# **Project Number 77-I4**

Title: Project 77-I. Fumigation.

Prepared by: Howard D. Nelson

### I. Objectives:



# Methyl Bromide

To obtain information on the amount of organic and inorganic bromide residues in almond hulls and shells when fumigated with Methyl Bromide at the rate of 2 and 4 lbs per cu ft for 24 hours. This information was requested by EPA before the present petition that has been presented to them can be processed.

### Hydrogen Phosphide (Phosphine)

It is still true that hydrogen phosphide is the only fumigant approved for use on inhull and inshell almonds if the shells and hulls are to be used for animal feed. Most of the work in the past has been done with hydrogen phosphide applied as pellets and relatively little with tablets. Studies were conducted this year in which stacks of inhull almonds covered with 6 mil clear polyethylene were fumigated with this fumigant applied as tablets. The prupose of which was to obtain needed information on the dosage and exposure required to produce satisfactory mortality of the early egg and pupae stages of the NOW.

# Influence of Various Stack Coverings Upon the Temperature build up within the Covered Almonds

In reference to the last annual report, there is evidence that damage to almond meats can result if subjected to temperatures of  $130^{\circ} F$  or higher. It has been found that almonds are being subjected to temperatures in excess of  $130^{\circ} F$  when fumigated in stacks covered with six mil clear polyethylene sheeting. In the light of this problem, additional studies were conducted in an effort to find a suitable covering that would keep the temperature below the danger level.

# Revision of Fumigation Manual

Since the supply of this manual is nearly exhausted it is planned to reprint the manual and in the process, bring it up to date.

# Aeration Systems for Use in Stacks of Inhull Almonds

For a number of years the grain industry has utilized the flow of air through bins of grain as a means of reducing temperature within the mass, reduction of moisture and to recirculate and evacuate fumigants at the end of the fumigation period. Such systems were developed by agricultural engineers and others. Considerable time was spent last year assembling information on this subject.

# II. Interpretive Summary:

### Methyl Bromide

Studies were conducted during the past almond harvest season that were geared to supply information that EPA requested relative to obtaining a tolerance for the use of methyl bromide as a fumigant for almond hulls and shells. The study which was conducted in cooperation with Kern Almonds, Inc. has been completed, except all of the residue analyses have not been made. The analyses should be completed by the end of January 1978, after which time, the data will be summarized and submitted to EPA through the IR-4 coordinator.

# Hydrogen Phosphide (Phosphine)

In cooperation with Kern Almonds, Inc., four stacks of Nonpareil inhull almonds were covered with 6 mil clear polyethylene sheeting and fumigated with hydrogen phosphide in tablet form. The dosage used was 20 tablets/ m cu ft and the exposure period was 72 hours. The stacks were about 90' long and the results indicated that in order to obtain satisfactory mortality of the NOW eggs and pupae, the tablets needed to be placed at two locations

along the sides of each stack.

### Influence of Different Coverings Upon Temperature within the Stacks

Studies conducted this year included seven different kinds of materials as possible stack coverings. Of the seven evaluated, it would appear that the 6 mil polyethylene white laminated plastic and the 6 mil regular white polyethylene plastic were the most desirable based upon performance, availability and cost. These studies were conducted in cooperation with Kern Almonds, Inc.

# Revision of Fumigation Manual

In view of the demand for this manual by the industry the original printing is in short supply. During the procedure of reprinting the manual will also be revised.

### Aeration Systems for Use in Stacks of Inhull Almonds

Considerable time and effort was expended in reviewing the literature and interviewing Ag engineers and others, as well as my own knowledge of the aeration systems currently used by the grain industry. It would appear that some of these systems could be adopted for use in stacks of inhull almonds.

#### III. Experimental Procedure:

#### Methyl Bromide (1977 Activities)

The procedure used in fumigating six stacks of inhull almonds with Methyl Bromide was the same as that used in fumigating similar almonds with hydrogen phosphide (see 1976 annual report). The differences were 1) that the mehtyl bromide was introduced into an aluminum pan placed on the surface of the almonds in the air dome on top of the stack. A ½" OD plastic tubing was used to transfer the methyl bromide from a measuring device mounted to the 50 lb. pressure cylinder into the tray on top of the stack.

2) Concentrations of methyl bromide were determined at intervals throughout the exposure period through the use of a fumiscope and 3) the organic and inorganic bromide residues in the nut meats, hulls and shells were determined by the following two procedures:

<u>Inorganic</u> - the inorganic bromide analysis consists of extracting the bromide from the ground almond sample, by using water as the solvent. Extraneous organic material is then eliminated from the sample by ashing in a muffle furnace. The bromide ion is then oxidized to the bromate ion by using sodium hypochlorite. The bromate ion is then titrated and the results are calculated as parts per million bromide ion. The sensitivity of this procedure is two parts per million.

