

primary metabolite found at all sampling periods was 3-hydroxycarbofuran with very low concentrations of 3-ketocarbofuran being noted. The concentrations of ^{14}C activity associated with the origin and calculated as carbofuran remained relatively constant in the 1-, 2-, and 5-week samplings but decreased in the 8-week sampling.

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Use of Selected Plastics in Controlled Release Granular Formulations of Aldicarb and Dimethoate

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Granular formulations of aldicarb prepared with cellulose acetate, polyamide, polyester, polyvinyl chloride, polyurethane, and urea-formaldehyde and granular formulations of dimethoate prepared with cellulose acetate, polyvinyl chloride, and petroleum charcoal released the insecticides more slowly into soil and water than did the standard corn cob formulations of the two insecticides. Greenhouse bioassays indicated that most plastic formulations of aldicarb were more

effective than the standard corn cob formulation in extending the period of systemic insecticidal activity of aldicarb against adult boll weevils, *Anthonomus grandis* Boheman. Greenhouse bioassays with cotton aphids, *Aphis gossypii* Glover, and radioassays of plants grown in soil treated with selected granular formulations indicated that certain plastic and charcoal formulations of dimethoate extended the uptake from soil and the biological activity.

Solid formulations of insecticides prepared with plastic materials have shown promise of extending the period during which the toxicant is released into the atmosphere or into an aqueous media. Probably the best known plastic formulations are the dichlorvos resin strips that release toxicant vapors into the atmosphere over extended periods. Smittle and Burden (1965) used formulations of dichlorvos in polyvinyl chloride to demonstrate the control of a number of insects of public health importance. Harvey and Ely (1968) used polyvinyl chloride strips or blocks that contained 20% dichlorvos to control some flying insects in homes and other buildings where strong drafts or extreme ventilation could be avoided and obtained good control of the short-nosed cattle louse (*Haematopinus eurysternus* Nitzsch.) when infested cattle were enclosed and exposed to the resin strips. Bailey *et al.* (1971) reported up to 7 weeks control of houseflies (*Musca domestica* L.) in poultry houses with dichlorvos applied in slow-release plastic (polyvinyl chloride) granules. In addition to these formulations that released toxicant vapors, several workers have described plastic formulations that released toxicants into aqueous media. For example, control of houseflies lasting as long as 5 months was obtained by formulating dichlorvos in wax or in a mixture of urea and formaldehyde and placing the blocks in aqueous sugar solution in chicken-watering devices (Kilpatrick *et al.*, 1962); pellets of polyvinyl chloride and polyamide containing Abate [*O,O,O',O'*-tetramethyl *O,O'*-(thiodi-*p*-phenylene) phosphorothioate], naled, and malathion showed promise of extending the activity of mosquito larvicides

(Whitlaw and Evans, 1968); and Miles and Woehst (1969) reported releasing Abate from foamed polyvinyl chloride formulations into water for control of *Aedes aegypti* (L.). The larvae of the southern house mosquito (*Culex pipiens quinquefasciatus* Say) have been controlled up to 26 weeks with slow release formulations of Dursban [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl)] (Wilkinson *et al.*, 1971).

Stokes *et al.* (1970) and Coppedge (1970) reported previously the chemical and biological evaluation of controlled release formulations of aldicarb. They found that certain compacted carbon formulations released aldicarb more slowly in laboratory water immersion tests than standard corn cob formulations and also extended the systemic activity of this insecticide against the boll weevil (*Anthonomus grandis* Boheman) after treatment of cotton plants with side dress applications. Therefore, a similar chemical and biological evaluation of the rates of release of aldicarb and dimethoate from selected plastic formulations was made.

MATERIALS AND METHODS

Formulations of Aldicarb. All granular formulations of aldicarb contained approximately 10% active ingredient by weight and were sized 10/20 mesh. The corn cob granules (Union Carbide Corp., Clayton, N. C.) and the petroleum charcoal granules (Great Lakes Research Corp., Elizabethton, Tenn.) were used as the fast and slow release standards, respectively.

