DISTRIBUTION AND RETENTION OF FUMIGANT COMPONENTS IN SHELLED CORN IN 3,250-BUSHEL METAL BINS

Marketing Research Report No. 897

Agricultural Research Service

UNITED STATES DEPARTMENT OF AGRICULTURE

PRECAUTIONS

Fumigants, because of their volatility and toxicity, are hazardous when inhaled. Fumigants should be used only by a qualified person who is thoroughly familiar with their hazards, who will assume full responsibility for their proper use, and who knows he must comply with all precautions on the labels. Fullface masks should always be worn by persons applying fumigants. The applicator of the fumigants is cautioned to be certain that the gas mask to be worn will provide protection against the fumigants involved. The gas mask, or the container in which it was shipped, should provide a listing of the fumigants for which protection is provided. If this information is not available for the particular mask available, a suitable mask must be obtained before applying fumigants.

If a person is overcome by the vapor of a fumigant, prompt, on-the-spot action is essential. Carry the victim outdoors or to a room free of gas and lay him down. Remove contaminated clothing and keep him warm. Administer first-aid treatment immediately. If breathing has stopped, give artificial respiration. Call a physician immediately. Fumigators should have kits properly equipped with antidotes required for first-aid treatment of a victim of the specific fumigant being used and instructions on treatments that are to be administered only by a physician.

The maximum average atmospheric concentration (threshold limit) for each fumigant, by volume, to which workers may be exposed for an 8-hour day without injury to health, is as follows: carbon disulfide—20 p.p.m.; carbon tetrachloride—10 p.p.m.; ethylene dichloride—50 p.p.m. These threshold limit values were adopted at the Annual Meeting of the American Conference of Governmental Industrial Hygienists, 1969.

Carbon disulfide is flammable and explosive. Never use it near heat or open flame.

The fumigants used in these tests are exempt from the requirement of a tolerance for residues when used on shelled corn.

PROTECT

Use Pesticides Safely
FOLLOW THE LABEL
U.S. DEPARTMENT OF AGRICULTURE

PREFACE

This is the report of 20 test fumigations conducted in 1961, 1962, and 1963, in a series of tests to determine the behavior and distribution of the various components of mixtures now in common use for fumigating grain in storage. Although these results were not published at that time, they are still valid, and these formulations are widely used by grain handlers. Other tests of the series are reported in Marketing Research Report No. 894, Distribution of Chloropicrin Used Alone or Mixed with 80:20 to Fumigate Wheat and Sorghum, which evaluates the distribution of chloropicrin used alone or in mixture with carbon tetrachloride and carbon disulfide.

This report evaluates the distribution of an 80:20 mixture of carbon tetrachloride with carbon disulfide and a 75:25 mixture of ethylene dichloride with carbon tetrachloride.

The tests were made at the Watseka Experimental Binsite, Watseka, Ill., in a cooperative study by the Watseka and the Manhattan, Kans., Stored-Grain Insects laboratories, Market Quality Research Division, Agricultural Research Service, U.S. Department of Agriculture.

Wilbur F. Bauer and Roy Tipton of the Watseka Binsite and Ralph L. Ernst of the Manhattan laboratory assisted in the tests.

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DISTRIBUTION AND RETENTION OF FUMIGANT COMPONENTS IN SHELLED CORN IN 3,250-BUSHEL METAL BINS

By

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SUMMARY

In 20 gravity-penetration fumigations of shelled corn in 3,250-bushel bins, during summer, fall, and early winter, 5 gallons of liquid fumigant, 80:20 (carbon tetrachloride, CCl_4: carbon disulfide, CS_2) or 75:25 (ethylene dichloride, EDC : carbon tetrachloride, CCl_4), were applied per 1,000 bushels. Distribution and retention of each fumigant component and the insect mortality were measured. Half of the bins had a prior history of aeration, and the other bins were nonaerated. During fumigation, fans in the vertical duct systems of the aerated bins were stopped.

The 80:20 components were more uniformly distributed than the 75:25 components at grain temperatures above 70° F., but they tended to settle to the bottom of the corn mass. With temperatures below 60° F., volatilization of the EDC in the 75:25 was delayed, and distribution was limited to the upper half of the corn mass.