Organic - in a 5 gram sample, ionized bromide is quantitatively converted to 2-bromoethanol by reacting with ethylene oxide in an acid medium using acetonitrile as the solvent. The 2-bromoethanol produced is then determined in processed acetonitrile extracts by gas-liquid chromatography. Residual methyl bromide and/or ethylene dibromide, neither of which react with ethylene oxide under conditions prescribed are separated and determined concurrently.

#### Hydrogen Phosphide (Phosphine)

The procedure used to fumigate the 4 stacks of inhull almonds was the same as described in the 1976 report. The tablets were put in phostrays and the trays were placed at one location by each of two stacks and at 2 locations by each of two stacks. One stack was used as a control.

# <u>Influence of Different Coverings</u> <u>Upon Temperature within Stacks</u>

There was no basic difference in the procedure used in 1977 from that used in 1976. Seven kinds of material were evaluated.

### Aeration Systems for Use in Stacks of Inhull Almonds

No actual experiments were undertaken, but as previously mentioned a considerable amount of preliminary work was done in preparation for such studies.

### IV. Results:

### Methyl Bromide

The results of this study are not complete at this time. As mentioned previously the results of the residue analyses should be available within a month. When these results become available they will be summarized and submitted along with the other data as an addendum to this report.

# Hydrogen Phosphide (Phosphine) 1977 Studies

Results of this study are presented in tables 1, 2, and 3. Table 1 contains the concentrations of hydrogen phosphide in PPM and temperature in <sup>O</sup>F found at 5 locations within stacks 9 and 10 during the 72 hour exposure period. The tablets were placed at 1 location along the side of each stack. Table 2 contains similar information except the tablets were placed at one location on each side of the stacks. In table 3 the percent mortality of the NOW eggs and pupa resulting from the fumigation may be found.

# <u>Influence of Different Coverings</u> Upon Temperature within Stacks

Results of a two-day study in which temperature readings were taken in seven stacks of inhull almonds covered with seven different kinds of material are presented in table 4.

#### V. Discussion:

# Methyl Bromide

As mentioned above, all of the data for this study is not available and will be submitted as an addendum to this report at a later date. It

would appear that the tests were conducted in a satisfactory manner and everything went along smoothly. It is hoped that EPA will find this data suitable and that a tolerance will be established and a label obtained for the use of methyl bromide as a fumigant for almond shells and hulls without further delay.

### Hydrogen Phosphide (Phosphine) 1977 Studies

As indicated in the annual report for 1976 preliminary studies on the use of aluminum phosphide applied in tablet form showed promise.

Studies this year (1977) in which tablets were used seemed to substantiate the preliminary findings. On the basis of this years study the following observations seem justified:

- 1. NOW pupae are much easier to kill than eggs less than 24 hours old.
- 2. A dosage of not less than 20 tablets per 1000 cu ft of space should be used with an exposure period of 72 hours.
- 3. When the stacks of almonds are long eg., up to 90 feet; the tablets should be divided into two groups and placed in two locations along the sides of the stacks.

During the coming year it is planned to use tablets at a higher dosage level, learn more about size of stack and placement of dosage relationship, study the effect of fumicels should they become available, and to see if broadcasting the tablets over the surface of the stack will solve the problem of fumigant distribution (particularly in the longer stacks).

# <u>Influence of Different Coverings</u> Upon Temperature within Stacks

Studies conducted this year indicated that 6 mil regular white and white laminated polyethylene sheeting would be a satisfactory material to

use as a covering for stacks of inhull almonds. It is my understanding that the white sheeting is available and the cost would not be prohibitive. The mylar coverings, though effective, are quite expensive. It is planned to discontinue this study at least for the near future.

### Aeration Systems for Use in Stacks of Inhull Almonds

In view of available information regarding aeration systems used in stored grain and other commodities it would appear that procedure could be developed or adopted for use in stored inhull almonds. It is planned to install an aeration system in at least one stack of inhull almonds during the 1978 harvest season.

### VI. Publications:

It is planned to reprint and revise the hydrogen phosphide fumigation manual during 1978.

Location of fumigation concentration and temperature sampling locations within the stacks of almonds referred to in tables 1, 2 and 3.

1/ = Within air space between top of stack and plastic cover.

