Chemical and Biological Evaluation of the Release of Aldicarb from Granular Formulations

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The relative rates of release of aldicarb (newly accepted common name for 2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime; Temik, UC-21149) from granular formulations into water and soil were affected by the type base material, the type and percentage of binder used, and the mesh size. Useful correlations between release rates in a laboratory water immersion test and extended biological activity were obtained. Bioassay of the new growth of treated cotton plants with boll weevils, *Anthonomus grandis* Boheman, showed that prolonged uptake of the toxicant in the plant occurred with formulations which had slow rates of release in a laboratory water immersion test. Also, mixtures of granular formulations with fast and slow rates of release gave a greater initial uptake than occurred with a formulation with a slow rate of release and a more prolonged uptake than occurred with a formulation with a fast rate of release.

Formulations capable of extending the biological activity of chemical compounds have been investigated for several years, and significant advances have been made. For example, successful pharmaceutical formulations for oral administration have been prepared by coating a drug, embedding it in a wax-fat vehicle or porous plastic base, binding the active substance to ion exchange resins, complexing it with a colloidal material, fusing it into a pellet, or encapsulating it (Lazarus and Cooper, 1961). Also pharmaceutical formulations have been surgically implanted into animal tissues where their hardness, insolubility, or other physical properties caused the active compound to be absorbed slowly into the system (Ballard and Nelson, 1962).

Pellets of fertilizer have been coated with polyethylene, resins, vinyl acetate, waxes, paraffin compounds, asphaltic mixtures, or sulfur (Brown *et al.*, 1966; Dahnke *et al.*, 1963; Lawton, 1961; Powell, 1968). Thus, Lunt *et al.*, (1961) demonstrated that coatings of polymeric resins can prolong the release of minerals from fertilizer for as much as 6 months, and Lunt and Oertli (1962) found that corn plants recovered from 25 to 45% of the applied nitrogen from resin-coated ammonium nitrate even though the plants were growing in sand through which 7 feet of water was passed.

Similar extension of the activity of insecticides dates back to the introduction of organic insecticides (Campbell and West, 1944; Lindquist *et al.*, 1945). Subsequently, the residual activity of chlorinated hydrocarbons, botanicals, and organophosphorus compounds was extended by incorporating the compounds into urea–formaldehyde resins (Bracey, 1957; Price, 1960), and that of sprayed deposits was extended by incorporating coumarone resins (van Tiel, 1962), pine gum-rosin (Jensen *et al.*, 1950), and chlorinated terphenyls (Hornstein and Sullivan, 1953; Sullivan *et al.*, 1955) in the solution. More recently, formulations of insecticides have been developed that release the toxicant into a different medium over an extended period. For example, Miles *et al.*, (1962) incorporated dichlorvos into solid blocks of montan wax and either hydrogenated cotton-seed oil or phthalic acid esters; these authors reported that the solid formulations were stable for long periods and released dichlorvos for extended periods when they were exposed to the atmosphere or immersed in water. Also, formulations of dichlorvos in polyvinyl chloride were used to control a number of insects that are important to public health (Smittle and Burden, 1965). Thus, as much as 5 months' control of houseflies, *Musca domestica* L., was obtained by formulating dichlorvos in wax or urea-formaldehyde and placing the blocks in sugar water in chicken watering devices (Geary, 1963; Kilpatrick *et al.*, 1962). In addition, pellets of polyvinyl chloride and polyamide containing Abate (*O,O*-dimethyl phosphorothioate *O,O*-diester with 4,4-thiodiphenol), Dursban (*O,O*-diethyl 0-3, 5,6-trichloro-2-pyridyl phosphorothioate), naled, and malathion showed promise of extending the control obtained with mosquito larvicides (Whitlaw and Evans, 1968).

Despite all this research, only a few studies have been made to find formulations that will control the release of conventional systemic insecticides applied in soil, though the potential applications are numerous. For example, Ridgway *et al.* (1969) found that multiple applications of aldicarb were more effective against the boll weevil, *Anthonomus grandis* Boheman, than single applications though the same amount of total toxicant was used. Thus they simulated controlled release and demonstrated that a formulation that would provide such release would probably extend the control obtained with a single application.