Total amounts and ratios of CS_2 and CCl_4 consistent with the applied amounts and ratio were recovered in each of the 80:20 fumigations. In the 75:25 fumigations, the total amounts of EDC and CCl_4 recovered were sharply less during October, November, and December fumigations than during the other months. The concentrations of EDC were consistently so low in comparison with those of CCl_4 that the fumigant mixture to which insects within the corn were exposed bore little similarity to the ratio of EDC and CCl_4 applied.

In general, the 75:25 components reached their peak concentrations later in the exposure period and persisted longer than did the 80:20 components.

Overall mortality of test insects and natural infestations did not differ materially at comparable temperatures for the 80:20 and 75:25 fumigations. More insects survived in the upper parts of the corn mass in the 80:20 fumigations and in the lower parts in the 75:25 fumigations.

Difference in gas distribution within aerated and nonaerated bins were of little significance in grain having temperatures above 70° F. Distribution within the corn mass was nearly identical in both aerated and nonaerated bins, although fumigant concentrations were slightly higher in aerated bins. When the grain temperature was below 60° F., there was little difference in gas distribution of aerated and nonaerated bins in the 80:20 fumigations. Temperature differentials of the aerated and nonaerated bins resulted in marked changes in the distribution patterns in the 75:25 fumigations.

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INTRODUCTION

A mixture of carbon disulfide (CS_2) and carbon tetrachloride (CCl_4) formulated with 4 parts of CCl_4 to 1 part of CS_2 and commonly known as 80:20, has been used as a grain fumigant for more than 5 decades. Due to the flammable nature of carbon disulfide, investigations were made in the 1920's by Neifert et al. (*10*),[4] to find nonflammable fumigants that might substitute for carbon disulfide. One material, ethylene dichloride (EDC), showed considerable promise. Cotton and Roark (*3*) recommended that it be substituted for carbon disulfide in atmospheric-vault fumigations. This mixture was a formulation of 3 parts EDC to 1 part CCl_4. Commonly known as 75:25, it has been used extensively as a spot fumigant in flour mills and as a general fumigant for bulk grain.

Many workers have investigated the insecticidal effectiveness of 80:20 and 75:25 mixtures and their individual components during the past 35 years. Cotton (*2*) recommended dosages of 3 to 5 gallons of 80:20 or 75:25 per 1,000 bushels for the control of insects attacking grain in farm storage. Lindgren and Vincent (*8*) noted that 1.3 times as much 75:25 was required for a 95 percent kill of the granary weevil and confused flour beetle 5½ inches below the surface of wheat as was required at the surface. Shepard and Lindgren (*13*) and Shepard et al., (*14*) found CS_2 more toxic than CCl_4 to stored-grain insects, but Harein (*4*) reported that formulations containing 30 percent or less of CS_2 failed to produce significantly higher mortalities than 100 percent CCl_4 to several species of stored-grain insects.

Few studies have been published on the distribution of 80:20 and 75:25 mixtures and their components in bulk grain during fumigation. Strand (*15*) was one of the first to measure penetration of fumigants in an extensive series of controlled experiments. He found that, contrary to general belief at that time, the heavier fumigants such as CS_2 and chloropicrin did not sink down very far in a mass of grain. He attributed this to sorption of the gases by the top layer of grain.

Because of the difficulty in analyzing the mixtures of fumigant and air in treated grain, most studies of distribution have been based on interpretation of insect kills obtained in various parts of a treated grain mass. The development of thermal conductivity (T/C) gas analyzers by Phillips (*12*) to measure fumigants permitted rapid estimation of concentrations within treated grain, but the T/C instrument did not indicate the concentrations of individual components of a mixture. Kenaga (*6*), and later Whitney and Kenaga (*16*), conducted studies in which fumigant component distribution in small towers of wheat was determined by mass spectrometric analyses of air samples. Storey[5] conducted a similar study in elevator tanks. Berck (*1*) developed a chemical technique for determining mixtures of methyl bromide, ethylene dibromide, and carbon tetrachloride in air and reported on the distribution and persistence of these materials applied in mixtures to 5-foot columns of wheat.