2 = SURFACE STACK OF ALMONDS

= Top corner 1 ft from edge of stack and 1 ft down from surface of almonds.

4 = Center of almonds from top to bottom 1/3 length of stack.

5) 4 = Opposite bottom corner from 2 above 1 ft above ground and 1 ft in from edge of stack.

Table N. 1 - Summary of Concentrations of hydrogen phosphide itemperatures found at four locations within 2 stacks of inhull almonds fumigated with aluminum phosphide lehostoxin ) in tablet form during a 72 hour exposure. The dosage was 20 table?

1 Mcu. ft. + were placed at one location along one side of each stack.

			0 +			Temperature									
		utrotion		migant		Location in Stack.									
Sample	1000		u Sta	Number 4	115										
Interval			PPM.		P.P.M.	NUMBERT	OF	OF	of	· OF					
hours	P.P.M.	PRM	PP. /FI	Tirini	7,77,77										
				stack	T Numb	er 8									
Began at 4:35 K.M															
1	20	مح	20	5	2	105	90	70.5	70 .	66.5					
2	40	15	45	15	15	81	90	71	7/	69					
4	20	20	40	20	20	82	89	74	72	66					
8	50	40	90	40	26	67	82	78	73'	72					
12	120	90	100	8 <i>5</i>	50	62	77	73	72	69					
24	175	125	150	190	60	155	101	77	74	69					
36	150	150	140	150	90	72	76	78	71	72					
48	100	100	100	150	120	120-	105	80'	79`	70					
	110	115	115	115	45	64	58	80'	77	74					
72	90	95	105	95	95	120+	95	_71_	76	62					
Total=	815	755	905	865	567	928	863	758,5	741	689.5					
Aug =		75.5	90.5	44.5	56.7	92.8	86,3	75.8	74.1	69.0					
N =	10				,		<b>n</b>								
0				5+	act Nu	mber C	<u>1</u>								
Beran at 3.50P.M															
1	10	15	20	15	/	114	60	70	72	64					
2_	20	20	25	10	3	85	90	70	72	65					
4	20	20	30	20	10	80	88	72	74	66					
. 8	30	30	. 56	90	15	70	76	73	75	68					
/2	90	80	110	110	50	63	81	72.	75	63					
24	150	125	100	200	120	116	102	74	76	67					
36	150	125	125	150	120	74	91	75	77	69					
48	100	110	100	100	100	120+	106	76	76	70 68					
60	105	110	100	90	90	91	93 00	78	78	60					
72	7.5	_ 85	95	_80_	_81_	130	99	_77	77_	660					
Tc., -1 =	•	720	755	865	589	945	880	737	752						
Aug =	75.0	72,0	75.5	86.5	588	44,3	88,0	73.7	15,2	F E 10					
N	10														
Ge Total -	1625	1475	// / 6	1730	1151-	1071	17:19	1495.5	1493	1344,5					
				86.5			87.2			67.5					
nie.	81.25	, 318	<i>ن.د</i> ن		٠/١٠ د	الما بدا	011-	71. 0	1118	-					

Table No. 2. Summary of concentrations of hydrogen phosphide + temper afures found at five locations within 2 stacks of inhall almonds funigated with Aluminum plosphide (Phostoxin®) in tablet form during a 72 hour exposure period. The dosage was 20 tablets/m cs. 7. + half of the tablets were placed at I location on one side of éach stack

