

Title: Project 77-I. Fumigation.

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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 inshell 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 inshell almonds covered with 6 mil clear polyethylene were fumigated with this fumigant applied as tablets. The purpose 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°F or higher. It has been found that almonds are being subjected to temperatures in excess of 130°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 methyl bromide was introduced into an aluminum pan placed on the surface of the almonds in the air dome on top of the stack. A 1/4" 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:

Inorganic - 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 in-hull 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.

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

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 °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.

##### Influence of Different Coverings 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).

#### Influence of Different Coverings 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

3/ ~~2/~~ = Top corner 1 ft from edge of stack and 1 ft down from surface of almonds.

4/ ~~3/~~ = 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 No. 3. - Summary of the effect of hydrogen phosphide, under conditions described in tables No. 1 & No. 2, on the early egg stage (less than 24 hrs. old) + the pupa stage of the NOW. In all four stacks the dosage + exposure period was the same. In stacks 8 & 9 the tablets were placed at one location by each stack + in stacks 10 & 11 tablets were placed at 2 locations by each stack. Stack No. 12 remained untreated.

stack identify	Fumigant location in stack	Insect location in stack	Fumigated in pupae stage		Fumigated in pupae stage	
			untreated	number	number	number
8	1 side	2 2	367	0	0	30
"	"	3 3	239	0	0	30
"	"	4 4	370	1	0	30
"	"	5 5	332	133	0	30
	Total	=	1675	134	0	120
	Avg %	=	419	34	0	30
		=	92.6	7.4	0	12.0
9	1 side	2 2	415	0	0	30
"	"	3 3	395	3	0	30
"	"	4 4	327	0	0	30
"	"	5 5	124	177	0	30
	Total	=	1271	180	0	120
	Avg %	=	318	45	0	30
		=	80.6	12.4	0	12.0
10	2 sides	2 2	326	0	0	30
"	"	3 3	361	0	0	30
"	"	4 4	478	0	0	30
"	"	5 5	285	0	0	30
	Total	=	1550	0	0	120
	Avg %	=	388	0	0	30
		=	100	0	0	12.0
11	2 sides	2 2	352	0	0	30
"	"	3 3	379	0	0	30
"	"	4 4	370	0	0	30
"	"	5 5	194	28	0	30
	Total	=	1295	28	0	120
	Avg %	=	324	7	0	30
		=	90.9	2.1	0	12.0

Table No 3 (Contd.) -

Stack identity	Fumigant location in stack	Insect location in stack	Fumigated in early egg stage		Fumigated in pupae stage		Total		
			Number	Number	Alive	Dead	Alive	Dead	
			Unsettled	Settled	Number	Number	Number	Number	
12	Met fumigated	2	133	236	0	0	27	3	
"	"	3	48	351	0	0	30	0	
"	"	4	34	301	0	0	27	3	
"	"	5	29	323	0	0	29	1	
	Total =		244	1211	0	0	113	7	
	Avg =		61	303			28	175	
	% =		16.8	83.2			94.1	5.9	
Place & holding room of laboratory									
			23	275	0	0	30	0	
			26	205	0	0	29	1	
			13	268	0	0	25	2	
			17	158	0	0	23	7	
			13	183	0	0	29	1	
			19	212	0	0	30	0	
	Total =		111	1301	0	0	169	11	
	Avg =		18.5	216.8			28	1.8	
	% =		7.9	92.1			93.9	6.1	

Table No. 4: - Summary of the Range and Avg. Temperatures in degrees F. recorded from four locations in each of seven stacks covered with different materials over a two day period.

Oct. 8 & 9, 1957

Location	White Plastic Laminated		White Plastic Regal		Black Plastic		Mylar Coated with Aluminum		Mylar Silver with Red Backing		Mylar Silver with White Backing		No. Covering		Clear Plastic	
	Range of	Avg of	Range of	Avg of	Range of	Avg of	Range of	Avg of	Range of	Avg of	Range of	Avg of	Range of	Avg of	Range of	Avg of
1. Almond surface on top of stack	58.5 - 124	98.0	62.2 - 112	90	59 - 134	108	58 - 96	83.5	58.2 - 108	89.2	60 - 112	93.0	53 - 100	82.0	62 - 154	118.4
2. Top corner 1 ft. from surface + 1 ft. from edge.	73 - 82	76.0	77 - 98	87	77 - 101	89.5	78 - 92	80.0	76.5 - 81	78.5	77.2 - 88	83.0	66.1 - 86	72.5	81.5 - 113	96.3
3. Center of stack	77 - 78	77.5	77.5 - 79	78.5	75 - 79	76	-	-	78 - 79	78.6	77 - 80	78.2	61.5 - 75	72.5	78 - 91	85.4
4. Opposite bottom corner from 2 about 1 ft. from sides + 1 ft. from bottom	54.5 - 66	58.5	53.8 - 63	57.5	59 - 68	62	67 - 76	70.0	54 - 69	64.2	66 - 71	67.9	70 - 73	70.5	65.5 - 79	71.8
Total =	244 - 350	372.07	270.5 - 352	374.5	320 - 382	402.9	203 - 254.8	280.0	267.7 - 337	3730.2	142 - 341	3865.6	250.6 - 334	298.1	287 - 437	1540.8
Avg. =	66 - 87.5	77.5	67.6 - 88.8	78.0	71.5 - 95.5	83.9	67.7 - 81.9	77.9	66.9 - 81.2	77.7	35.8 - 90.2	80.5	62.7 - 80.5	74.5	71.8 - 109.7	91.7

477-I

Fumigation of Inhull Almonds on the Farm

By

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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<sup>®</sup>) 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.