US ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES PROGRAMS
REGISTRATION DIVISION (TS-767)
WASHINGTON, DC 20460

NOTICE OF PESTICIDE: ☐ REGISTRATION ☒ REREGISTRATION

(Under the Federal Insecticide, Fungicide, and Rodenticide Act, as amended)

EPA REGISTRATION NO. 11491-7

DATE OF ISSUANCE JUL 31 1995

TERM OF ISSUANCE

NAME OF PESTICIDE PRODUCT

Carbon Dioxide

PM 14
11491-7
10/24

NAME AND ADDRESS OF REGISTRANT *(Include ZIP code)*

Liquid Carbonic
810 Jorie Boulevard
Oak Brook, IL 60521-2216

5488279 675/22

5488280 675/22

NOTE: Changes in labeling formula differing in substance from that accepted in connection with this registration must be submitted to and accepted by the Registration Division prior to use of the label in commerce. In any correspondence on this product always refer to the above U.S. EPA registration number.

On the basis of information furnished by the registrant, the above named pesticide is hereby Registered/Reregistered under the Federal Insecticide, Fungicide, and Rodenticide Act.

A copy of the labeling accepted in connection with this Registration/Reregistration is returned herewith.

Registration is in no way to be construed as an indorsement or approval of this product by this Agency. In order to protect health and the environment, the Administrator, on his motion, may at any time suspend or cancel the registration of a pesticide in accordance with the Act. The acceptance of any name in connection with the registration of a product under this Act is not to be construed as giving the registrant a right to exclusive use of the name or to its use if it has been covered by others.

Based on your response to the Reregistration Eligibility Document, EPA has reregistered the product listed above. Enclosed is a copy of your label stamped "Accepted". This action is taken under the authority of section 4(g)(2)(C) of the Federal Insecticide, Fungicide, and Rodenticide Act, as amended. Reregistration under this section does not eliminate the need for continual reassessment of pesticides. EPA may require submission of data at any time to maintain the registration of your product.

Make the revisions specified below before you print the final labeling for this product.

1. On the Front Panel, rewrite the WARNING statement to read:

   WARNING: May be fatal if inhaled. Do not breath vapor. For handling activities in enclosed areas during **and after fumigation**, use either a supplied-air respirator with MSHA/NIOSH approval number TC-19C or a self-contained breathing apparatus (SCBA) with MSHA/NIOSH approval number TC-13F.

☐ ATTACHMENT IS APPLICABLE

SIGNATURE OF APPROVING OFFICIAL

10/24

DATE JUL 31 1995

EPA Form 8570-6 (Rev. 5-76)

PREVIOUS EDITION MAY BE USED UNTIL SUPPLY IS EXHAUSTED.

US GPO: 1992-312-018/60303

7. Under Paragraph 2 of PRECAUTIONS AND PROCEDURES DURING DISCHARGE, add the following sentence:

   See the text under WARNING on the Front Panel for the specific type of approved respiratory device.

Submit one copy of your final printed labeling before you release the product for shipment. Refer to the A-79 Enclosure for a further description of final printed labeling.

Registrants may sell or distribute products bearing old labeling for **one year** after the date of this Notice. **Non-registrants** may sell or distribute products bearing old labeling for **three years** after the date of this Notice.

If these conditions are not complied with, the registration will be subject to cancellation in accordance with FIFRA section 6(e). Your release for shipment of the product bearing the amended labeling constitutes acceptance of these conditions.

A stamped copy of the labeling is enclosed for your records.

Robert A. Forrest
Product Manager (14)
Insecticide-Rodenticide Branch
Registration Division (H7504C)

Enclosures: 1. Stamped label
2. A-79 Enclosure

Peacock WP#6:A:38719-5.CO2:305-5407,-6600:7/31/95

Address Label:

Liquid Carbonic
810 Jorie Boulevard
Oak Brook, IL 60521-2216

Attention: Mr. Brian Curtis

CARBON DIOXIDE

ACTIVE INGREDIENT:	CARBON DIOXIDE	99.95%
INERT INGREDIENTS:		0.05%
		100.00%

KEEP OUT OF REACH OF CHILDREN

ACCEPTED
with COMMENTS
In EPA Letter Dated

JUL 31 1995

Under the Federal Insecticide, Fungicide, and Rodenticide Act as amended, for the pesticide registered under EPA Reg. No. 11491-7

WARNING

EXPOSURE MAY CAUSE SUFFOCATION & DEATH

STATEMENT OF PRACTICAL TREATMENT

If inhaled: Remove to fresh air immediately; keep victim lying down and warm. If breathing is difficult, give oxygen. Call physician immediately.

PRECAUTIONARY STATEMENTS

WARNING: May be fatal if inhaled, Do not breath vapor. For handling activities in enclosed areas during fumigations, use either a supplied-air respirator with MSHA/N10SH approval number prefix TC-19C, or a self-contained breathing apparatus (SCBA) with MSHA/N10SH approval number TC-13F.

AERATION: After fumigation, aerate treated areas until the level of CO_2 as measured by (the registrant must identify one or more direct-reading detection devices suitable for use with the product and provide or reference instructions on its use), is below 5,000 ppm.

RE-ENTRY (Below 5,000 PPM): If CO2 levels are below 5,000 ppm persons may re-enter the treated area without respiratory protection.

RE-ENTRY (5,000 - 30,000 PPM CO2): If CO2 levels are between 5,000 and 30,000, persons may re-enter the treated area without respiratory protection for 15 minutes or less. For periods longer than 15 minutes, person must wear the respiratory protection device specified above under WARNING.

RE-<u>ENTRY (Over 30,000 PPM CO2):</u> If CO2 levels are over 30,000 ppm CO2, person must always wear the respiratory protection device specified above under WARNING.

The USDA has set a limit of 0.5% (5,000 ppm) maximum CO_2 concentration in work areas.

DIRECTIONS FOR USE

It is a violation of Federal Law to use this product manner inconsistent with this labeling.

GENERAL USE RESTRICTIONS: This product is used to fumigate storages, trucks, trailers, sealed railroad cars and ships. The following may be treated – all raw and processed agricultural products such as: Corn, including popcorn, barley, oats, rice (milled and/or enriched), sorghum, wheat, rye and other small grains, cocoa beans, coffee beans, flour, cereal and related products, all dry beans, peas, macaroni and pasta products, dry milk and products made with dry milk, nuts including peanuts, almonds, walnuts, pecans, filberts, cashews and brazil nuts, dried fruits including apples, apricots, currants, dates, figs, peaches, prunes, pears and raisins, raw and processed tobacco, brewer's grits, candy; all spices, all herbs, animal feed in bulk or bags, birdseed, man mal skins, stuffed animals, herbarium specimens, rare books and wood products such as carvings.

It is effective against the following storage products inserts: Beetles including granary weevil, rice weevil, broadnose grain weevil, lesser grain borer, larger grain borer, confused flour beetle, red flour beetle, American black flour beetle, longhead flour beetle, slenderhead flour beetle, larger flour beetle, yellow meal worm, dark meal worm, black carpet beetle, karpa beetle, warehouse beetle, trogoderma inclusum, trogoderma glabrum, warehouse beetle, rusty grain beetle, flat grain beetle, cryptolestes pusilloides, saw toothed grain beetle, merchant grain beetle, foreign grain beetle, corn sap beetle, cigarette beetle, drugstore beetle, cowpea weevil, adzuki bean weevil, pea weevil, broadbean weevil, bean weevil, coffee been weevil, cadelle; Booklice including psocids, booklice and death watch; Moths including Angoumois grain moth, Indian meal moth, almond moth, tobacco moth, raisin moth, meal moth, Mediterranean flour moth, rice moth, navel orange moth, webbing clothes moth and clothes moth.

Dosage rates very from 60% atmosphere to 100% atmosphere. Treatment times vary from 2 days to 4 days. See our Bulletin MB-84-2 for details on treatment specifics. Call 708-572-7500 for additional help.