The urea-formaldehyde formulations were prepared by the methods described by Geary (1963) or by slight modifications of these methods. The specified quantities of aldicarb, urea-formaldehyde, and additives were mixed, 2

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Table 1. Release of Aldicarb from Plastic Formulations into Water

Formulation	Percentage of theoretical aldicarb found in water at indicated hour of immersion			
	0.5	2	6	24
C. cobs ^a	100	100	100	100
U. 1-formaldehyde ^b	53	74	87	100
Polyvinyl chloride	52	72	88	91
Polyamide	25	48	66	100
Polyurethane	28	43	52	67
Petroleum charcoal with 20% hydrocarbon binder ^c	23	32	40	48
Cellulose acetate ^d	5	8	12	23
Polyester	1	1	2	3

^aFast release standard. ^bPrepared with 50% urea by weight. ^cSlow release standard. ^dPrepared with technical grade cellulose acetate and no plasticizer.

drops (approximately 0.2 g) of 85% phosphoric acid were added, and the mixture was stirred until it solidified.

The polyamide formulations were prepared by dissolving aldicarb and Elvamide 8061 (E. I. duPont de Nemours & Co., Wilmington, Del.) in refluxing methanol. This slightly turbid solution was poured into glass containers and after the methanol evaporated sheets of white opaque resin were obtained. Granules from a single batch were used in all reported tests because the thickness and consistency were difficult to reproduce from batch to batch. (The thickness apparently made a significant difference in the release rates obtained. Although a definite cause and effect relationship was not established, it was observed that the rates of release from batches with different thickness were not identical.)

The polyurethane formulations were prepared by incorporating aldicarb in Isofoam PE-20 (Isocyanate Produce, Wilmington, Del.) by using the methods previously described by Whitlaw and Evans (1968).

The polyvinyl chloride formulations were prepared by mixing aldicarb and a polyvinyl chloride plastisol (Thuron Industries Inc., Dallas, Tex.) and then heating small portions (1 g) of the mixture at 260° for 1 min in small metal planchets. Chemical analyses of these formulations for total aldicarb revealed very little decomposition at the molding temperature.

The cellulose acetate and cellulose acetate butyrate formulations were prepared by dissolving aldicarb, cellulose acetate (acetyl 39.8%, ASTM visc. 3), or cellulose acetate butyrate (17% butyryl, ASTM visc. 15), and plasticizers in refluxing acetone. When the hot acetone solutions were poured into glass containers and allowed to evaporate, a clear film of plastic remained. Cellulose triacetate formulations were prepared similarly, except that tetrachloroethane was used as the solvent.

The polyester formulations were prepared by modifying the procedures described by Lloyd (1967). Aldicarb was mixed with Plaskon 9407 resin (W. R. Grace and Co., Linden, N. J.) and 1 or 2 drops of 60% methyl ethyl ketone peroxide in dimethyl phthalate were added. These mixtures usually gelled in 30 to 40 min without noticeable generation of heat.

Formulations of Dimethoate. All formulations of dimethoate contained technical dimethoate (97% pure; American Cyanamid Co., Princeton, N. J.) and/or ³²P-labeled dimethoate (initial specific activity of 10 mCi per mmol; >97% pure; purchased from Amersham/Searle Corp., Des Plaines, Ill.) and were approximately 10% active ingredient by weight and were sized 10/20 mesh.

The polyvinyl chloride formulations containing unlabeled dimethoate and the polyvinyl chloride plastisol used in the formulation containing ³²P-labeled dimethoate

were supplied by Thuron Industries Inc. (Dallas, Tex.). [This labeled formulation (PVC No. 4) was prepared by mixing 1.5 g of technical dimethoate, 20 mg of ³²P-labeled dimethoate, and 13.5 g of the plastisol and then heating 1-g portions at 260° for 1 min in small metal planchets.] It should be noted that the composition of the PVC formulations obtained commercially was confidential; reported differences in release rates, therefore, probably resulted from unspecified changes in the plasticizers used.

The cellulose acetate formulation was prepared as described by dissolving a mixture of 1.5 g of unlabeled dimethoate, 20 mg of ³²P-labeled dimethoate, 2.25 g of triphenyl phosphate, and 11.25 g of cellulose acetate (acetyl 39.8%, ASTM visc. 3) in refluxing acetone.