The studies reported here were made at the Chemical and Physical Methods Investigations Laboratory and The Cotton Insects Systemic Chemicals and Nutritional Investigations Laboratory at College Station, Texas, in 1967 to develop methods of evaluating formulations of systemic insecticides and to find formulations that would prolong the period of effectiveness of aldicarb when it is applied for control of cotton insects, particularly the boll weevil.

EXPERIMENTAL

Granular Formulations. The granular formulations (all containing about 10% aldicarb by weight) included granules of petroleum charcoal made with a water soluble binder or a water insoluble hydrocarbon binder, 5, 10, 20, or 30% binder, and three mesh sizes (supplied by Great Lakes Research Corp., Elizabethton, Tenn.); granules of corn cobs made by absorbing aldicarb on 16/30 mesh corn cobs and then coating the granules with a water soluble coating (supplied by Union Carbide Corp., Clayton, N. C.); compacted granules of flour with the aldicarb distributed throughout the granule (supplied by Union Carbide Corp., Clayton, N. C.);

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granules of calcium sulfate prepared by mixing additives and calcium sulfate and then adding aldicarb and water; granules of cellulose acetate prepared by dissolving 4.5 grams of cellulose acetate and 0.5 gram of aldicarb in acetone, evaporating the acetone, and breaking up and sieving the hard brittle material to the desired mesh size.

Analysis of Formulations. The petroleum charcoal granules (40 to 60 mg.) were weighed into small beakers, and chloroform was added. This dark slurry was filtered into a 100-ml. volumetric flask, and sufficient additional chloroform was used in rinsing the filter paper to fill to the mark. Aliquots (10 ml.) of the solution were then added to 250-ml. flasks containing 5 ml. of distilled water, and the resulting two-phase mixture was swirled as the chloroform was evaporated by a stream of air. After the chloroform layer disappeared, 95 ml. of additional water was added, and this solution was filtered. Aliquots (5 ml.) were then analyzed by a colorimetric procedure. When the filter paper and residue were re-extracted with 50 ml. of chloroform and the chloroform was concentrated under vacuum, distilled water was added, and the remaining chloroform was carefully evaporated by air stream, the residue was found to yield only 0.1 to 0.4% of the aldicarb found in the original 100 ml. of solution.

The calcium sulfate granules (40 to 60 mg.) were weighed, crushed to a powder, and extracted with 100 ml. of distilled water for 24 hours. Then the aqueous mixture was filtered, and 5-ml. aliquots were analyzed by a colorimetric procedure.

Analytical Procedure. Aqueous solutions containing aldicarb were analyzed by the following modified version of the method described by Johnson and Stansbury (1966). Aqueous aliquots (5 ml.) containing 0 to 8 μg. per ml. of aldicarb were transferred to test tubes, and 1 ml. of 0.45*N* NaOH was added. After the tubes were heated in a water bath at 68 $\pm$ 2° C. for 20 minutes, 1 ml. of 0.55*N* HCl and 1 ml. of sulfanilic acid reagent (1.0 gram in 200 ml. of 12.5% acetic acid) were added. These acidic mixtures were then heated for an additional 20 minutes at 68 $\pm$ 2° C. and after they again cooled to room temperature, 0.2 ml. of iodine solution (1% in acetic acid) was added and the solutions were stirred vigorously and allowed to react for 3.0 minutes. Then 0.2 ml. of 50% potassium acetate and 0.3 ml. of 2% sodium thiosulfate were added, followed immediately by 0.3 ml. of freshly prepared 1-naphthylamine (1.0 gram in 165 ml. of 30% acetic acid). This solution was stirred, 3.0 ml. of 50% acetic acid were added, and the absorbance was measured at 530 mμ with a colorimeter (Bausch and Lomb, Rochester, N. Y.).

Also, a calibration curve was prepared by analyzing 5.0-ml. samples of known concentrations of aldicarb in the 0 to 8 μg. per ml. range by the same procedure. The reagent blank (containing no aldicarb) routinely gave values of absorbance of 0.020 to 0.040. A set of blanks were determined concurrently with each set of samples analyzed and a correction made using the average of at least two blanks. When corrected values were plotted against μg. per ml. of aldicarb, a straight line with a slope of 0.078 abs. unit per μg. per ml. was obtained.

Water Immersion Test. About 25 mg. of granules were weighed into 10-gram screw-cap vials. Distilled water (25 ml.) at 30° C. was added, and the vials were capped and maintained at 30° C. for the specified time. Then the solution was filtered into a flask and diluted to an appropriate range of concentration. Aliquots (5 ml.) of this diluted solution were then assayed colorimetrically.