Do not fumigate if grain temperature is low (less than 40°F). Area should be as gas tight as possible before treatment. Maintain as near to 60% CO_2 as possible.

This carbon dioxide can be used in food handling, manufacturing, processing and storage facilities at a rate from one to eleven pounds per 1,000 cubic feet, as an atmospheric conditioner or carrier in conjunction with an EPA registered pesticide (as long as the pesticide is also for use in food handling, manufacturing, processing, and storage facilities).

TRAINING: All persons working with this product should be knowledgeable of the hazards of this chemical, and trained in the use of required respirator equipment and detector devices, emergency procedures and use of the product. When used for fumigation of enclosed spaces, (boxcars, silos, ship containers, and other transport vehicles), two persons familiar with the use of this product must be present during introduction of the fumigant, initiation of aeration, and after aeration when testing for reentry. Two persons do not need to be present if monitoring is conducted remotely (outside of area being fumigated).

PLACARDING STATEMENT: The applicator must placard or post all entrances to the fumigated area with signs conforming to the following requirements:

a) The sign shall be at least 14 inches by 16 inches in size and the letters shall be at lease 1 inch in height unless a smaller size sign is necessary because the treated area is too small to accommodate a sign of this size. Letters shall be clearly legible.

b) The signal word, "DANGER/PERLIGRO" must be on the placard.

c) The statement, "Area under fumigation, DO NOT ENTER/NO ENTRE".

d) The date of fumigation.

e) The name of the fumigant (carbon dioxide).

f) Name, address and telephone number of the applicator or pesticide handler.

These signs must be posted at eye level and must be visible from all visible points of entry to the treated area. They must remain posted during application and throughout the restricted-entry interval until the concentration of carbon dioxide is below 5,000 ppm. Each separate treated area (i.e., boxcar, silo, ship container) must be posted or placarded with this sign.

The applicator or person responsible for monitoring levels of carbon dioxide may remove the placard when the concentration of carbon dioxide is at or below 5,000 ppm.

FUMIGATION DIRECTIONS: Purge bin to 60% Atmosphere. We recommend two day treatment for adult kill, four days for all life stages. For specific flows, contact qualified Liquid Carbonic or fumigation engineer.

TRUCKS & TRAILERS: Treat as above. Do not move Truck or Trailer during treatment. They must be aerated before movement is allowed.

SHIPBOARD, INTRANSIT SHIP OR SHIPHOLD FUMIGATION

IMPORTANT

Shipboard, intransit ship or shiphold fumigation is also governed by U.S. Coast Guard Regulations. Refer to and comply with these regulations prior to fumigation.

PROCEDURES

PREFUMIGATION PROCEDURES:

1. Prior to fumigating a vessel for intransit cargo fumigation, the master of the vessel or his representative and the fumigator must determine whether the vessel is suitably designed and configured so as to allow for safe occupancy by the ship's crew throughout the duration of the fumigation. If it is determined that the design and configuration of the vessel does not allow for safe occupancy by the ship's crew throughout the duration of the fumigation, then the vessel will not be fumigated unless all crew members are removed from the vessel. The crew members will not be allowed to reoccupy the vessel until the vessel has been properly aerated and a determination has been made by the master of the vessel and the fumigator that the vessel is safe for occupancy,

2. The person responsible for the fumigation must notify the master of the vessel, or his representative, of the requirements relating to personal protection equipment, detection equipment and that a person qualified in the use of the equipment must accompany the vessel with cargo under fumigation. Emergency procedures, cargo ventilation, periodic monitoring and inspection, the first aid measures must be discussed with, and understood by, the master of the vessel or his representative.

3. During the fumigation or until a manned vessel leaves port or the cargo is aerated, the person is charge of the fumigation shall insure that a qualified person using gas or vapor detection equipment tests spaces adjacent to spaces containing fumigated cargo and all regularly occupied spaces for fumigation leakage. If leakage of the fumigant is detected, the person in charge of the fumigation shall take action to correct the leakage, or shall inform the master of the vessel, or his representative, of the leakage so that corrective action can be taken.

4. If the fumigation is not completed and the vessel aerated before the manned vessel leaves port, the person in charge of the vessel shall insure that at least two units of personal protection equipment and one gas or vapor detection device, and a person qualified in their operation be on board the vessel during the voyage.

PRECAUTIONS AND PROCEDURES DURING VOYAGE:

Using appropriate gas detection equipment, monitor spaces adjacent to areas containing fumigated cargo and all regularly occupied areas for fumigant leakage. If leakage is detected, the area should be evacuated of all personnel, ventilated, and action taken to correct the leakage, before allowing the area to be occupied. Do no enter fumigated areas except under emergency conditions. If necessary to enter a fumigated area, appropriate personnel protection equipment must be used. Never enter fumigated areas alone. At least one other person, wearing personal protection equipment, should be available to assist in case of emergency.

PRECAUTIONS AND PROCEDURES DURING DISCHARGE:

If necessary to enter hold prior to discharge, test spaces directly above grain surface for fumigant concentration, using appropriate gas detection and personal safety equipment. do not allow entry to fumigated areas without personal safety equipment unless fumigant concentrations are at safe levels, as indicated by a suitable detector.

"Personal protection equipment means a gas mask or respirator for the fumigant, jointly approved by the Mining Enforcement and Safety Administration and the National Institute of Occupational Safety and Health".

STORAGE AND DISPOSAL

STORAGE: Do not contaminate water, food, or feed by storage or disposal. Store in bulk CO_2 vessels which are permanent or semi-permanent installations or in approved CO_2 cylinders.

Store cylinders in dry, cool, well-ventilated area under lock and key. Post as a pesticide storage area.

Store cylinders upright, secured to a rack or wall to prevent tipping. Cylinders should not be subjected to rough handling or mechanical shock such as dropping, bumping, dragging or sliding. Do not use rope slings, hooks, tongs or similar devices to unload cylinders. Transport cylinders using hand truck or fork truck to which the cylinder can be firmly secured.

Do not remove valve protection bonnet and safety cap until immediately before use. Replace safety cap and valve protection bonnet when cylinder is not in use

SPILL AND LEAK PROCEDURE STATEMENT:

Evacuate immediate area of leak. Use respiratory device (see Precautionary Statement) for entry into affected area to correct problem.

LEAKING BULK CO2 VESSEL OR ITS ATTACHED PIPING:

In the event of leakage from a bulk CO_2 vessel or its attached piping, close the upstream valve to isolate the leaking section. Depressurize the affected section and remove or repair the leak. If shutting off the valves at the vessel fail to stop the leakages, contact local CO_2 service personnel to pump out or unload the vessel before proceeding with repairs.

LEAKING OR DAMAGED CYLINDERS

Move leaking of damaged cylinder outdoors or to an isolated location, observing strict safety precautions. When completely empty, return to manufacturer if instructed or dispose of leaking or damaged cylinders or containers in accordance with State and Local waste disposal regulations.

Do not permit entry into spill area by unprotected persons until concentration of carbon dioxide is determined to be less than 5,000 ppm.

PESTICIDE DISPOSAL:

Bulk CO_2 vessels are generally moved empty and depressurized. The usual method to dispose of excess CO_2 is to dilute it with air by venting. Care must be exercised to prevent accumulations of high concentration of vented CO_2 gas in an enclosed or low lying area. This is usually accomplished by very slow venting of the CO_2 to avoid a local asphyxiation hazard.

CONTAINER DISPOSAL:

Bulk CO_2 vessels should be removed and disposed of only by qualified CO_2 service personnel.

Return empty CO_2 cylinders for reuse or disposal.

When cylinder is empty, close valve, screw safety cap onto valve outlet and replace protection bonnet before returning to shipper. Only the registrant is authorized to refill cylinders. Do not use cylinders for any other purpose. Follow registrant's instruction for return of empty or partially empty cylinders.