The petroleum charcoal formulation was prepared by mixing 2.25 g of technical dimethoate, 30 mg of ³²P-labeled dimethoate, 4.5 g of asphalt (supplied by the Texas Transportation Institute, Texas A&M University), and 15.7 g of petroleum charcoal (supplied by Great Lakes Research Corp., Elizabethton, Tenn.) in a chloroform slurry. This slurry was poured into glass containers, and the chloroform was allowed to evaporate. The resulting dry residue was scraped from the glass surface and ground to a fine powder with a mortar and pestle; then small portions (approximately 5 g) were pressed into pellets at a pressure of 20,000 lb/in.² and a temperature of 60° with hydraulic press equipped with a constant temperature hot plate (Fred S. Carver, Inc., Summit, N. J.).

The corn cob formulation was prepared by mixing 1.5 g of technical dimethoate, 20 mg of ³²P-labeled dimethoate, and 13.5 g of corn cob grits in an acetone slurry. The acetone was evaporated with frequent stirring to yield dry corn cob granules.

Extraction and Analysis of Formulations. For analyses of all the plastic formulations of aldicarb except polyamide, 25-mg samples were refluxed in chloroform for 4 hr, undissolved granules were removed by filtration, and the filtrate was diluted quantitatively to 100 ml. Aliquots (10 ml) of this solution were transferred to 250-ml flasks that contained 10 ml of distilled water, and the resulting two-phase mixture was swirled while the chloroform was evaporated by a stream of air. After the chloroform layer disappeared, an additional 40 ml of water were added and the solution was filtered. Aliquots (5 ml) of the final solutions were analyzed with the colorimetric procedure. Formulations containing polyamide were analyzed by refluxing 30-mg samples in 30 ml of methanol until the granules dissolved. After 50 ml of water were added, the mixtures were filtered quantitatively and diluted to 500 ml. Aliquots of 5 ml were then analyzed by the colorimetric procedure. This method of analysis of the polyamide formulations was useful for obtaining an approximation of the aldicarb content but would be unsatisfactory if high accuracy were required because quantities of dissolved or suspended polyamide in the final aliquot produced cloudy solutions which caused a high absorbance (0.08 to 0.12) in the blanks. The petroleum charcoal and the corn cob formulations were analyzed as previously described (Stokes *et al.*, 1970).

For the analysis of dimethoate, the polyvinyl chloride (PVC) formulations were extracted by refluxing weighed quantities (40 to 60 mg) of granules in 50 ml of chloroform for 6 hr. After removal of the granules by filtration, the chloroform extracts were diluted to 100 ml. Extracts of PVC formulations that contained ³²P-labeled dimethoate were radioassayed; those that contained unlabeled dimethoate were analyzed by gas chromatography. In the case of the other formulations that contained ³²P-labeled dimethoate, the following methods were used. Weighed quantities of the cellulose acetate formulation were dissolved in 100 ml of acetone, and aliquots were radioassayed. Weighed quantities of the corn cob formulation were im-

mersed in 100 ml of distilled water for 24 hr, the granules were removed by filtration, and aliquots of the final solutions were radioassayed.

Analytical Procedures. The modified version of the colorimetric method described by Johnson and Stansbury (1966), which was used for all analyses of aldicarb, was described by Stokes *et al.* (1970). The analysis of dimethoate was done with a F&M Model 402 gas chromatograph (Hewlett-Packard, Avondale, Pa.) that was equipped with a flame photometric detector (Tracor, Inc., Austin, Tex.) that contained a 524 μ interference filter for the detection of phosphorus-containing compounds. A U-shaped glass column (76 cm \times 3 mm i.d.) packed with 5% QF-1 fluorosilicone on 60/80 mesh Gas Chrom Q (Applied Science Laboratories, State College, Pa.) was used at an oven temperature of 192°. Temperatures of the injection port, transfer line (column to detector), and detector were 195, 175, and 150° (external), respectively. The flow rate of nitrogen (carrier) was 145 ml per min. No special column conditioning was used but the peak heights of unknown samples were frequently compared with those of known samples. The retention time for dimethoate at these conditions was about 0.9 min.

