placed in a centrifuge tube (15 mL). Solvent was removed under a slow stream of N_2, the residue was dissolved in methanol (0.5 mL), diazomethane (2.0 mL) of known concentration was added, and the whole mixture was mixed thoroughly on a vortex mixer for ≃45 s and then allowed to stand at room temperature (20 ± 1 °C). At different time intervals, centrifuge tubes, in duplicate, were removed and excess diazomethane and ether evporated under N_2. The residues were redissolved in hexane and the solvent was again removed under N_2. The residues were redissolved and taken to volume in hexane. Aliquots were analyzed on a gas chromatograph.

Extraction of Samples and Treatment with Diazomethane. Samples were extracted as detailed previously (Zitko and Sergeant, 1977; Akhtar, 1982). Extracts were dried over anhydrous $MgSO_4$, filtered, concentrated, and transferred into a centrifuge tube (15 mL), solvent was removed under N_2, and the residue was dissolved in 0.5 mL of methanol, treated with diazomethane (2 mL, concentration 20 mg/mL), and then allowed to stand overnight (≃16 h) at room temperature. After usual workup as detailed above, aliquots were analyzed on a GC.

Analysis of Reaction Mixtures. The reaction mixtures were analyzed on a Perkin-Elmer gas chromatograph equipped with a 1.07 m × 4 mm (i.d.) galss column packed with 3% SE-30 on Chromosorb WHP, 80–100 mesh, and an electron capture detector (^{63}Ni). Other operating temperatures were 175, 150, and 400 °C for injector, oven, and

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