LIQUID CARBONIC INDUSTRIES CORPORATION
810 Jorie Blvd.
Oak Brook, Illinois 60521-2216
E.P.A. REG. NO. 11491-7

LIQUID CARBONIC

Subsidiary of Houston Natural Gas Corporation

MB-84-2

CARBON DIOXIDE MARKETING BULLETIN

ACCEPTED
JUL 31 1995
Under the Federal Insecticide, Fungicide, and Rodenticide Act, as amended, for the pesticide registered under EPA Reg. No. 7/491-7

CO_2 GRAIN FUMIGATION MARKETING PROGRAM

INTRODUCTION AND HISTORY

The use of modified or controlled atmospheres is an adaptation of the ancient practice of hermetic storage. Hermetic storage involves sealing up grain, beans or oilseeds, generally in underground pits, and allowing the respiration of the commodity plus that of any insects present to deplete the oxygen to a level that will asphyxiate the insects. The reduced amount of oxygen in the atmosphere of a hermetically sealed storage also protects the commodity from fungal attack and thus the condition tends to maintain higher quality over extended storage periods. Hermetic storage, in pre-industrial times, was probably the only means of keeping large quantities of grain free from insect attack for significant lengths of time in areas with mild winters.

Hermetic storage was used on a large scale in Argentina during and immediately after World War II when facilities for storage of over 2.5 million tons of grain were constructed and utilized. Today there are reported active but primitive hermetic storages in operation in India, and underground storages are still in use in Yemen, Somalia, Sudan and Egypt. Modern concrete hermetic storage bins have been built in Cyprus and Kenya for corn storage and are primarily for protection against famine.

Obviously, the potential of hermetic storage is a viable one, as it eliminates the need for the use of grain protectants and fumigants and also assists in maintaining product quality over extended storage periods. It also could be of value when large crops and carryover produce a grain surplus. However, it is not a reasonable alternative for the majority of the current and projected storage needs in the U.S. In most instances, before this method could be implemented, the construction of new storage facilities as the alteration of existing facilities would be required.

The use of modified atmospheres offers a more practical method of stored product insect control. It will control insect pests much quicker than hermetic storage and does not leave chemical residue as do conventional fumigants and protectants. It usually does not require extensive modification of existing storage facilities although some sealing will usually be needed. The method simply involves changing the existing atmosphere in the storage structure by purging with CO_2 which is lethal to insects.

CO_2 ATMOSPHERES - LABORATORY STUDIES

A considerable amount of literature is available on the use of modified atmospheres for insect control. Dr. Ed Jay, Research Entomologist, Stored-Product, Insects Research and Development Laboratory U.S.D.A., has done extensive work in this area over the past fifteen (15) years. Many of these studies involved only one life stage, usually the adult, of one or a few species. Keep in mind, the adult is generally the easiest life stage to kill. Also, many researches have used mixtures of CO_2, oxygen (O_2) and N_2. From this data (refer to Table I), we can see that increasing the N_2 concentration from 97 to 100% greatly increases mortality as does increasing the CO_2 concentration from 37 to 60%. However, increasing the CO_2 concentration to 99% produced less mortality than that obtained at 60%. Laboratory studies such as this suggest that CO_2 is more effective than N_2 and there is probably no need to increase the CO_2 concentration above 60% when purging. Also, the table indicates longer exposures may be required to obtain complete control of this species.

TABLE I -- (Mean number of adult insects emerging from wheat infested with 1-5 week old immatures and exposed for 1-4 days to indicated atmosphere at 80°F.)

Atmosphere 1	Mean Emergence
Air (control)	70.7
97% N_2	51.6
99% N_2	36.0
100% N_2	33.3
37% CO_2	30.5
46% CO_2	17.1
99% CO_2	14.5
60% CO_2	9.7

In the U.S., research has been directed toward the use of CO_2 for stored product insect control. The following are some obvious advantages:

(a) Lower costs

(b) Less stringent sealing requirements

(c) Faster insect mortality

(d) Less influence on performance caused by slight fluctuations in concentrates

TEMPERATURE AFFECTS CO_2 CONTROL

The effect of temperature on the length of time necessary to obtain good control with CO_2 is as important as it is with any conventional fumigants. Temperature of the grain should be above 70°F during the treatment with CO_2. What happens at lower temperatures can be seen in Table II. Here it can be seen that it takes between 3-6 days for the 60% CO_2 atmosphere to give complete kill and that the cold air is no longer as effective in reducing emergence.

TABLE II -- (Percent reduction in emergence when immature rice weevils were exposed to CO_2 at two different temperatures for 8 days.)

Atmosphere	% Reduction in Emergence (35°F)			
	1 Day	3 Days	6 Days	8 Days
98% CO_2	99.8%	100.0%	100.0%	100.0%
60% CO_2	95.6%	94.4%	98.8%	98.8%
	(60°F)			
98% CO_2	97.4%	97.2%	99.6%	99.9%
60% CO_2	80.5%	99.0%	100.0%	100.0%

FIELD STUDIES AND TESTS

Except for laboratory studies, little interest was shown in the technique of using CO_2 atmospheres in grain storage until 1970. It was then USDA researches attained and maintained a 35% CO_2 concentration for 2, 4 and 7 day periods in an upright concrete silo containing 68,000 bushels of in-shell peanuts at Columbus, GA. This lack of interest was undoubtedly due to the success of conventional fumigants and grain protectants. Later in 1973, researches successfully controlled a natural infestation of the rice weevil and the grain moth in 28,000 bushels of corn in an upright concrete silo at the terminal elevators in North Charleston, SC. In this test, a CO_2 concentration of about 60% was successfully attained for a 96-hour period. The success of this test is shown in Table III, where more than a 99.9% reduction of all species of insects was obtained. This Table shows that over 99% reduction in damaged kernels was also observed in the test.

TABLE III -- (Average number of insects per sample and damage to 28,000 bu. of corn treated with 60% CO_2 atmosphere at the terminal elevator in North Charleston, SC. Samples collected before and after a 4-day treatment of the corn with CO_2.)

Sample Examined	No. Insects		% Damage	
	Before Treatment	After Treatment	Before Treatment	After Treatment
Initially	1	1	1.3	0.7
1 month	25	1	2.5	0.2
2 months	204	1	16.3	0.6

AUSTRALIAN STUDIES

Australian researches began large scale field tests with CO_2 in 1976. In the first test, gaseous CO_2 was released at 3 points into the base of a welded metal bin containing 7000 tons of wheat. The pressure of the CO_2 eventually pushed the existing atmosphere out of the top of the bin. Since 1976 Australian researches have conducted several additional studies on large grain storage facilities including sealing and treating a 16,000 ton flat storage with CO_2. Also, they have studied sealing extensively as CO_2 costs are much higher in Australia than in the United States.

Currently in Australia, all ten (10) terminal elevators in the State of Victoria have been sealed and modified for the use of CO_2. In western Australia, the Co-Operative Bulk Handling, LTD plans to have, in the near future, 25 horizontal grain storage units with an average of 25,000 ton capacity sealed for CO_2 as well as many of their vertical steel and concrete storages.

U. S. STUDIES

Interest in using CO_2 to protect grain against insect infestation has increased in the U.S. but not to the extent it has in Australia. Several large CO_2 producers, including Liquid Carbonic, has applied to the EPA for labels for CO_2 and Airco has already obtained one. The USDA has recently cooperated in pilot tests with us (LCC) and Airco in treating grain storage facilities with CO_2 ranging from terminal elevators to on-farm storage.

The publication written by Dr. Jay (1980) gives details on the actual techniques involved in using CO_2 in upright concrete silos and describes field tests using these application methods. Three methods are discussed for purging the atmosphere of a silo with CO_2:

(1) Applying the CO_2 into the top of a full bin -
(2) Applying CO_2 into the bottom of a full bin -
(3) Adding the CO_2 into the grain stream as the silo is filled.

Recently, a test was conducted at a large Texas terminal elevator in an upright concrete silo containing approximately 40,000 bushels of wheat. Carbon dioxide was supplied on site from a 6 ton vessel equipped with vaporizers. Infested wheat was used in the test and a 96 hour treatment produced a 100 percent reduction in emergence when samples were examined after 7 days. At 30 and 60 days after treatment, the percent reduction decreased to 99.5 and 95.4. However, insects that emerged after treatment were not able to reproduce.