All qualitative and quantitative thin-layer chromatography (tlc) was done with glass plates coated (0.25 mm) with silica gel G (Brinkmann Instruments, Inc., Westbury, N. Y.) and a solvent mixture of 1:1:1 acetone-chloroform-hexane. Radioactive areas were located by autoradiography, identified by cochromatography, and radioassayed. The R_f value for dimethoate with this system was 0.65.

All radioassays were made at ambient temperatures by liquid scintillation. Appropriate corrections were made for quenching and radioactive decay.

TEST PROCEDURES AND RESULTS

Water Immersion Tests. Approximately 25 mg of the various granular formulations were weighed into 1-dram vials, and 25 ml of warm (30°) distilled water were added. Then the vials were capped and held at 30° with occasional shaking. After the specified times, the mixtures were filtered and the filtrates were retained for analysis. Filtrates containing aldicarb were analyzed colorimetrically; those containing ^{32}P -labeled dimethoate were analyzed radiometrically. With formulations that contain only unlabeled dimethoate, 20-ml aliquots of the filtrate were extracted with two 25-ml portions of chloroform. The combined chloroform extracts were dried with anhydrous sodium sulfate, evaporated, and then diluted to 10 ml. In some cases, these samples were diluted further to adjust the concentration of dimethoate to a convenient working range (10 to 50 μg per ml). Samples of these final solutions were then assayed by the gas chromatographic procedure.

Table II. Effect of Composition on the Release of Aldicarb from Urea-Formaldehyde Formulations into Water

Percentage urea	Additive	Percentage of theoretical aldicarb found in water at indicated hour of immersion	
		0.5	24
33	None	51	100
50	None	40	97
67	None	39	46
50	10% glycerine	33	95
50	10% dioctyl phthalate	54	73
50 ^a	None	40	78

^aFormaldehyde replaced by benzaldehyde.

Table III. Effect of Type of Cellulose Acetate on the Release of Aldicarb from Cellulose Acetate Formulations into Water

Type of cellulose acetate	Percentage triphenyl phosphate	Percentage of theoretical aldicarb found in water at indicated hour of immersion	
		0.5	24
Technical (acetone soluble)	0	5	23
	15	4	23
Acetyl 39.8% ASTM visc. 3	0	4	21
	15	3	17
Triacetate (tetrachloroethane soluble)	0	3	11
	15	3	23
Butyrate (17% butyryl ASTM visc. 15)	0	1	4
	15	3	8

Marked differences in the rates of release of aldicarb from the various types of plastic formulations into water were obtained (Table I). The cellulose acetate and the polyester formulations released aldicarb more slowly than did the petroleum charcoal slow release standard, and the rates of release from all formulations were slower than that from the corn cob fast release standard. None of these granular formulations appeared to disintegrate or dissolve in water during the 24-hr tests.

The rates at which aldicarb was released from the urea-formaldehyde formulations were apparently affected by the relative proportions of urea and formaldehyde and to a lesser extent by the additives used in the preparations (Table II). Apparently, release was slowest from the urea-formaldehyde formulation that contained 67% urea.

No important differences were observed in the rates at which aldicarb was released from the two partially acetylated grades (technical and with 39.8% acetyl) of cellulose acetate; however, the release from both the cellulose triacetate and the cellulose acetate butyrate formulations was slower (Table III). The rate that aldicarb was released from both the cellulose triacetate and the cellulose acetate butyrate formulations was apparently increased when triphenylphosphate was added. With cellulose acetate, the effect of the addition of triphenylphosphate was less noticeable. Also the type and relative amount of plasticizer used in the preparation of another cellulose acetate (acetyl 39.8%) series was apparently an important factor in altering the release of aldicarb from these formulations into water (Table IV). With phthalate plasticizers the rates increased as the number of carbons in the plasticizer increased, and the use of higher concentrations of each

Table IV. Effect of Plasticizers on the Release of Aldicarb from Cellulose Acetate Formulations into Water