The development of gas-liquid partition chromatography by James and Martin (*5*), Phillips (*11*), and Keulemans (*7*) permitted qualitative and quantitative determinations of nearly all components of gaseous and liquid fumigant mixtures. Lindgren and Vincent (*9*) used gas chromatography to determine concentrations of various single- and multiple-component fumigants recirculated through corn in small metal towers. They found the 75:25 mixture no more effective against the confused flour beetle and rice weevil than carbon tetrachloride or ethylene dichloride alone. The rate of sorption of the two 75:25 components differed considerably. Seventy-two percent of the ethylene dichloride had disappeared within 15 minutes after application, but the carbon tetrachloride lost only 41 percent of its original concentration. In similar tests with 80:20, the rate of sorption by corn was similar for both components.

Each year large quantities of 80:20 and

[4] Italic numbers in parentheses refer to Literature Cited, page 12.

[5] Unpublished data.

75:25 liquid grain fumigants are applied to corn in commercial storage for the control of insects. The Commodity Credit Corporation has used these two mixtures for many years. Very little is known about the distribution, retention, and separation of the two components in the corn. This type of basic knowledge might make possible a more effective treatment. It was speculated, also, that the presence of standard vertical aeration systems, widely used in CCC bins, might influence the effectiveness of the fumigation.

From September to December, over a 3-year period, 20 bins of corn were fumigated with the 80:20 and 75:25 formulations at the Watseka, Ill., Experimental Binsite. Data were collected on the following: The distribution, concentration, and retention of individual components of the 80:20 mixture and of the 75:25 mixture; the effect of the presence of a vertical-duct aeration system on fumigant distribution, even though the fan was not operating during fumigation; and insect mortality achieved by each formulation.

PROCEDURE

The fumigations were conducted in shelled corn in 3,250-bushel U.S. Department of Agriculture standard circular metal bins. Fumigant mixtures were applied at a rate of 5 gallons per 1,000 bushels of corn.

In September 1961 two bins, one aerated and one nonaerated, were fumigated with 80:20. The following year, 80:20 was again used to fumigate aerated and nonaerated pairs of bins in July, September, and November. In July and September other pairs of bins were fumigated with 75:25 in the same manner. The third year, 80:20 was used in July, and 75:25 in September, October, and December for aerated and nonaerated bins. All of the fumigants were applied between 7:30 a.m. and 10:00 a.m.

A gasoline engine powered a vane-type pump (fig. 1). The fumigant was delivered through a ½-inch neoprene hose, which had a flow meter next to the pump and a gate valve and nozzle attached to the end. The fumigant was sprayed evenly over the surface of the corn through the opening in the center of the roof (fig. 2). The nozzle was a ½-inch galvanized pipe which delivered a coarse flat stream of fumigant. Sixty percent of the fumigant was applied to the outside 5 feet of grain and the remaining 40 percent to the inside 4 feet. The fumigant was applied to each bin in about 4 minutes.

Gas sample readings were taken with the T/C unit from 7 tiers of gas sample probes at intervals of 1, 4, 24, 48, and 72 hours, and 1 week after application of the fumigant. The T/C readings, expressed as units on the galvanometer scale, indicate the total gases present, but do not differentiate between the individual components of the mixture. Each tier of probes was composed of combination gas sample and test insect points placed at the grain surface and at 2-, 4-, 8-, and 12-foot or bottom levels. Four sampling tiers were placed in the outer periphery of the grain mass near the wall of each bin. Two sampling tiers were 4 feet from the bin wall toward the center of each bin. The seventh sampling tier was in the center of each bin. Gas samples were drawn

BN-35516

FIGURE 1—Pump and meter used to supply the liquid fumigants.

BN-35517

FIGURE 2.—Application of liquid fumigants through roof opening using a hand-held nozzle.

through plastic tubes connected to each sample probe (fig. 3).

Gas samples were collected in 125-ml. glass tubes with stopcocks at each end for gas chromatographic analyses of the individual 80:20 and 75:25 components. The collection tubes were placed ahead of the T/C unit on the sample lines, and the T/C readings were taken at the same time as the samples. The gas chromatographic analyses were made by the Manhattan laboratory. There were 60 samples from each bin.

A sample of wheat containing immature rice weevils and a small screen cage of adult confused flour beetles were placed inside a short section of perforated pipe attached to the bottom of each gas-sampling probe. Control insects were held in the culture room. The adult test insects were held in the laboratory rearing room for 2 weeks after the 1-week exposure period for observation of mortality. Mortality estimates for the immature rice weevils were based on relative numbers of adults emerging

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FIGURE 3.—Glass collection tubes and purging apparatus used to trap fumigant samples for gas chromatography analyses.

from treated and untreated samples 6 weeks after their exposure to the fumigant.