Studies have also been conducted on a natural infestation in wheat stored in two Harvestore bins on a farm in South Carolina. One bin had a capacity of 14,000 bushels and the other 6,000 bushels. The wheat was heavily infested with several species and life stages of stored product insects including the granary weevil and various grain beetles. Carbon dioxide concentrations of 62-80% were maintained for 120 hours in these bins. Insect control ranged from 95.3% in the top of the 14,000 bushel bin to 99.9% in the bottom of the bin, while a 99.9% control was observed in all grain samples taken from the 6,000 bushel bin. Temperatures of the grain ranged from 82-92°F.

ECONOMICS

The economics of using CO_2 versus other fumigants has been monitored but not adequately investigated. Several factors enter into the cost of CO_2 treatments. Next to labor, which is variable, the most important factor is the cost of the CO_2. Another factor is, of course, the method to which it is applied. For example, reports and testing have indicated that recirculation of CO_2 may be necessary. This is to prevent persistent regions of low CO_2 which may form, and also eliminate concentration differential in the storage area. Taking this into consideration, we know that using CO_2 is very competitive with conventional fumigants. Continental Grain in Texas has run cost comparisons and results showed that the cost for liquid fumigant (methyl bromide) was 0.7¢/bushel and 0.76¢/bushel for CO_2.

16 of 24

Safe Replacement For EDB

It's as effective as chemical[illegible] and costs about the same

ZAHRADNIK

NEW [illegible] 1984

[illegible]h di[illegible] harmless gas that [illegible] to soft drinks, is being [illegible] dangerous chemicals [illegible] ethylene dibromide to co[illegible] ts in hundreds of thousands [illegible] stored grain around the world. [illegible] government scientist wh[illegible] essfully used [illegible] to pr[illegible] against hordes of hungry [illegible] the [illegible] South for 18 years. [illegible] our climate could [illegible] st about anywhere. We have [illegible] ul natural pest population," says [illegible] Jay, a research entomologist [illegible] USDA's Stored Product Insects [illegible] atory in Savannah, Ga.

[illegible] fact, several large-scale grain stor[illegible] and handling firms using carbon [illegible] de (CO_2) for pest control are [illegible] d in the deep South, where intense [illegible] her heat and humidity and mild [illegible] ers combine to create some of the [illegible] try's most challenging pest con[illegible] conditions.

[illegible] EDB is one headache we don't have," [illegible] Eves J. Menard, assistant man[illegible] of the Riviana Foods plant in [illegible] eville, La. The firm's 30 concrete [illegible] n storage silos, each 100 feet high [illegible] fitted with hoses and valves tha[illegible] from a central CO_2 storage tan[illegible] insect can survive when the atmo[illegible] ere within the silo hits 60 percen[illegible]," says Menard.

"It works without a doubt," says [illegible] uck Knutson, terminal manager for Continental Grain Company's [illegible] eat and soybean export facility [illegible] Beau[illegible] Knutson says Conti[illegible] nental's [illegible] of its 44,000-bushe[illegible] under CO_2 [illegible] this summer.

"C[illegible] costs have been com[illegible] parable [illegible] chemical costs in our [illegible]s," adds Knutson. Costs for chemical fumi[illegible] gation and CO_2 treatment fall in the .7 [illegible] 1 cent per bushel range, according [illegible] grain storage industry studies.

On the other side of the world, Aus[illegible] tralia has made a major commitment to using CO_2 instead of chemical insec[illegible] ticides. More than one-eighth of that nation's total grain storage [illegible] tons of grain — is now protected by the odorless, tasteless gas, says John Banks, an entomologist with Australia's Commonwealth Scientific and Industrial Research Organization.

"We're trying to get away from using chemicals," says Banks. "That's one reason why modified atmosphere (CO_2) storage has increased here." Commercial-scale testing of CO_2 for pest control began in Australia in the early '70s. The method "really took off" in 1979, says Banks. Australia has what may be the world's largest grain storage facility to be protected by CO_2, the 330,000-ton-capacity Cooperative Bulk Handling Ltd. plant in Perth. Firms in Israel, France, and Italy also use CO_2 to protect stored grain, says Jay.

But CO_2 is becoming practical for farm-scale grain storage, too. "I'd like to see it used more often. It sure beats that EDB," says H.H. LeMaster, who grows several different types of grains and soybeans on 750 acres near [illegible]ney, S.C. Last year LeMaster worked with USDA to store wheat in [illegible]000-bushel silos with only CO_2 to protect the harvest from the bugs. "We stored that wheat all winter with just one [illegible] application and it looked beautiful when it came out."

CO_2 Protects Fruit

While EDB is no longer approv[illegible] for grain fumigation, it's still being used to fumigate citrus for import or expo[illegible] EDB levels [illegible]0 times higher than the government safety standards of 30 par[illegible] per billion have been detected in [illegible] rus fruit pulp, Food and Drug Admini[illegible] tration tests revealed. USDA is in the midst of a feverish search for alterna[illegible] tives and, at the special request of Congress, recently completed a report on alternatives to EDB.

Carbon dioxide fumigation may pro[illegible] vide an answer. "Although CO_2 is slower acting than conventional fumigants, [illegible] could have practical application (on fruit)," says Clarence Benschoter, a researcher with USDA's Subtropical Horticulture Research Unit in Miami, Fla. Extensive testing in Miami proved that CO_2 can kill 95 percent to 100 percent of citrus pests in 48 hours of exposure.

In another development, Edwin L. Soderstrom and David G. Brandl, researchers with USDA's Agricultur[illegible] Research Service in Fresno, Calif., have found CO_2 an effective alternative to chemicals in a variety of fruit storage and quarantine situations. The re[illegible] searchers successfully controlled insect pests in stored raisins with CO_2 and will continue their work on other fruit[illegible]

Current costs per ton for storing and treating for insects are: CO_2, 18.[illegible]; methyl bromide, \$7.61; and aluminum phosphide (phosphine), \$9.77.

Carbon dioxide protects hard wheat and soybeans stored at Continental Grain Co., Beaumont, Texas. "It works without a doubt," says Chuck Knutson, terminal manager. Each concrete silo holds 44,000 bushels of grain.

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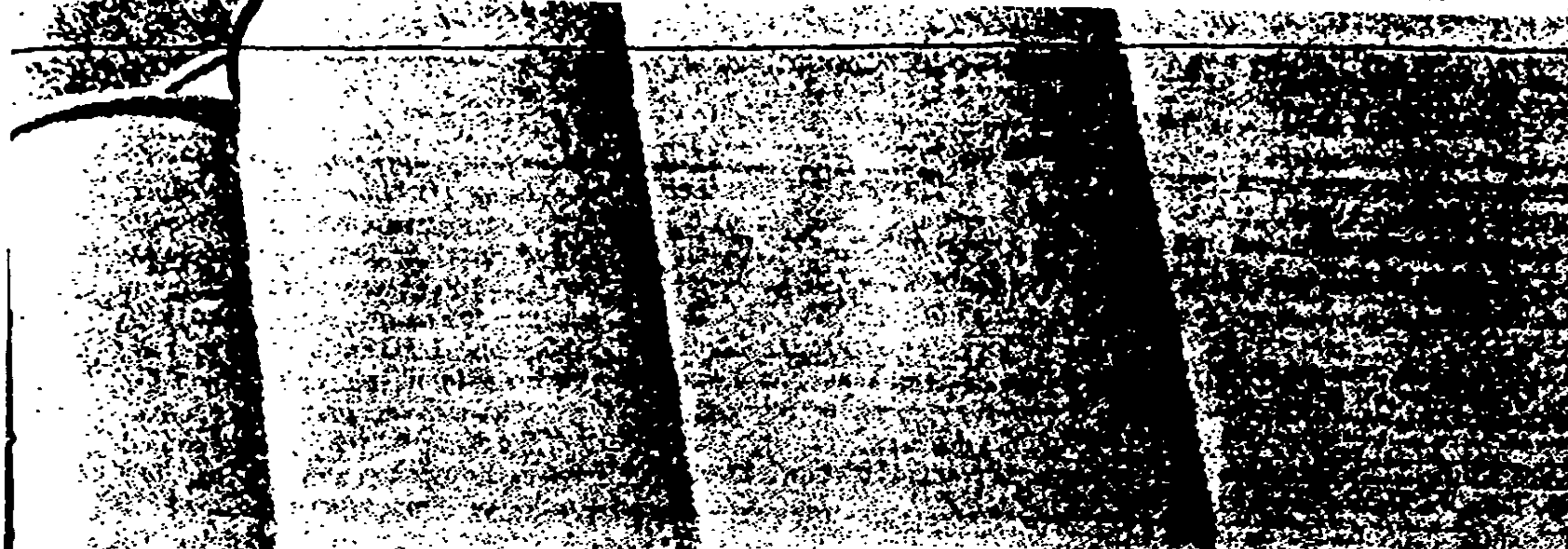