C4 7.	+ half o	f the tal	blefs wi	ete place	ed a+1	location	Shows	side of	each s	fact						
+ tht	rt main	1ng /2	ONTHE	other	SIGEO	Temperature										
-		entrafie	ı	11 14 19 Q M	-	Location in Stack										
Sample	Loca	number 24	n Stac	K #4	(10.10 5) - 1	1 1 1 1 1	Number 2	Number 3	Kumber 4	Number 515						
Interval 1	PPM PPM	number 24 PPM	PPM.		P.P.M.	P.P.M.	P.P.M.		P.P.M.	P.P.M.						
hours	<i>P.P.</i> ///	· P.P.III	F. 1. 111.	1,1,111	· · · · · · · · · · · · · · · · · · ·			-								
				Stack	Numb	er 10	_		-							
8eqan 3:10 P.M					,				•	·						
/	40	3	10	15.	5	112	82,5	8b'	88	93,5						
2	45	15	15	40'	25	81	81	85"	86	83.						
4	50.	10.	20.	90.	30	70.	87	85	86'	74						
8.	60.	10	40	120	40	62	84	84	85	67						
12	110.	50	100	100	110	59	81.	89	83.	61						
24	100	145	115	100	190	///	101	84	84	78						
36	140	120	125	140	120	69	85	85.	85	£8						
48	120	110	100	110	100	102	120+	83	85	82						
1 k	90	110	90.	90	90	60	86	87	88	56 68						
72	80.	_85	70	_75	70	120	85	-8/	84.	730,5						
Total =	835	660	685	880	780	846	892,5 89.2	849	854 85,4	73.0						
QUE =	83.5	66.0	68.5	88,0	78.0	84.6	81,2	419	8517	10,0						
N = 10 Stack Number 11																
				STACE	T NUM	ner 11										
Gegan of 3:10 pm																
1	25	<b>O</b> -	10	5	5	114.	83	88	85	71.						
2	25	5	15	15	25	90	82	86	83	70						
4	20.	5	15.	50	20	70	86	88	83	73						
. <b>E</b>	60	15	90	120	20	62	71	87.	83	73						
12	120	60	120	125	30	58	77	86.	80	67						
24	100	100	150	190	105	149	100	86	77	71						
26	120	100	140	150	95	70	87	81	82	72						
48	100	100	110	110.	100	120	100	84	79	7/						
10	90	80	90	90	90	58	86	88 12	<del>8</del> 9	7/ 65						
12	60	10	50	_65_	60	128	82	<u>\$3</u>	74	704						
Total.	= 720	525	790	920	600	919	860	863	815 81.5							
avg. =	72.0	52.5	79.0	92,0	62.0	91.9	86.0	86.3		70.4						
Scitotal -	1555	1185	1475	1800	1400	1765	1752.5	1712	1669	1434.5						
Aug =	77.8	59.2	73.8	90.0	70.0	₹8,25	87.6	85.6	<u> </u>	_71.7_						

Table. No 3. - Summary of the effect of hydrogen phosphide, under conditions described in tables No. 17 No. 2, on the early egg stage (less than 24 hrs. old) title pupa. stage of the NOW. In all four stacks the dosage texposure period was the Sawie. In stacks 8rg the tablets were placed at 128 location by each stack tin stacks lot! tablets were placed at 2 locations by each stack. Stack No. 12, remained Universited.

	,	-												e												
			ESSENTEN																							
				,								٠														
	e Stage	Toval	elive grad	Number number																						
	tred in page	1.dult>	Live Read	Humber Damber Humber			-												•							
	7 um 199 ho	ak	dead .	Humber W	4	30	35	o M	30	12.0	80	32	7% O	w O	07/	•	3 D	. 08	30	120		30	30	30	0/20	300
	. Anna de Carrella	Purp	Alive	namb es		0	Ø	٥	0	٥	٥	0	0	d	90			0	٥	00		ଦ	Q	٥	00	
o A	101 ha	Stage	batched	humber Humber	¢	0	0	_	133	747	. 0	W	0	177	08/	5.0	0	٥	O	0	>	٥	0	0	28	7.5
ノングトセロトウロ	Form 190 ted	Karly	un hatchee	humber		367	239	3.70	332	15700	415	3 93	327	134	1221	31.6	326	361	478.	285					194	620
1 parl	ניוז פרב.	20 cq tion	4707S	MCMID & L							त्त्र त्त्र त्र					, ,,	7 7				V 11	127		H +	-1 14	
2 remaine	Fumigant	10cq+100	Stack	hocation )		1 51de	. 2	2	=	A SO A	I side	~	¥	z	16tal	70	2 sides	=	<i>-</i> -	70+ A [	400	2 sides	e	Ξ	otal Aug	40
1001		54ach	1 dentity	Member	1	æ	4	b	ï		6	=	z	æ			01	<u>۔</u>	z	' ب		17	Ξ	≥.	~	

	te/	dead.	Vimber Dumber Dumber Dumber				-			•	. ·										
Stape	Total	411VE	Dumber														:				
	(43	gead	Number		M	٥	M	-	1	175	5,9		٥	_	d	~	~	0	//	8'/	60)
Funigored in purac	#du(#5	A114			77	30	77	2.9	1/3	, By	140		30	76	4	4	2	200	691	28	93,9
owigared	6	grad	Number		4	۵	Φ	0	0				Q	0	٥	٥	0	0	0		t
FU	Bupge	Alive	number			٥	Đ	0	0			•	٥	ð	O	Ø	ව	0	۵	•	
rd In	260156	hatched	wwher number humber number Nawber		236	3	301	27.3	12.11	W 0 .	83.2		275	705	568	158	183	2.12	1301	2163	- 3 - 3
fumicated in	Early egg stage	wholehed hatched	MUWhit		133	#	75	29	244	9	16.8		87		13	17	%	5	=	18,5	2.9
143864	Voca From	S tack	Manber				T F	3/2	,	Į,	11		way room	Pry	•,				"	اء '	11
Fuminum turket	location	Stack	Location	7	Suniqueted				10+2	10 ×	, 60°	•	Place d in Kolding room	labora tory	٥	ت	Ξ	~	10ra/	A 00	80
	Stack	Identity	Tadiana		7	ē	Ξ	<b>2</b>					Placed	to							