Plasticizer	Percentage plasticizer	Percentage of theoretical aldicarb found in water at indicated hour of immersion	
		0.5	24
None		4	21
		3	17
Triphenyl phosphate	5	3	17
	15	3	17
Dimethyl phthalate	10	4	16
	20	4	19
Diethyl phthalate	10	5	22
	20	6	30
Dibutyl phthalate	10	5	24
	20	10	47
Dimethyl sebacate	10	6	28
	20	15	72

Table V. Release of Dimethoate from Granular Formulations into Water

Formulation	Percentage of theoretical dimethoate found in water at indicated hour of immersion			
	0.5	2	6	24
Corn cobs ^a	66	84	100	100
Polyvinyl chloride no. 4	39	60	80	100
Petroleum charcoal with 20% asphalt binder ^b	41	60	71	74
Polyvinyl chloride no. 2	10			57
Polyvinyl chloride no. 3	6			34
Cellulose acetate	4	9	18	30
Polyvinyl chloride no. 1	1			3

^aFast release standard. ^bSlow release standard.

plasticizer resulted in increased rates of release. The fastest rate of release was obtained with formulations that contained dimethyl sebacate; the slower were obtained with triphenylphosphate and dimethyl phthalate.

Marked differences in the rates at which dimethoate was released from the test formulations into water were also observed (Table V). The slowest was obtained with a polyvinyl chloride formulation (no. 1); less than 3% of the theoretical dimethoate was found in water after immersion for 24 hr. The fastest rate of release was obtained with the corn cob formulation; 60 and 100% of the theoretical dimethoate were found in the water after immersion for 0.5 and 24 hr, respectively.

Release of Aldicarb into Moist Sand in the Greenhouse. Weighed quantities (25 mg) of granular formulations were mixed with 10 g of dry sand, sealed in saran screen packets (52 × 52 mesh), and buried in 1-gal pots containing Lufkin fine sandy loam. Each container received 200 ml of water on alternate days (an equivalent of 1.75 in. of simulated rainfall per week). At the specified times after treatment, the packets were removed from the pots and the granules were recovered and analyzed for aldicarb content.

The results indicated a wide range in the rates at which aldicarb was released from the plastic formulations into greenhouse soil (Table VI). (Since aldicarb was unstable in the polyurethane and the polyester formulations, those preparations were deleted from the test; also, the polyamide formulation was deleted because of inconsistency in the results obtained in water immersion tests of different batches.) The rates at which aldicarb was released from

Table VI. Release of Aldicarb from Plastic Formulations into Soil

Formulation	Percentage of theoretical aldicarb lost from granules at indicated day posttreatment			
	3	7	14	28
Corn cobs ^a	75	96	100	100
Polyvinyl chloride	12	93	100	100
Cellulose acetate with 20% dimethyl sebacate	45	58	80	90
Cellulose acetate with 20% dibutyl phthalate	36	48	75	98
Petroleum charcoal with 20% water-insoluble binder ^b	28	69	92	98
Cellulose acetate with 15% triphenyl phosphate	6	18	57	75
Cellulose triacetate with 15% triphenyl phosphate	31	23	22	51
Cellulose butyrate	9	13	14	35

^aFast release standard. ^bSlow release standard.**Table VII. Release of Dimethoate from Granular Formulations into Soil**

Formulation	Percentage of theoretical dimethoate lost from granules at indicated day posttreatment					
	3	7	14	21	28	42
Corn cobs ^a	85		100	100	100	100
Polyvinyl chloride no. 4	28	52	69	88	92	100
Petroleum charcoal with 20% asphalt binder ^b	41	50	57	62	66	74
Cellulose acetate with 15% triphenyl phosphate	2	6	10	18	25	57

^aFast release standard. ^bSlow release standard.

the polyvinyl chloride formulation and from the cellulose acetate formulations had the same relative order obtained in the water immersion tests. That is, the rates of release from the cellulose acetate (15% triphenylphosphate), cellulose triacetate, and cellulose acetate butyrate formulations were slower than the rates from the petroleum charcoal standard, and the rates of release of the two other cellulose acetate formulations (20% dibutyl phthalate and 20% dimethyl sebacate) and the polyvinyl chloride formulation were intermediate between those of the petroleum charcoal and the corn cob formulations.