Moist Sand Tests. Dry purified sand (10 grams) and 20 of the appropriate granules (3 to 15 mg. were weighed to the nearest 0.1 mg.) were mixed in screw-cap vials, and 0.5 ml. of water was added. Then at the specified times, the contents of the vials were transferred to a petri dish, the granules were removed with forceps, and the sand was transferred quantitatively to a flask containing 100 ml. of water. After the mixtures stood with occasional shaking, they were filtered, and 5-ml. aliquots were used for colorimetric determination. Recovery of aldicarb from moist sand after 0, 1, 3, 7, and 14 days ranged from 89 to 98%, an average of 93%.

In another test in a greenhouse, 50 granules (weighed) mixed with 20 grams of dry sand were sealed in Saran packets and buried in 1-gallon pots containing Lufkin fine sandy loam. Each container received 1.75 inches of water per week. At specified intervals, the packets were removed and the granules were separated from the sand and analyzed by the method of chloroform extraction.

Assays of Biological Material. Cotton plants used were of the Delta-pine Smoothleaf variety grown in the greenhouse. Insects used for bioassay were 6- to 9-day-old adult boll weevils from insecticide-susceptible laboratory colonies reared at controlled environmental conditions.

Boll Weevil Bioassay. Specified quantities (170 to 340 mg.) of the different granular formulations were distributed in four 2-inch deep holes spaced evenly around cotton plants (12 to 14 inches tall) that were grown individually in 1-gallon containers in the greenhouse. From 1 to 35 days after treatment, new leaves (leaves formed since the preceding bioassay) and old growth (the growth present at time of treatment) were removed and fed to adult boll weevils held in a ventilated glass container. Mortality was recorded after 72 hours. Four replicates of 10 weevils each were used to bioassay each plant part.

RESULTS

Water Immersion Test. The results of the tests indicated that there were significant differences in the rates of release of aldicarb from the granular formulations (Table I). However, the wheat flour and corn flour compacted granules and the petroleum charcoal granules containing the water soluble binder disintegrated rapidly when they were immersed in water. Granules made with corn cobs, calcium sulfate, cellulose acetate, or petroleum charcoal (water insoluble binder) did not appear to disintegrate appreciably. The rates of release of aldicarb from the formulations of calcium sulfate and petroleum charcoal were affected by the size of the individual granules (Table II); as the size increased, the rate of release decreased. Lloyd (1967) noted a similar increase in the aqueous release of diazinon and dimetilan with decreasing size of the polyvinyl chloride pellets.

In addition, the rate of release of aldicarb from the petroleum charcoal granules was affected by the type and percentage of binder (Table III). Granules containing 20% water insoluble binder had significantly slower rates of release than those containing 20% water soluble binder, and the rates apparently decreased as the percentage of the water insoluble binder increased. The incorporation of dextrin, methyl cellulose, talc, cellulose acetate, and castor oil in calcium sulfate granules appeared to cause increased rates of release rates (Table IV) and calcium sulfate granules containing these additives disintegrated rapidly in water. Several attempts to coat the granules of calcium sulfate with thin films of cellulose acetate, carnauba wax, and silicone rubber gave inconclusive results.

Table I. Release of Aldicarb from Granular Formulations into Water

Granular base	Mesh Size	Percent Aldicarb in Water at Indicated Hr. 0.5	24
Corn cobs	16/30	100	100
Wheat flour	16/30	80	100
Corn flour	16/30	96	100
Calcium sulfate	10/20	60	81
Cellulose acetate	20/40	15	53
Petroleum charcoal (20% water soluble binder)	16/30	70	100
Petroleum charcoal (20% water insoluble binder)	16/30	23	48

Table II. Effect of Mesh Size on Release of Aldicarb from Granular Formulations into Water

Formulation	Percent Aldicarb in Water at Indicated Hr. 0.5	24
Calcium sulfate		
30/60 mesh	81	90
20/30 mesh	72	84
10/20 mesh	60	81
Petroleum charcoal (20% water insoluble binder)		
+60 mesh	79	100
16/30 mesh	23	48
8/16 mesh	17	31

Table III. Effect of Type and Percentage of Binder on Release of Aldicarb from 16/30 Mesh Formulations of Petroleum Charcoal Granules into Water