Samples of the shelled corn were drawn before and after each fumigation to determine numbers of living and dead insects, moisture content, and amount of foreign material. Each sample was taken to the laboratory in a plastic-lined, kraft envelope for examination. The samples were screened; the numbers of living stored-grain insects were noted and recorded. The samples were taken with a 4-foot grain trier equipped with extensions and handle, at 2-foot intervals from the grain surface to the floor. Each sample contained about 250 grams of shelled corn. The samples were taken at the points where three tiers of gas sample probes were placed: At the outer periphery near the bin wall by the door; in the center of the bin; and toward the center 4 feet from the bin door on the east wall.

Temperatures were measured at the points where the corn samples were drawn.

RESULTS

80:20 Fumigations

The temperature and moisture content of the grain mass in the aerated bins was fairly uniform from top to bottom. In the nonaerated bins, the corn tended to be warmer and more moist in the upper layers than it was in the lower depths of the grain. Moisture and dockage were similar in the aerated and nonaerated bins. The lowest temperatures were recorded in the aerated bin during November fumigations (table 1).

T/C signals recorded for paired tests of aerated and nonaerated bins did not differ significantly (table 2). In the July and September fumigations the total T/C signals recorded in tiers of probes located at the wall, 4 feet from the wall, and center of the bins were similar. In the November fumigations the total signals recorded in the wall tiers of probes were considerably lower than those detected in tiers of probes 4 feet from the wall and in the center of the bins.

Distribution of the 80:20 indicated by gas chromatography analysis of the individual components was similar to the distribution as indicated by the T/C signals in each fumigation (table 3). Within paired tests, differences between aerated and nonaerated bins did not materially affect the distribution of the individual components. During the July and September fumigations somewhat more CS_2 and CCl_4 was recovered in the aerated bins than in the nonaerated bins. In the cooler corn in the November fumigations, the nonaerated bins contained slightly more of each gas than the aerated bins.

A comparison was made of the percentages of carbon tetrachloride and carbon disulfide detected during the 1-, 4-, 8-, 24-, and 48-hour

TABLE 1.—*Moisture, temperature, and dockage in grain fumigated with 80:20 (CCl_4:CS_2) with and without aeration*

Date of fumigation	Temperature [1]		Moisture [1]		Dockage content [1]	
	Nonaerated	Aerated	Nonaerated	Aerated	Nonaerated	Aerated
	°*F.*	°*F.*	*Percent*	*Percent*	*Percent*	*Percent*
July 9	65	75	12.9	11.7	0.5	0.5
July 24	68	82	12.2	11.9	0.4	0.5
September 19	75	76	12.4	12.2	0.5	0.4
September 26	88	72	12.4	12.6	0.7	0.5
November 6	74	52	12.8	12.9	0.6	1.0

[1] Average of 15 sample locations.

TABLE 2.—*Distribution of 80:20 (CCl_4:CS_2) fumigant at stated intervals after application at a rate of 5 gallons per 1,000 bushels of corn in aerated and nonaerated 3,250-bushel bins by gravity penetration*

Date of fumigation	Gas recovery [1] at stated intervals after application						
	1 hour	4 hours	8 hours	24 hours	48 hours	72 hours	1 week
	T/C units	*T/C units*	*T/C units*	*T/C units*	*T/C units*	*T/C units*	*T/C units*
July 9:							
Nonaerated	314	179	122	47	23	18	10
Aerated	357	206	148	69	35	26	15
July 24:							
Nonaerated	398	168	119	58	39	27	8
Aerated	380	222	186	103	55	50	25
September 19:							
Nonaerated	397	232	146	96	54	43	19
Aerated	392	209	161	105	63	42	12
September 26:							
Nonaerated	322	160	102	66	30	12	0.5
Aerated	300	213	78	49	20	6	0.8
November 6:							
Nonaerated	304	216	157	88	46	34	2
Aerated	194	166	139	58	38	35	9

[1] Average of 35 sample locations per bin measured by thermal conductivity unit deflections on a galvanometer scale.

sampling intervals within each paired test by date (table 4). The initial tests in the 80:20 series, September 26, 1961, were excluded from this comparison because the sampling pattern was changed in the subsequent 80:20 fumigations.