Greenhouse Tests with Granular Formulations of ³²P-Labeled Dimethoate. Formulations (340 mg) that contained ³²P-labeled dimethoate were divided among four 2 in. deep holes spaced evenly around cotton plants (Deltapine Smoothleaf variety) growing in a greenhouse (23–38°) in 1-gal containers of greenhouse potting soil (3:1 mixture of sand and peat moss). Then the holes were covered with soil and the locations were marked for later recovery of granules. At the specified days after treatment, some granules (at least 25 to 50 mg) and new growth (leaves formed after application of the granules) from three treated plants (three replicates, one plant per replicate) were collected (an exception was the 42-day harvest when only the granules were collected). The granules were removed from the soil with forceps, dried overnight at ambient temperature, and then analyzed for ³²P-dimethoate. The new growth was weighed immediately after harvest and then homogenized with a mixture (2:1 v/v) of acetone and water (10 to 15 ml per g) and again with acetone. The homogenates were combined, filtered, evaporated to a convenient volume, and radioassayed. These mixtures were then evaporated to near dryness, filtered, and analyzed by the tlc procedures.

The results of analyses of the granules indicated that the ³²P-labeled dimethoate was released from the several formulations into soil at rates having the same relative order as that obtained in the water immersion tests (Table VII). Thus, no dimethoate was found in corn cob granules recovered after 14 days, and essentially all the dimethoate was gone from the polyvinyl chloride formulation after 42 days. The dimethoate was released rapidly from the petroleum charcoal formulation during the first 3 days post treatment (41%), but the rate thereafter was slow and steady. The rate of release from the cellulose acetate formulation actually increased during the test since more dimethoate per day was released during the last 14 days of the test than during the first 14 days.

Measurements of the ppm (μ g of dimethoate per g of leaf) in the new growth of cotton plants growing in treated soil indicated that the concentrations in plants treated with the corn cob and the polyvinyl chloride formulations reached a peak at 14 days (Table VIII). However, concentrations from plants treated with the petroleum charcoal formulation were maximum at 7 days and decreased thereafter, and those from plants treated with the cellu-

Table VIII. Uptake of Dimethoate by Cotton Plants after Soil Treatment with Granular Formulations

Formulation	Dimethoate (μg per g of leaf) found in new growth at indicated day posttreatment			
	7	14	21	28
Corn cobs ^a	62	120	14	5
Polyvinyl chloride no. 4	50	105	35	23
Petroleum charcoal with 20% asphalt binder ^b	62	49	14	7
Cellulose acetate with 15% triphenyl phosphate	12	6	12	20

^aFast release standard. ^bSlow release standard.

lose acetate formulation increased during the 28-day test. Thereafter, even though only 25% as much dimethoate was released by the cellulose acetate formulation, the new growth of treated plants contained almost as much dimethoate after 28 days as that from plants treated with the polyvinyl chloride formulation.

Assays of Biological Materials. Bioassays with new growth from cotton plants treated with the formulations were conducted in the greenhouse with 5 to 8-day-old adult boll weevils from the laboratory culture and with cotton aphids (*Aphis gossypii* Glover) of mixed ages. Side dress treatments were simulated by distributing 340 mg of the aldicarb formulations or 680 mg of the dimethoate formulations in four 2-in. holes spaced evenly around cotton plants 12 to 14 in. tall. All bioassays were conducted as described by Coppedge (1970).

The results indicated that the three cellulose acetate formulations and the petroleum charcoal slow release standard extended control of the boll weevil longer than did the cellulose butyrate, the cellulose triacetate, and the corn cob formulations (Table IX). Also the cellulose butyrate and cellulose triacetate formulations extended control more than the corn cob formulations.