Binder Type	Binder Percentage	Percent Aldicarb in Water at Indicated Hr. 0.25	0.5	2.5	24
Water insoluble	30	17	19	20	36
	20	25	23	34	48
	10	33	42	65	100
	5	...	73	...	100
Water soluble	20	65	70	100	100

Table IV. Effect of Various Additives on Release of Aldicarb from 10/20 Mesh Calcium Sulfate Granular Formulations into Water

Additive	Percent Additive	Percent Aldicarb in Water after 0.5 Hr.
None	...	60
Dextrin	5	66
	10	83
	40	100
Castor oil	1	77
	5	79
	10	91
Cellulose acetate	5	59
	10	70
Methyl cellulose	5	68
	10	68
Talc	10	92

Moist Sand Tests. Studies on the release of aldicarb from selected granular formulations into moist sand indicated differences in these rates (Figure 1). The transfer of aldicarb from the corn cob granules to moist sand was essentially complete within the first 3 days; the transfer from the petroleum charcoal granules occurred throughout the 14-day test. The Saran packets buried in the pots transferred aldicarb steadily for 28 days from the 16/30 mesh petroleum charcoal granules (water insoluble binder) into the soil (Figure 2).

Bioassays with Boll Weevils. Bioassays with boll weevils showed that the uptake of toxicant into new growth of cotton plants 4 weeks after treatment was greater after treatment with some formulations of petroleum charcoal granules than after treatment with corn cob or compacted flour granules (Table V). Also, the larger granules gave more prolonged activity in new growth than the smaller granules (Table VI). However, differences in activity in new growth after treatment with petroleum charcoal granules containing different percentages of binder were variable, and no clear pattern was observed (Table VII). Formulations of calcium sulfate and cellulose acetate granules appeared to have patterns of activity similar to those obtained with corn cob granules (Table VI, VII). A mixture of petroleum charcoal and corn cob granules had an initial systemic activity equal to that obtained with corn cob granules alone and the activity of new growth after 5 weeks was similar to that obtained with the petroleum charcoal granules alone (Table VII).

Table V. Systemic Activity of 16/30 Mesh Granular Formulations of Aldicarb Applied as a Sidedress Treatment at the Rate of 34 mg./Plant

(Granules being applied 2 in. deep and 2 in. from the plants)

Formulation	Percent Net Mortality of Boll Weevils in 3 Days at Indicated Days after Treatment 1	7	14	21	28
Petroleum charcoal[a]					
20% binder	0	64	79	55	50
10% binder	0	83	76	55	32
Corn cobs	53	91	60	45	15
Wheat flour	19	91	73	10	9
Corn flour	50	91	26	0	4

[a] Petroleum charcoal formulations contained the water insoluble binder.

Table VI. Systemic Activity of Several Granular Formulations of Aldicarb Applied as a Sidedress Treatment at the Rate of 17 mg./Plant

(10 percent granular formulation applied 2 in. deep and 2 in. from stems of plants)

Formulation	Mesh size	Old Growth 3	7	14	21	New Growth 7	14	21	35
Petroleum charcoal[a]	16/30	12	47	56	89	36	64	65	17
Petroleum charcoal[b]	16/30	15	75	83	73	45	85	68	40
Petroleum charcoal[a]	8/16	6	39	64	65	9	79	42	47
Calcium sulfate	30/60	27	78	72	57	66	50	7	5
Calcium sulfate	10+	0	68	83	76	63	82	47	0
Corn cob	14/60	6	97	86	84	81	91	60	0
Control	...	17	5	7	5	17	15	5	0

(Percent Net Mortality of Boll Weevils at Indicated Days after Treatment)

[a] 20% water insoluble binder. [b] 10% water insoluble binder.

DISCUSSION

The results of the chemical and biological evaluations of granular formulations containing aldicarb demonstrated the value of simple laboratory tests in the study of rates of release. Also, the assumption that moisture is a key to the process by which aldicarb is released from formulations appears to have validity since formulations that had slower rates of release in the water immersion tests generally had extended biological activity. For example, petroleum charcoal granules (with water insoluble binder) had slower rates of release in the water immersion tests than the corn cob, corn flour, or wheat flour granules and also gave more extended biological activity. Also, the larger granules of petroleum charcoal and calcium sulfate with slower release rates in immersion tests had more extended biological activity.