The total amounts of CS_2 and CCl_4 measured in each of the paired aerated and nonaerated 80:20 fumigations were similar. The highest concentrations of each gas observed in aerated and nonaerated fumigations were found in the September fumigations. The lowest concentrations of each component in the aerated bins were found in the November fumigation, and the lowest concentrations in the nonaerated bins were detected in the July 24 fumigation.

The components were originally applied at the ratio of 4 parts CCl_4 to 1 part CS_2. Air samples obtained from 2½-foot to bottom levels in the corn mass 1 hour after application of the fumigant mixture contained each component at ratios very similar to the original 4 to 1 applied ratio. Four hours after application, the component ratio had increased to 7 to 1, and at the 8-hour readings the ratio was 8 to 1. This recovery ratio pattern was consistent throughout fumigations in July, September, and November.

Test insect mortality was excellent in all of the 80:20 fumigations, and natural infestations were virtually eliminated (table 5). However, mortality of the immature rice weevils at the surface locations was exceptionally low in the July 24 nonaerated bin, the September 26 aerated bin, and in the November 6 aerated bin.

75:25 Fumigations

The temperature and moisture content of the grain and the content of foreign matter is shown in table 6.

As in the 80:20 fumigations, the T/C signals and the gas chromatography analyses gave similar indications of the distribution of the 75:25 during each sampling interval (tables 7 and 8). Within each pair of tests, similar T/C signals were recorded in the two bins. T/C signals were considerably lower in the December fumigations, particularly in the aerated bin, than were the signals recorded in the bins

TABLE 3.—*Distribution of carbon tetrachloride (CCl_4) and carbon disulfide (CS_2) at stated intervals after fumigation of corn in nonaerated and aerated 3,250-bushel bins with 5 gallons of 80:20 fumigant per 1,000 bushels of corn by gravity penetration*

Date of fumigation	Concentration of gas in bin at stated time after application													
	1 hour [1]		4 hours [1]		8 hours [1]		24 hours [1]		48 hours [2]		72 hours [3]		1 week [4]	
	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2
	Mg./l.	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*
July 9:														
Nonaerated	314	54	214	26	154	17	67	7	28	6	0	0	10	2
Aerated	394	62	257	24	148	21	107	9	42	12	44	6	43	7
July 24:														
Nonaerated	196	45	98	16	95	12	38	5	37	5	36	4	12	2
Aerated	242	51	154	20	117	16	63	11	61	7	80	15	24	7
September 19:														
Nonaerated	311	52	236	29	204	20	121	12	92	8	108	9	43	5
Aerated	354	58	221	27	214	19	132	11	95	10	98	10	63	8
September 26:														
Nonaerated	214	31	152	19	119	17	49	10	31	5	9	1	([5])	([5])
Aerated	192	58	234	22	21	4	51	7	41	8	30	6	16	4
November 6:														
Nonaerated	185	36	201	25	152	19	92	11	63	9	75	8	4	1
Aerated	133	45	144	21	124	11	59	6	40	13	29	3	9	2

[1] Average of 9 to 14 sample locations.
[2] Average of 5 to 11 sample locations.
[3] Average of 2 or 3 sample locations.
[4] Average of 1 or 2 sample locations.
[5] No samples taken.

TABLE 4.—*Total concentrations of carbon tetrachloride (CCl_4) and carbon disulfide (CS_2) recovered in eight fumigations of corn with 80:20, and percentage of each component detected at stated sampling intervals*

Date of fumigation	Average corn temp.	(CS_2) recovered						(CCl_4) recovered					
		Total	1-hr.	4-hr.	8-hr.	24-hr.	48-hr.	Total	1-hr.	4-hr.	8-hr.	24-hr.	48-hr.
	°F.	*Mg./l.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Mg./l.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
July 9:													
Nonaerated	65	1,116	51.4	24.6	14.5	6.3	3.2	8,549	40.4	27.5	19.9	8.6	3.6
Aerated	75	1,189	52.6	20.0	15.5	7.6	4.3	9,333	42.4	27.5	14.3	11.5	4.5
July 24:													
Nonaerated	68	930	53.9	20.5	14.6	5.6	5.4	5,128	42.1	21.4	20.5	8.1	7.9
Aerated	82	1,152	48.8	19.8	15.0	9.5	6.9	7,147	37.3	23.8	18.0	11.5	9.4
September 19:													
Nonaerated	75	1,316	43.2	23.9	15.7	9.7	7.5	10,567	32.6	25.7	20.0	12.6	9.1
Aerated	76	1,392	45.9	21.4	15.4	9.4	7.9	11,407	34.1	21.3	21.8	13.6	9.2
November 6:													
Nonaerated	74	1,091	36.6	26.1	18.8	10.9	7.6	7,651	26.6	29.3	21.8	13.2	9.1
Aerated	52	954	51.8	24.3	12.6	6.4	4.9	5,553	26.4	29.3	24.6	11.8	7.9