More than 20 million pounds of EDB were used annually for pest control in the United States before the chemical was banned for grain and soil fumigation purposes. The grain storage and handling industry relied on EDB as an inexpensive, fast and effective fumigant since it was approved for use as a pesticide in 1948. The chemical was also valued because its residue lingered on machinery and in silos for a lasting pest-killing effect.

Unfortunately, it also lingered all the way into consumer food products.

EDB is "bad stuff . . . a very potent carcinogen, but we don't have any evidence that it has harmed anyone, nor do we have any that it hasn't," says William Ruckelshaus, administrator of the U.S. Environmental Protection Agency.

EDB was found in foods sold by Duncan Hines, Pillsbury, General Mills, Quaker, Nabisco, Procter & Gamble, Frito Lay, and even Fearn Natural Foods. Nationwide, more than one-third of the off-the-shelf, grain-based food products tested so far contain detectable amounts of EDB, government tests show. Only a small percentage of these foods violate the federal guidelines of 900 parts per billion for raw grains, 150 parts per billion for foods requiring further preparation, and 30 parts per billion for ready-to-eat food.

States are free to set their own guidelines and the health departments of Massachusetts, New York, New Jersey, Maine, Connecticut, New Hampshire, and Vermont have set stricter standards, citing not only the cancer risk of EDB, but evidence linking low levels of EDB to reproductive disorders.

The federal guidelines "are deficient in adequately protecting the public from the mutagenic, carcinogenic, and reproductive consequences of both the short- and long-term effects of this pesticide," says Dr. David Axelrod, New York state health commissioner.

Other Chemicals Dangerous

But federal and state health officials may not have heard the last of chemicals in food. Many food processors are turning to the chemicals methyl bromide and aluminum phosph[illegible] that EDB is banned, says [illegible]rd Johnson, leader of the EPA EDB review team. "We have evidence that residues of aluminum phosphide have been detected in fruit shipped from Florida to California," says Johnson. The review team also received a study linking methyl bromide with cancer in laboratory test animals.

Could CO_2 completely replace these chemicals? Some authorities doubt it. "CO_2 is an alternative with limitations," says Arvid Hawk, who is in charge of grain storage and handling for the [illegible] Grain Co., Minneapolis, Minn. "Right now it would be impractical to use carbon dioxide as a fumigant for grain handling and milling machinery," he says. A nearly airtight seal is needed to make CO_2 effective, Hawk explains, and this would be difficult to achieve around the machines.

This need for near airtightness where CO_2 is applied is a limitation for farm storage, too. "With a typical bolted steel farm storage bin, it would take a good bit of retrofitting and sealing, which may or may not be cost-effective in the long run," says Hawk.

Some companies such as American Rice Industries, a Houston-based co-op serving South Texas, abandoned chemicals several years ago in favor of CO_2. The move was made mostly for safety reasons, says Preston Hill, American Rice's sanitation and building manager.

"Carbon dioxide is safer than methyl bromide because it doesn't leave any residue," Hill says. "It's safer during application, too. We don't have to shut down part of the plant. That's good for us and the workers."

If CO_2 is so safe for workers, then how does it kill food pests? When the atmosphere within a silo reaches 60 percent CO_2, explains USDA's Edward Jay, the lack of oxygen causes insects to consume their own body moisture and die. A high-CO_2 atmosphere also inhibits the growth of mold and fungus.

Other advantages of CO_2 include:

- Less complicated application equipment since the gas is safer than chemical pesticides, says Hill.
- Being heavier than air, CO_2 displaces normal atmosphere quickly, whether applied from top or bottom of a silo.
- No hold time or mandatory aeration period as with chemicals. "We can use the grain anytime," says Eyes J. Menard of Riviana Foods.
- Little chance of insect resistance developing. "The high-CO_2 atmosphere disrupts basic life functions of the insects," says Jay.

Although CO_2 occurs naturally in the atmosphere, industrial gas firms don't separate the carbon dioxide out of normal air, says Kevin [illegible], a spokesman for [illegible] Industrial Gases, Murray Hill, N.J. Carbon dioxide is recovered [illegible]

Methods of Applying Carbon Dioxide for Insect Control in Stored Grain

By Edward Jay[1]

ABSTRACT

Three methods of applying carbon dioxide to grain stored in siloe are described. One method involves purging a full silo from the top, another involves purging a full silo from the bottom, and the third involves introducing carbon dioxide in the grain stream as a silo is being filled. Comparative purge times, carbon dioxide requirements, and costs are given. Modification of storage-facility atmospheres is a promising method to achieve residue-free insect control, and the merits of using carbon dioxide and nitrogen for this purpose are compared. Index terms: carbon dioxide, insect control, modified atmospheres, nitrogen, stored-product insects.

INTRODUCTION

Since the publication by Jay (1971) on using carbon dioxide (CO_2) to control stored-grain insects, considerable interest has developed worldwide on the use of this technique and on the use of nitrogen (N_2) and on combinations of atmospheric gases to achieve control. This interest has been generated because of the increasing worldwide problem of insect resistance to conventional insecticides and fumigants and also because of the residues associated with the use of these materials. Jay and Pearman (1973) showed that a 4-day CO_2 treatment of shelled corn having a natural infestation of stored-grain insects gave almost 100% control. Shejbal et al. (1973) showed that similar control could be obtained by using N_2, but the time needed to obtain control was 10 days. Banks and Annis (1977) conducted trials with N_2 in commercial, upright, welded-steel silos. Lethal atmospheres were attained and maintained in these silos for periods up to 30 days.

Both CO_2 and N_2 have merit in a residue-free insect-control program. Nitrogen has the advantage of filling 78% of the interstitial spaces initially. However, atmospheric oxygen (O_2) in these interstitial spaces must be reduced to less than 1% to obtain effective insect control, a situation difficult to achieve and maintain in storage facilities that are not gastight. Therefore, CO_2 is considered by the author to be more efficient than N_2 in situations where tight sealing is physically impossible or where it is not economically feasible to seal the storage structure to rigid gastight specifications. A CO_2 concentration of about 60% will give over 95% control of most stored-grain insects after a 4-day exposure at temperatures of 27° C or higher (Jay 1971), and the CO_2 concentration can fluctuate ±10% and still provide effective control. The low-oxygen N_2 atmosphere, on the other hand, must be held for 10 or more days at 27° C or above to be effective against life stages of stored-grain pests. Even so, Shejbal et al. (1973) reported that control of insect eggs was not obtained in a 10-day exposure to 0.5% O_2 and 99.5% N_2. Unpublished laboratory

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as a byproduct of some other industrial processes, such as natural gas processing, ammonia production, or ethanol fermentation, he says.

Carbon dioxide is also being tested for use in rail hopper cars, truck-ship type containers, barges, and oceangoing ships.

Instead Of Irradiation

Carbon dioxide also compares favorably with the irradiation of food, an alternative pest control proposed by the Food and Drug Administration and Margaret M. Heckler, federal Health and Human Services secretary. Irradiation involves exposing food to gamma rays from radioactive isotopes. The FDA would allow irradiation doses of up to 100 kilorads to kill insects in fruits, vegetables, and stored grains. But as USDA has stated, "There are some questions regarding consumer acceptance of irradiated food products."