15,4083 4.811 89.3 21.8 85.4 Clear 82.8 42- 154 81.5-113 11.8 169. 70,5 65,5- 79 187 487 16 - 86 Range 72.5. 298.1 14.5 72.5 Covering 38656 2506-334 - 73 93.0 53 - 100 62.7-65,5 151 - 75 Range 83°D 66,1 - 86 2 with white backing 78.2 500 61.9 Summary of the Runge and Aug. Temperatures in degrees F recorded from Mylar Coated with Myler Silver with Mylar Silver おどの 2201 AVG . Banger 17.7 35.8 - 90.2 3730.2 142 - 341 Seven Stacks Covered with different makerials over a 18,5 77.2 - 68 OCK, 878 18,6 17-80 12-99 4/19 85,5 512-108 89,2 60.112 Red Back 1249 Range 60 203-254,8 2.800, 4 267,7-337 18 16.9 - 84.2 29 54-181 7655-70.0 0,00 17.9 A V 9 MY WILLIAM 108-85 - 96 - 828 67 - 76 RAMINE COMME 81.8 -- 212 86,5 | 78 76 7 ે દ 4029 A V 9. 639 Black Plaskic 282 - 382 59 - 134 79 5'56-51 101 -57,5 | 59-68 Range 75 -47 78.5 ., 68 3745 78.0 white plasfic ,06 A16 REGULAF. 98,0 62,2-112 Total = 244 -350 37207 985-352 77.5 167.6-88.0 Rayor 58.5 538- 63 26-64 77.5 775 - 79 IJ. FOUR locations In each of 76.00 White Mostic Lyminated Range 1 top doruet / 23 - 82 518-99 1. Almond Surface | 59,5 - 124 4. Opposite bollow 545 - 66 84 - 26 Table No. 4: -2 about 18:W 1 Ct. from bottom on top of stack From sides + corner from day period Center of Location 77875 Stack Location Bagt. ev.

M7-I

Fumigation of Inhull Almonds on the Farm

Ву

Howard D. Nelson

USDA-ARS-Stored Product Insects Research Laboratory, Fresno, CA Dec. 1977

# Methyl Bromide:

A petition to obtain a tolerance for the use of methyl bromide as a fumigant for almond shells and hulls was presented to EPA (Environmental Protection Agency). Before EPA would act on the petition, they requested the following:

- 1. Fumigate, with methyl bromide, 6 stacks of inhull almonds stored on the farm and covered with 6 mil polyethylene sheeting.
- 2. Three of the stacks to be fumigated at the rate of 2 lbs of methyl bromide per 1000 cu ft for 24 hours and remaining three stacks at the rate of 4 lbs per 1000 cu ft for 24 hours.
- 3. Obtain fumigant concentration and temperature readings within the enclosure at intervals during the fumigation period as well as the amount of organic and inorganic bromide residues present in the almonds as a result of the fumigation.

The almonds were fumigated as requested and fumigant concentrations and temperature readings were taken and samples of almonds obtained for residue analyses. These analyses will be completed by February 1978. All of the data will then be compiled and forwarded to EPA through the Coordinator of IR-4.

### Hydrogen Phosphide:

This year's studies indicated that stacks of inhull almonds can be fumigated effectively with hydrogen phosphide (Phostoxin) when applied as tablets at the rate of not less than twenty per 1000 cu ft for 72 hours. When fumigating stacks that are up to 90 feet long, the tablets should be placed in at least two locations along the sides of the stacks. Temperature Studies:

Of the seven kinds of stack coverings studied the 6 mil white plastic was the most satisfactory based upon performance, cost and availability.

For Information of cooperators only — do not use in sales promotion or advertising that expresses or implies endorsement of a product by the U. S. Department of Agriculture. Preliminary unpublished data — do not reproduce, quote in print, or make available to persons not directly involved in the studies without clearance from the Stored-Product Insects Research Laboratory, Agricultural Research Service, USDA,