TABLE 5.—*Mortality of test insects and number of live insects in samples of corn after fumigation with 5 gallons of 80:20 (carbon tetrachloride:carbon disulfide) per 1,000 bushels of corn in 3,250-bushel bins by gravity penetration*

Date of fumigation	Mortality of test insects [1]		Insects per 1,000 grams of corn [2]	
	Adult confused flour beetles	Immature rice weevils	Before fumigation	After fumigation
	Percent	*Percent*	*Number*	*Number*
July 9:				
Nonaerated	99.9	97.0	0.5	0
Aerated	100	98.0	2.1	0
July 24:				
Nonaerated	96.0	93.0	11.0	0
Aerated	99.0	100	14.3	0
September 19:				
Nonaerated	100	99.0	2.1	0
Aerated	99.0	98.0	18.4	.3
September 26:				
Nonaerated	100	98.0	17.0	0
Aerated	98.0	94.0	6.7	0
November 6:				
Nonaerated	100	98.0	32.3	.3
Aerated	99.9	91.0	3.2	0

[1] Average of 35 sample locations.
[2] Average of three 1,000-gram samples.

TABLE 6.—*Moisture, temperature, and dockage in grain fumigated with 75:25 (EDC:CCl_4) fumigant with and without aeration*

Date of fumigation	Temperature [1]		Moisture [1]		Dockage content [1]	
	Nonaerated	Aerated	Nonaerated	Aerated	Nonaerated	Aerated
	°F.	*°F.*	*Percent*	*Percent*	*Percent*	*Percent*
July 25	69	80	12.4	12.1	0.4	0.4
September 10	71	77	12.3	11.5	.5	.6
October 8	70	77	11.7	11.1	.5	.5
November 27	52	42	12.7	12.4	.6	.5
December 11	53	48	11.3	12.2	.5	1.1

[1] Average of 15 sample locations.

with warm grain. In most instances the highest T/C signals were recorded in the center tier of probes, where the highest temperatures were also recorded. In the September nonaerated bin, the average center and wall temperatures were identical and the T/C signals were nearly equal in probes at the wall, 4 feet from the wall, and center tiers.

At temperatures below 60° F., the 75:25 components, especially EDC, volatilized more slowly, so that higher concentrations were recorded after 4 hours than after 1 hour. Much less total fumigant was recovered in the November and December fumigations than in the July and September fumigations.

Use of aerated or nonaerated bins within paired tests did not significantly affect the distribution of the individual components of 75:25 during July, September, and October fumigations. In the November and December fumi-

TABLE 7.—*Distribution of 75:25 (EDC:CCl_4) fumigant at stated intervals after application at a rate of 5 gallons per 1,000 bushels of corn in aerated and nonaerated 3,250-bushel bins by gravity penetration*

Date of fumigation	Gas recovery [1] at stated intervals after application						
	1 hour	4 hours	8 hours	24 hours	48 hours	72 hours	1 week
	T/C units	*T/C units*	*T/C units*	*T/C units*	*T/C units*	*T/C units*	*T/C units*
July 25:							
Nonaerated	231	164	87	50	35	24	16
Aerated	256	231	119	53	34	28	20
September 10:							
Nonaerated	224	160	93	47	34	12	10
Aerated	315	196	108	62	53	41	31
October 8:							
Nonaerated	141	131	84	46	25	20	8
Aerated	161	170	92	58	44	40	21
November 27:							
Nonaerated	86	96	85	35	13	11	3
Aerated	62	91	86	53	31	26	16
December 11:							
Nonaerated	72	97	96	69	24	7	1
Aerated	46	62	55	22	9	4	2

[1] Average of 35 sample locations measured by thermal conductivity unit deflections on a galvanometer scale.