Besides the possible dangers of irradiation and problems of public acceptance, the method is too costly and complex for farm use, says Bill McGaughey, of the U.S. Grain Marketing Research Center, Manhattan, Kan. That's a serious drawback, since 60 percent of the nation's grain is stored on farms. "Could you imagine a farmer discovering a serious pest problem in his grain, then hauling the whole load up to Chicago for pre-sale irradiation treatment?" asks McGaughey.

The use of low-oxygen, tightly sealed grain storage dates back to the ancient Egyptians. The first large-scale tests on CO_2 storage were conducted in underground pits near Paris from 1819-1830, adds USDA's Jay. So why have chemical fumigants, rather than CO_2, emerged as the dominant pest control?

"The chemicals have been promoted within the industry for years," says Jay. "A lot of momentum developed. If you're using a product for years, it's familiar, it works, it's inexpensive, you stay with it. Maybe CO_2 hasn't had the same push because nobody can patent it and make it their own." □

Pests 1, Farmers 99

HEREFORD, Texas—Arrowhead Mills stores, processes, packages and sells more than 2 million pounds of wheat, other grains and beans each year. When the Texas Department of Agriculture swept through the state's supermarkets and pulled hundreds of grain products from the shelves for sampling earlier this year, one-third of the products contained detectable levels of EDB residue. Arrowhead Mills' products were tested, too, but all 39 samples were found to be residue-free. That's because Arrowhead Mills doesn't use EDB or other harsh fumigants. Preventive measures and rapid turnover are the mainstays of the company's pest control program, which begins at the farm.

"We know personally each farmer who supplies us," says Boyd Foster, president of Arrowhead Mills. Buying grain directly from organic farmers in the region assures Arrowhead Mills that their grain is fresh, and didn't spend time in a line elevator, where it might have been fumigated or mixed with fumigated grain.

When grain reaches Arrowhead Mills, it's cleaned and screened to remove pieces of vegetative matter, which can harbor insect eggs. Next, grain is placed into one of 100 cylindrical metal bins, each of which holds 4,000 bushels and stands 50 feet high. Fans circulate air through the bins, drying grain down to 10 percent moisture, and keeping the grain cool. Air is circulated in the evening to take advantage of cooler temperatures.

"The bugs like a damp, warm and dirty environment, so we keep things dry, cool and clean," says Foster.

One full-time worker observes and samples all stored grains and grain products to detect insect or mold infestations before a serious problem develops. Foster estimates that less than 1 percent of the grain is lost to pests. Any infested grain is immediately removed from the property and sold to nearby farmers for livestock feed, says Foster.

Arrowhead Mills uses carbon dioxide, too, not as fumigant, but to preserve grain that is sold in five-gallon, sealed buckets for long-term storage.

Foster says the firm's relatively small size and "know-the-farmer" philosophy allows for the type of vigilance and spot treating with natural pesticides necessary to maintain the prevention program. (For a free catalog of Arrowhead Mills' products, write: Arrowhead Mills, P.O. Box 2059RA, Hereford, Texas, 79045.)

Natural Pesticides For Grain Storage

Diatomaceous earth—Talc-like powder mined from the earth kills insects on contact. DE's microscopic needles of silica pierce insect exoskeletons, causing dehydration and death. Yet, DE is harmless to other forms of life. Mixed with stored grain, DE is a very effective insect control, according to field-scale tests by USDA's Grain Marketing Research Service. In a three-year study, DE provided protection equal to malathion. DE is also used commercially by the 3,000-acre Lundberg farm, Richvale, Calif. "We've mixed it into storage with the rice, and we've used it under the bins," says Gordon Brewster, farm manager. DE is blown or washed out of rice after storage, he says.

Bacillus thuringiensis—B.t. is an insecticide made of living bacteria which paralyze the gut of crop-destroying worms. Harmful only to insects, B.t. is exempt from tolerance restrictions. B.t. infects and kills larvae of Lepidopteran order pests, such as the Indian meal moth and the almond moth. B.t. also controls moths that are resistant to chemical pesticides.

Pheromones—Useful for trapping and monitoring stored food product pests. More research in this field may lead to pheromone controls.

Cold treatment—Storing fruit at 34 degrees F kills Caribbean fruit flies and other citrus pests that have been targets of EDB fumigation, USDA says. Cold treatment takes at least 26 days, making this method costly.

—FRED ZAHRADNIK

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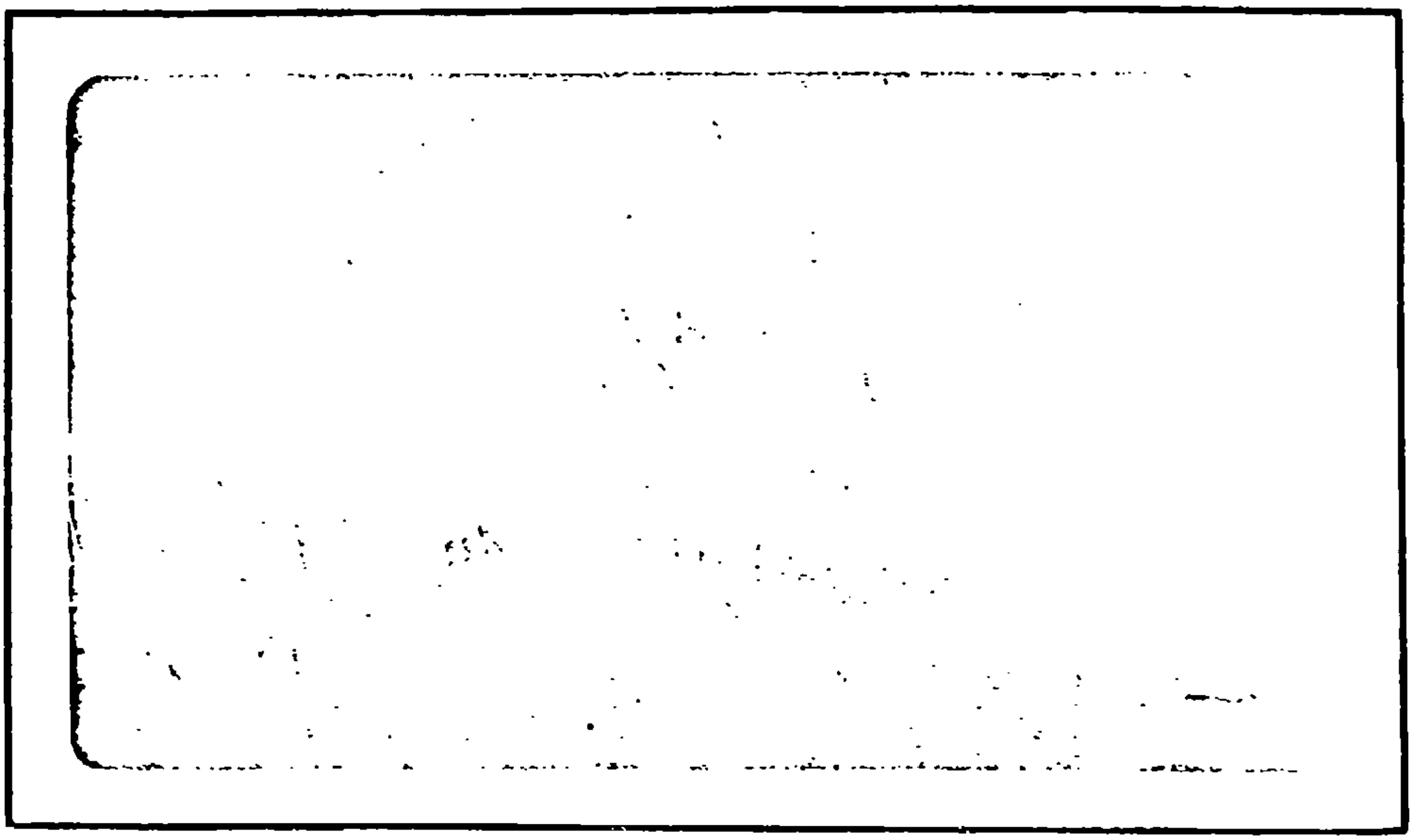
Methods of Applying Carbon Dioxide for Insect Control in Stored Grain