The results of bioassays with dimethoate indicated that none of the test formulations extended the insecticidal activity of the compound appreciably compared with the corn cob formulation. In fact, the formulations that had slower rates of release in the water immersion tests appeared to give the least control of the boll weevil (Table X). However, when these same formulations were tested with the aphid bioassay, all formulations appeared to ex-

Table IX. Systemic Activity of Cellulose Acetate Formulations of Aldicarb Applied as a Side Dress Treatment at the Rate of 34 mg of Toxicant/Plant

Formulation	Percentage net mortality of boll weevils after 3 days exposure to treated plant material obtained at indicated day after treatment					
	2	14	21	28	35	42
Corn cobs ^a	100	75	46	11	3	0
Cellulose acetate with 20% dimethyl sebacate	100	100	100	81	10	14
Cellulose acetate with 20% dibutyl phthalate	100	100	100	74	17	
Petroleum charcoal with 20% water-insoluble binder ^b	92	100	96	51	13	22
Cellulose acetate with 15% triphenyl phosphate	100	96	96	59	31	33
Cellulose triacetate with 15% triphenyl phosphate	78	67	89	29	0	11
Cellulose butyrate	85	71	85	29	3	0

^aFast release standard. ^bSlow release standard.

Table X. Systemic Activity of Granular Formulations of Dimethoate Applied as a Side Dress Treatment at the Rate of 68 mg/Plant

Formulation	Percentage net mortality of boll weevils after 3 days exposure to treated plant materials obtained at indicated day after treatment			
	3	7	14	21
Corn cobs ^a	89	70	57	24
Polyvinyl chloride no. 4	82	77	46	36
Petroleum charcoal with 20% asphalt binder ^b	92	81	15	16
Polyvinyl chloride no. 2	71	48	38	20
Polyvinyl chloride no. 3	82	74	26	16
Cellulose acetate	28	29	34	0
Polyvinyl chloride no. 1	7	0	11	8

^aFast release standard. ^bSlow release standard.

tend activity compared with the corn cob formulation (Table XI).

DISCUSSION

The results of the water immersion tests and the experiments in the greenhouse with both aldicarb and dimethoate suggested the possibility of designing plastic formulations with widely varying rates of release. With a given plastic, different release characteristics could usually be obtained by using different types of plasticizers and by changing the percentage of a given plasticizer. The cellulose acetate and the polyvinyl chloride systems appeared to offer the most versatility.

Usually, the relative rates of release of the toxicants into soil could be predicted from the laboratory water immersion data, but predictions of biological activity based on the laboratory data were not as clear cut. This difference was particularly evident with dimethoate since one of the polyvinyl chloride formulations (no. 1) released dimethoate so slowly that it was not effective against boll weevils, although it was reasonably effective against cotton aphids. The difference in the effectiveness of formulations was probably caused by the difference in the susceptibility of the target insects (Coppedge, 1970). This observation emphasizes the difficulty of comparing controlled release formulations with conventional formulations when both are used at the same dosage. When more data are available concerning the relationship between the release of toxicants from formulations into soil (including degradation to nontoxic metabolites), the uptake of toxicants by plants growing in treated soil, and the minimum lethal concentration in foliage necessary to kill the target insect a more rational basis for selecting desirable release characteristics of formulations should evolve.

Table XI. Systemic Activity of Granular Formulations of Dimethoate Applied as a Side Dress Treatment at the Rate of 68 mg/Plant

Formulation	Percentage net mortality of cotton aphids at indicated days after treatment of cotton plants						
	10	16	20	24	27	31	37
Corn cobs ^a	100	75	75	28	0	15	27
Polyvinyl chloride no. 4	100	100	100	100	99	97	100
Petroleum charcoal with 20% asphalt binder ^b	100	100	100	96	96	100	100
Polyvinyl chloride no. 2	100	100	100	100	100	100	89
Polyvinyl chloride no. 3	100	100	100	100	100	100	100
Cellulose acetate	100	100	100	100	100	100	100
Polyvinyl chloride no. 1	100	98	72	35	44	50	37

^aFast release standard. ^bSlow release standard.