TABLE 8.—*Distribution of ethylene dichloride (EDC) and carbon tetrachloride (CCl_4) at stated intervals after fumigation of corn in nonaerated and aerated 3,250-bushel bins with 5 gallons of 75:25 fumigant per 1,000 bushels of corn by gravity penetration*

Date of fumigation	Concentration of gas in bin at stated time after application													
	1 hour [1]		4 hours [1]		8 hours [1]		24 hours [1]		48 hours [1]		72 hours [2]		1 week [3]	
	EDC	CCl_4	EDC	CCl_4	EDC	CCl_4	EDC	CCl_4	EDC	CCl_4	EDC	CCl_4	EDC	CCl_4
	Mg./l.	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*
July 25:														
Nonaerated	77	137	78	108	81	64	46	43	20	22	16	22	9	9
Aerated	86	173	118	126	58	70	30	36	15	21	5	9	13	9
September 10:														
Nonaerated	98	155	116	84	72	44	36	22	23	11	19	12	13	4
Aerated	138	139	137	93	90	43	32	15	27	10	([4])	([4])	13	6
October 8:														
Nonaerated	20	66	23	69	15	48	17	39	10	15	5	13	([4])	([4])
Aerated	36	87	63	104	41	46	23	27	14	14	12	14	11	5
November 27:														
Nonaerated	12	44	15	50	22	53	18	18	7	4	3	1	1	1
Aerated	9	23	16	47	26	53	21	20	20	9	23	11	11	12
December 11:														
Nonaerated	10	57	23	65	20	43	22	34	12	15	2	2	<1	<1
Aerated	2	9	8	34	19	43	17	13	5	2	<1	<1	<1	0

[1] Average of 11 sample locations.
[2] Average of 2 to 4 sample locations.
[3] Average of 1 to 2 sample locations.
[4] No sample taken.

gations, previous aeration became a significant factor due to the temperature differentials between aerated and nonaerated bins. Lower surface temperature, particularly in the aerated bin fumigated in December, not only delayed volatilization of the 75:25, but severely limited the penetration of the EDC down through the corn mass. The components had been applied at the ratio of 3 parts EDC to 1 part CCl_4. By the end of the first hour, the component ratios were nearly reversed; 3 parts CCl_4 were recorded to 1 part EDC. This was particularly evident in the cool-weather fumigations in October, November, and December. In the September fumigations, when the corn mass was at its highest temperature, the initial recovery ratio was about 1 to 1. At later sampling intervals in the September fumigations the ratio increased nearly to the original 3 to 1 (EDC to CCl_4) ratio. In the cool-weather fumigations the return to nearly normal ratios was delayed in some instances until 24 hours after the 75:25 had been applied.

Except in the aerated bin fumigated in December, mortality of the test insects was excellent in all of the 75:25 fumigations (table 9). In the aerated bin fumigated in December, mortality of immature rice weevils averaged 93.8 percent at the wall, 85.6 percent 4 feet from the wall, and only 76.8 percent in the center. These mortalities are a direct result of the influence of temperature on volatilization and penetration. Most of the surviving immature rice weevils were found at the bottom level. Natural infestation in the aerated bin was reduced to an average of less than 0.5 live insects per 1,000 grams of corn. No live insects were found in the nonaerated corn samples.

As in the 80:20 fumigations, a comparison was made of the percentage of each fumigant component detected at each of the 1- through 48-hour sampling intervals (table 10). The total amount of EDC and CCl_4 found in the 75:25 fumigations was highest in the warm-

TABLE 9.—*Mortality of test insects and number of live insects in samples of corn after fumigation with 5 gallons of 75:25 (ethylene dichloride:carbon tetrachloride) per 1,000 bushels of corn in 3,250-bushel bins by gravity penetration*

Date of fumigation	Mortality of test insects [1]		Insects per 1,000 grams of corn [2]	
	Adult confused flour beetles	Immature rice weevils	Before fumigation	After fumigation
	Percent	*Percent*	*Percent*	*Percent*
July 25:				
Nonaerated	100	99.0	12.3	0.3
Aerated	100	98.0	11.7	.3
September 10:				
Nonaerated	100	99.9	10.3	0
Aerated	100	99.9	13.3	0
October 8:				
Nonaerated	100	99.9	10.4	0
Aerated	100	99.0	12.5	0
November 27:				
Nonaerated	100	100	13.8	0
Aerated	100	97.0	4.0	0
December 11:				
Nonaerated	100	98.0	19.5	0
Aerated	96.0	89.0	10.4	.5

[1] Average of 35 sample locations.
[2] Average of three 1,000-gram samples.