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Science and Education Administration
Advances in Agricultural Technology • AAT-S-13/April 1980

red flour beetle, *Tribolium castaneum* (Herbst), do not hatch in atmospheres above 20% CO_2 when the O_2 level is as high as about 19%. Similarly, AliNiazee and Lindgren (1970) reported that the percentage of egg hatch of *T. castaneum* and *T. confusum* Jacquelin duVal was inhibited partially or completely delayed in CO_2 atmospheres, while in similar N_2 atmospheres there was about the same percentage of egg hatch as there was in those eggs exposed to air. The author (unpublished laboratory studies) found that a concentration of about 62% CO_2 and 9% O_2 gave over 90% control of 0- to 25-hour-old eggs of the cowpea weevil, *Callosobruchus maculatus* (F.), in 2 days' exposure, while concentrations of 99.2% N_2 (balance O_2) took 3 days to produce the same results. One-week-old insects of the same species were controlled (90% or more mortality) in 2 days in the atmosphere containing 62% CO_2, while concentrations of 99.7% N_2 (balance O_2) took more than 3 days to give the same control.

In summary, CO_2 generally kills insects faster than N_2. It can be used in situations where leakiness may be a problem, and the concentration of 60% CO_2 can be allowed to fluctuate ±10% (or more, down to a low of 35%) leading to good control. (However, lower overall concentrations will necessitate longer exposure times.) In addition, sorption of CO_2 by grain or oilseeds may make it more effective against species whose immature stages feed inside the kernel. On the other hand, CO_2 is 1½ times as heavy as air and will sink from the top to the bottom of the treated storage facility unless it is tightly sealed. This sinking necessitates either adding CO_2 into the headspace periodically or recirculating the CO_2. (See Jay et al., 1970, for a description of this method. The method should be modified so that the recirculation fan is placed outside the storage facility to eliminate explosion hazard.)

If the above advantages and disadvantages of using CO_2 have been taken into consideration and there still remains a question of whether to use CO_2 or N_2, then economic factors enter into the decision. The comparative cost of the two treatments will depend on the availability of the gases, their unit cost (a unit is a ton, pound, cubic foot, cubic meter, etc.), the number of units required for effective insect control, the amount of grain to be treated per year (as the volume of gas used increases, unit costs will be reduced), of vaporization equipment and storage containers (if equipment is purchased, can it be depreciated annually?).

The above advantages, disadvantages, and economic considerations obviously involve a decisionmaking process for which a flow chart is presented in figure 1.

This paper presents three methods of applying CO_2 to stored grain. The information presented by Jay (1971) on suggested conditions for using CO_2 should be consulted in conjunction with the material presented here. If a decision is made to use N_2 instead, Banks and Annis (1977) should be studied. However, some techniques described for CO_2 could be used for N_2 with slight modifications. Another method of creating modified atmospheres, the burning of air to reduce its oxygen content, is not considered.

METHODS OF APPLYING CO_2

Since the publication by Jay (1971) became available, the author has conducted several additional field tests. One of these was described by Jay and Pearman (1973) and is summarized here (method 1) for comparative purposes with other application methods. The three methods described attain and maintain a concentration of about 60% CO_2. The tests were conducted in 1,038-m^3 (36,644-ft^3) upright concrete silos measuring 24.7 m (81 ft), excluding depth of discharge chute, by 7.3 m (24 ft). The silos each contained about 711 metric tons (28,000 bu) of shelled corn (maize) having an 11% to 16% moisture content. (In some tests the corn was moved into a silo as the CO_2 was being applied.) The equipment used in all tests for applying the CO_2, including supply tank, vaporizers, and regulators for monitoring and controlling the concentration after the desired concentration was reached, was similar to that described by Jay and Pearman (1973). Deviations will be described in the individual tests.

Method 1: Purge a Full Silo From the Top

This is essentially the method described by Jay and Pearman (1973) and will not be dealt with at length. It involves introduction of gaseous CO_2 into the headspace above the surface of the grain.

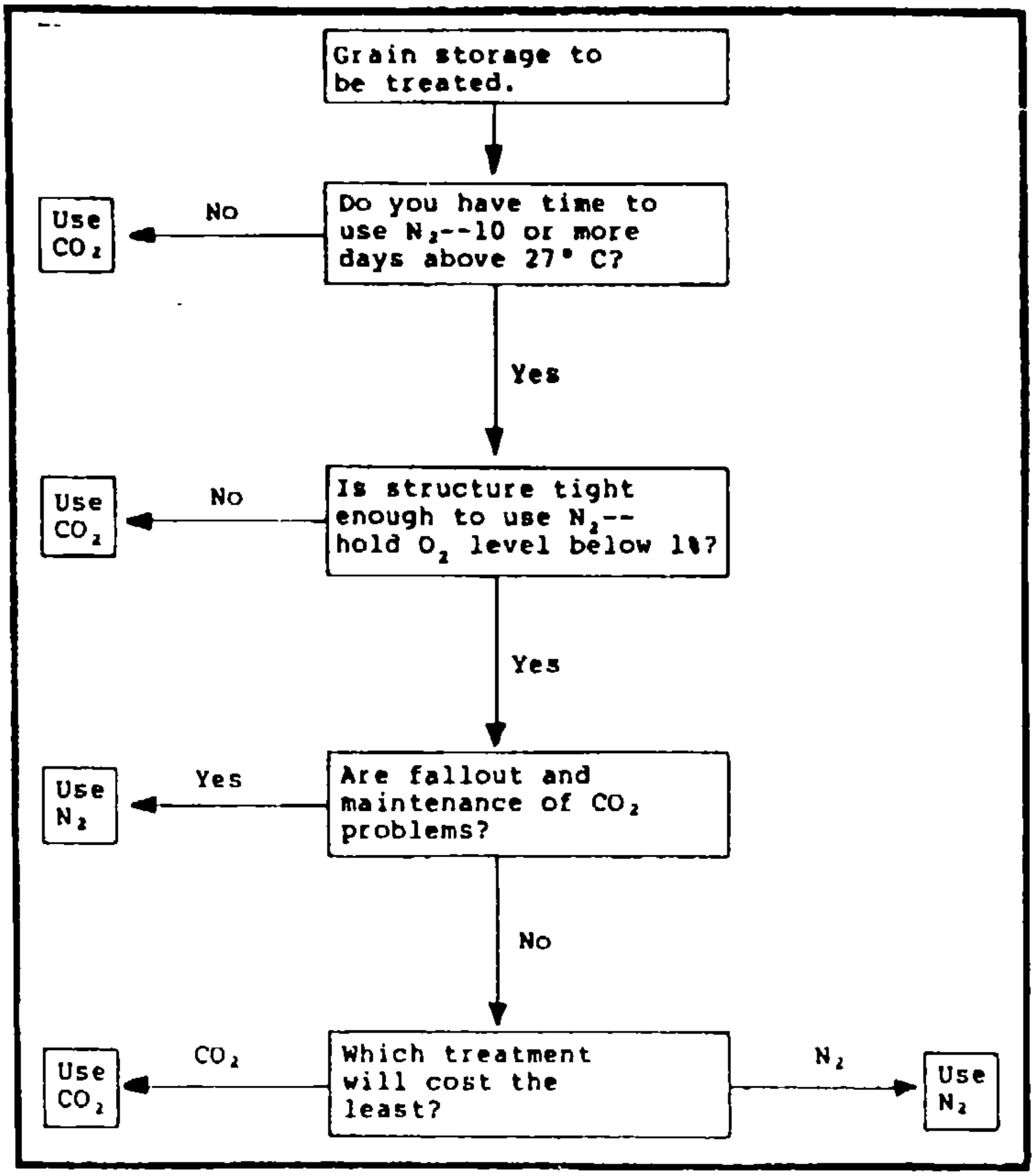

FIGURE 1.—Determining which modified atmosphere to use, CO_2 or N_2.