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Thermal and Acid Dealkylation of Some Uracil Derivatives

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The dealkylation of *N*-alkyl-5-halo-6-methyluracils and *N*-alkyl-6-methyluracils was investigated. Heating these compounds at 240 to 250° resulted in the elimination of the alkyl groups at position 3 yielding 6-methyluracils and certain olefins. This indicated that there may be a reaction mechanism similar to the β -*cis*-elimination (Chugaev reaction). A systematic study of the ef-

fect of halogen in position 5 and of the nature of the alkyl group in position 3 on the reaction of dealkylation at elevated temperatures indicated that the reaction is affected by these two factors. In some compounds, the dealkylation by the action of concentrated HI was detected, but only *N*-*tert*-butyl-5-halo-6-methyluracil and *N*-*tert*-butyl-6-methyluracil dealkylated completely.

Uracil derivatives are commonly used as herbicides. However, little is known concerning their metabolism in plants. Gardiner *et al.* (1969) detected 5-bromo-3-*sec*-butyl-6-hydroxymethyluracil and several unknown metabolites in soil and orange seedlings treated with bromacil (5-bromo-3-*sec*-butyl-6-methyluracil).

According to Wegler (1970), for herbicidal activity of the uracils, it is necessary that position 1 remain unoccupied or be substituted by an easily detached group. There should also be an alkyl group at position 3. The methyl group in position 6 is particularly important for the activity of these compounds.

We believe that *in vitro* reactions may demonstrate possible changes *in vivo*. Our previous research (Tadić and Ries, 1971) demonstrated that hydrocarbon groups were eliminated from triazine herbicides by high temperature or sonication *in vitro*. These dealkylated triazines have been isolated from plants by Shimabukuro (1972). However, the mode of dealkylation in plants has not been elucidated.

It was postulated that the elimination of the alkyl group could proceed in a reaction similar to that described previously (Tadić and Ries, 1971). If a cyclic transition state occurs at all in the intermediate reaction, it would be accomplished by breaking of the N-C bond, with one of the two carbonyl oxygens being the proton acceptor (Figure 1).

Although the conclusions based on experiments performed under high temperature or acidic conditions at low

temperature cannot be directly related to *in vivo* studies, these observations may elucidate the action in plants.

MATERIALS AND METHODS

Chemicals. 3,6-Dimethyluracil, 3-ethyl-6-methyluracil, and 3-isopropyl-6-methyluracil were synthesized by the same method as 6-methyluracil (Donleavy and Kise, 1943). 3-*tert*-Butyl-6-methyluracil was synthesized by the same method as 3-cyclohexyl-6-methyluracil (Senda and Suzui, 1958). 5-Bromo-3,6-dimethyluracil was synthesized according to Schmedes (1925). 5-Bromo-3-ethyl-6-methyluracil and 5-bromo-3-isopropyl-6-methyluracil were obtained according to Bückendorff (1911). 5-Chloro-3-ethyl-6-methyluracil, 5-chloro-3-isopropyl-6-methyluracil, and 5-bromo-3-*tert*-butyl-6-methyluracil were products of E. I. du Pont de Nemours & Co. 5-Chloro-3-*tert*-butyl-6-methyluracil was obtained from terbacil (Sinbar) by chloroform extraction and recrystallization from ether; 5-iodo-3-isopropyl-6-methyluracil was prepared according to Loux and Luckenbaugh (1966). 5-Iodo-3,6-dimethyluracil and 5-iodo-3-ethyl-6-methyluracil were obtained by the same method as 5-iodo-6-methyluracil (Karlinkaya and Hromov-Borisov, 1960). Solutions of Hg(ClO₄)₂ and LiCl were prepared according to Young *et al.* (1952). Hydroiodic and hydrobromic acid were commercial products, manufactured by Fluka A.G., Buchs S.G. Hydroiodic acid was distilled before use in the presence of a small quantity of NaH₂PO₂. Silica gel G, according to Stahl (1965), was used for thin-layer chromatography. Ethylene, propylene, and isobutylene were products of Matheson Co., Joliet, Ill. Standards were prepared by adding 100 and 200 μ l of olefin to 1.0l. of air.

Trapping of Gases. Dealkylation reactions were performed by heating 1.0 mmol of substance in the apparatus of Tadić and Ries (1971). Releasing of trapped olefins

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