TABLE 10.—*Total concentrations of ethylene dichloride (EDC) and carbon tetrachloride (CCl_4) recovered in 10 fumigations of corn with 75:25, and percentage of each component detected at stated sampling intervals*

Date of fumigation	Average corn temp.	Ethylene dichloride (EDC) recovered						Carbon tetrachloride (CCl_4) recovered					
		Total	1-hour	4-hour	8-hour	24-hour	48-hour	Total	1-hour	4-hour	8-hour	24-hour	48-hour
	°F.	*Mg./l.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Mg./l.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
July 25:													
Nonaerated	69	3,304	25.7	25.8	26.9	14.9	6.7	4,109	36.7	29.0	17.2	11.3	5.8
Aerated	80	3,388	28.0	38.5	18.9	9.8	4.8	4,683	40.6	29.7	16.3	8.5	4.9
September 10:													
Nonaerated	71	3,574	30.2	29.2	22.2	11.2	7.2	3,305	51.6	22.8	14.7	7.2	3.7
Aerated	77	4,467	30.9	33.6	22.3	7.1	6.1	3,133	44.5	32.5	15.0	4.8	3.2
October 8:													
Nonaerated	70	921	21.7	28.1	18.2	20.3	11.7	2,546	25.8	29.9	20.9	16.9	6.5
Aerated	77	2,057	26.3	33.4	21.7	11.3	7.6	3,033	31.5	37.8	16.7	9.0	5.0
November 27:													
Nonaerated	52	821	16.4	19.9	30.1	24.6	9.0	1,852	25.9	29.8	31.6	10.4	2.3
Aerated	42	994	9.9	16.0	28.6	23.5	22.0	1,619	15.8	28.9	35.6	13.6	6.1
December 11:													
Nonaerated	53	962	10.9	26.5	23.0	24.8	14.8	2,336	26.7	30.4	20.2	15.9	6.8
Aerated	48	544	4.2	15.8	37.0	32.9	10.1	1,105	9.2	33.5	42.4	12.9	2.0

weather fumigations and lowest in the cool-weather fumigations. More than two-thirds of the total EDC and more than one-half of the CCl_4 detected during the five fumigations was found in the July and September fumigations. Of the total gas recovered from the five aerated bins, less than 5 percent of the EDC and less than 10 percent of the CCl_4 was recovered from the aerated bin fumigated in December.

CONCLUSIONS

At the rate of 5 gallons per 1,000 bushels of corn, average mortalities of test insects were similar with 80:20 and 75:25 fumigants. More insects survived in the upper part of the corn mass in the 80:20 fumigations and in the lower part in the 75:25 fumigations.

The distribution behavior of the 80:20 and the 75:25 showed more definite contrasts. The components of the 80:20 volatilized and penetrated the grain fairly rapidly in both warm and cool grain. Fairly similar total amounts of CCl_4 and CS_2 were recovered from each fumigation. One hour after application, as the fumigant moved down through the corn mass, the concentrations of the individual components were still in about the same ratio as when they were applied. At later sampling intervals, it was apparent that the concentrations of CS_2 were decreasing more rapidly than the concentrations of CCl_4. This suggests that the CS_2 was more affected by sorption and/or leakage than CCl_4.

The distribution of the CCl_4 in the 75:25 fumigations was very similar to its distribution in the 80:20 fumigations in warm corn. The amounts of EDC recovered within the corn were remarkably small considering the amounts of CCl_4 recovered at the same time. The ratio of the two components in the corn mass at various intervals showed little similarity to the ratio at which they had been applied.

The 75:25 components reached their peak concentrations later in the exposure period and persisted longer than the 80:20 components. In addition, component ratios in the 75:25 fumigations returned more nearly to the applied ratio during the 24- and 48-hour sampling intervals. These factors suggest a rapid loss by sorption of the EDC component as the fumigant is applied to the grain surface, followed by a slow desorption of the EDC during the exposure period. At the lower grain temperatures, the degree of sorption appeared to increase and the rate of desorption to decrease.

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