Table VII. Systemic Activity of Granular Formulations of Aldicarb Applied as a Sidedress Treatment at the Rate of 34 mg./Plant
(2 in. deep and 2 in. from plants)

Formulation	Percent Net Mortality of Boll Weevils at Indicated Days after Treatment										
	Old Growth						New Growth				
	3	7	14	21	21	28	7	14	21	28	35
Petroleum charcoal[a]											
10% binder	35	78	83	94	97	100	77	28	58	53	46
20% binder	23	81	72	94	94	92	25	14	56	58	52
30% binder	23	67	75	86	92	89	11	31	46	51	37
Corn cobs	85	100	100	97	92	92	94	51	58	33	17
Cellulose acetate	67	91	81	97	94	100	88	51	76	61	17
Petroleum charcoal 20% binder + corn cobs (1:1 w:w)	85	97	81	91	94	84	91	4	61	53	46

[a] Petroleum charcoal formulations contained the water insoluble binder.

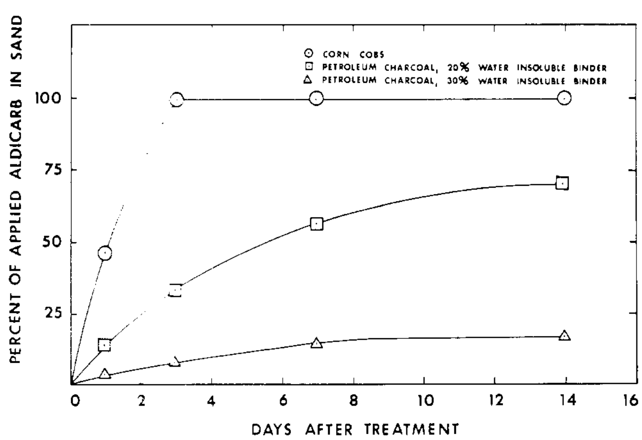

Figure 1. Release of aldicarb from 16/30 granular formulations into sand containing 5% moisture

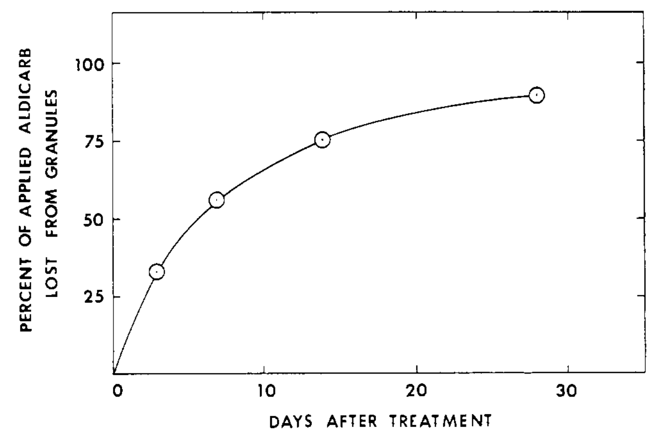

Figure 2. Release of aldicarb from 16/30 mesh petroleum charcoal granules (with 20% water insoluble binder) into soil in the greenhouse

However, granules with slower rates of release in the immersion tests did not always have extended biological activity against the boll weevil. Thus, though distinct differences were observed between petroleum charcoal granules with different percentages of binder in both the water immersion and moist sand tests, distinct differences in biological activity were not detected. Also, the release of aldicarb from cellulose acetate granules was much slower than that from corn cob granules in the water immersion tests, but the cellulose acetate granules did not appear to have extended biological activity.

The lack of correlation between some bioassays and some laboratory tests could have been caused by one or more of the following conditions: in the laboratory, the granules were completely immersed in distilled water to represent the optimum condition for release; in the bioassays, the granules were in contact with soil that had an undetermined and variable moisture content, the bioassay with boll weevils was less sensitive and more variable than the chemical assay, and microbial degradation of granular material placed directly in the soil may have affected releases.

Regardless of the noted exceptions, the results of the present study indicated that the characteristics of release of granular formulations observed in laboratory tests were useful in estimating the rates of release in the greenhouse. However, further studies of the effects of moisture levels, soil types, soil temperatures, and microbial activity on the rates of release of aldicarb from the granules and on the degradation of aldicarb in the soil will probably be required to predict more precisely the rates of release in the greenhouse and in the field.

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