The CO_2 is forced down into the grain by positive pressure on the headspace of the storage facility. The CO_2 mixes with and displaces a portion of the existing atmosphere and creates a modified atmosphere lethal to any insects present. Its advantages are that it can be used where no other method is available, it requires only one application line, labor requirements are minimal, and costs may be lower than with the other methods. Its disadvantages are that CO_2 is lost in mixing and "blowback," purging time is longer than in method 3, and vaporization requirements are high.

METHOD 2: LIFT THE ATMOSPHERE OUT

In this test and in method 3, a set of air-sampling lines was placed into a silo through each of the two access openings in the flat top prior to filling. These lines differed from those which were probed into the corn in method 1. One of the two openings was about 1.2 m (4 ft) in from the wall, where the corn was discharged into the silo, and the other opening was about 1.2 m (4 ft) from the center of the top. Each set of sampling lines was made up of six 0.6-cm-i.d. (¼-inch)

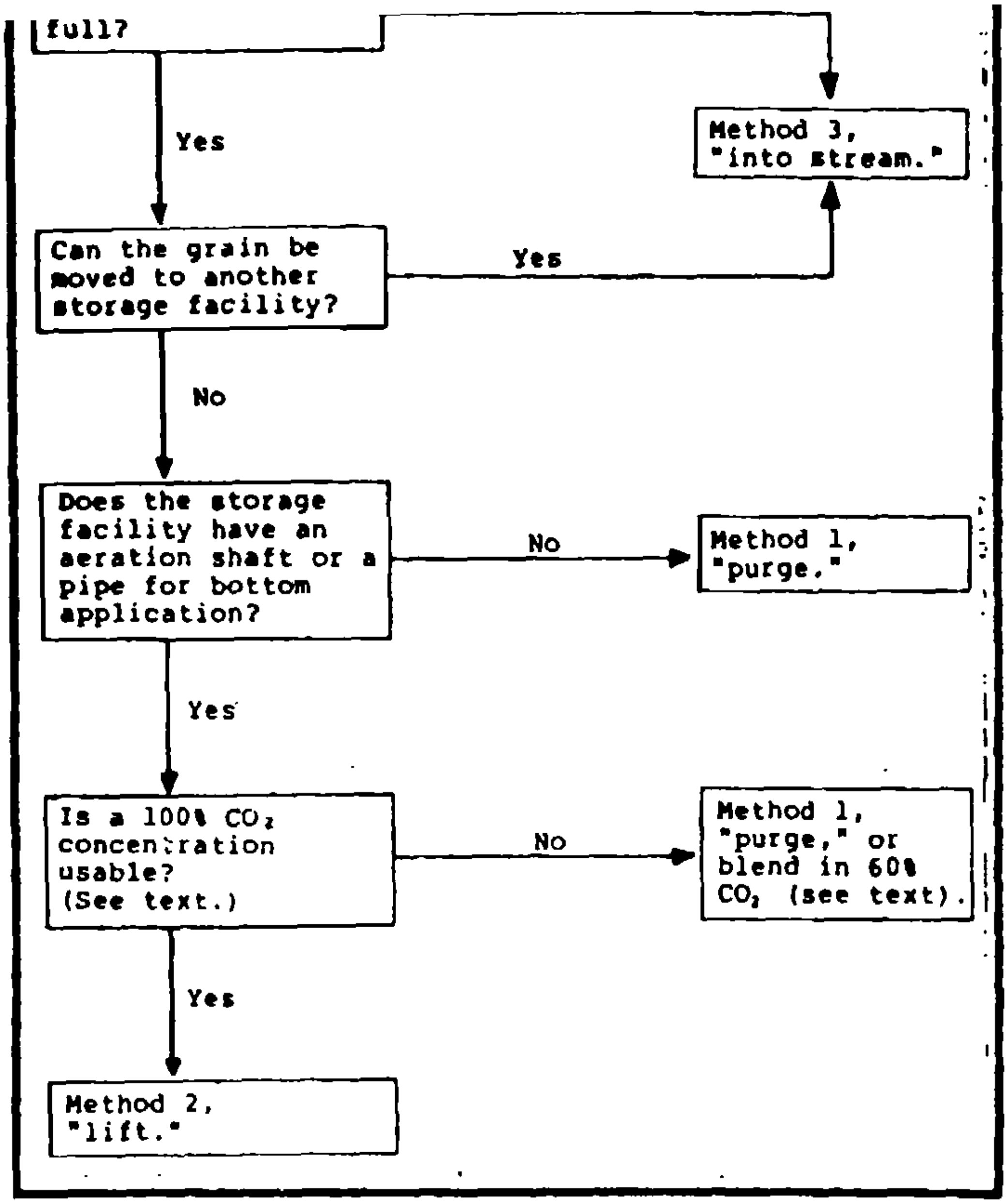

FIGURE 2.—Selecting a method for applying CO_2.

METHOD 3: APPLY CO_2 IN THE GRAIN STREAM

This test was conducted with liquid CO_2 from the same tank previously described. The CO_2 emerged from the equipment in a semisolid form called "snow" by the CO_2 industry. However, the snow soon sublimated and produced CO_2 gas. A CO_2 "horn" was attached to copper tubing (1.9-cm i.d., or ¾-inch), which was run from the liquid line on the CO_2 tank to the top of the silo. The tubing and horn were thoroughly grounded to prevent any sparks around the discharge area. Liquid CO_2 flow was started into an empty silo at the outer access opening, and in 10 min about 49.4 m^3 (200 lb) had been introduced. Corn flow was then started into the silo and continued, with two brief interruptions of 3 min each, until the silo was filled with about 711 metric tons (28,000 bu) of corn in 2.33 h. At this point about 642 m^3 (2,600 lb) of CO_2 had been introduced into the silo at a rate of 4.6 m^3/min (18.6 lb/min). Carbon dioxide application was continued an additional 0.5 h, except for a 10-min interruption. At this time an

Factors That Influence Insect Infestations

Regional Climates

Many insects that attack stored grain were originally from the tropics. They spread and adapted to colder climates by living in manmade food storage shelters. Because stored-grain insects cannot remain active at low temperatures, their potential for development and damage is much greater in the southern regions of the United States (see fig. 1) where warm temperatures permit them to reproduce and develop the year round. Infestation often starts in warm regions while the grain is still in the field and then is carried into storages with the harvested grain.

Harvest Conditions

Harvesting grain too wet not only provides an environment for insects to develop but quickly leads to invasion and development of storage fungi. Fungal spores can then be distributed further throughout the grain storage by migrating insects. During harvest, mechanical damage to grain also can affect development. Some stored grain pests cannot survive in whole grain; others will survive on unbroken kernels. Their development, however, is aided if broken kernels and dockage are present. Crops should be harvested as dry as possible, and the combine should be adjusted properly to eliminate chaff and as many weeds and weed seeds as possible while still holding cracked or unbroken kernels to a minimum.

Small residues of grain in conveyers, trucks, and harvesters are particularly susceptible to stored-grain insects and storage fungi, and under certain temperatures and moisture conditions will provide the necessary habitat for large populations to develop. Therefore, inspecting, removing, and treating these small grain residues before harvest is advisable to prevent contaminating newly harvested grain.

Grain Temperature and Moisture

Most insect pests of stored grain have a short period from egg to adult, their reproduction rate is high, and their adult lifespan is long. Two factors that influence these characteristics are temperature and moisture. Most stored-grain insects require temperatures of more than 60° F (15° C) to develop damaging populations, and many require temperatures of 70° F (21° C) or higher. Although some grain insects are more cold hardy than others, winter temperatures common in the grain-producing areas (except for the South) are generally lethal to many stored-grain insects when the low temperatures extend throughout the grain. Furthermore, temperatures not low enough to kill insects

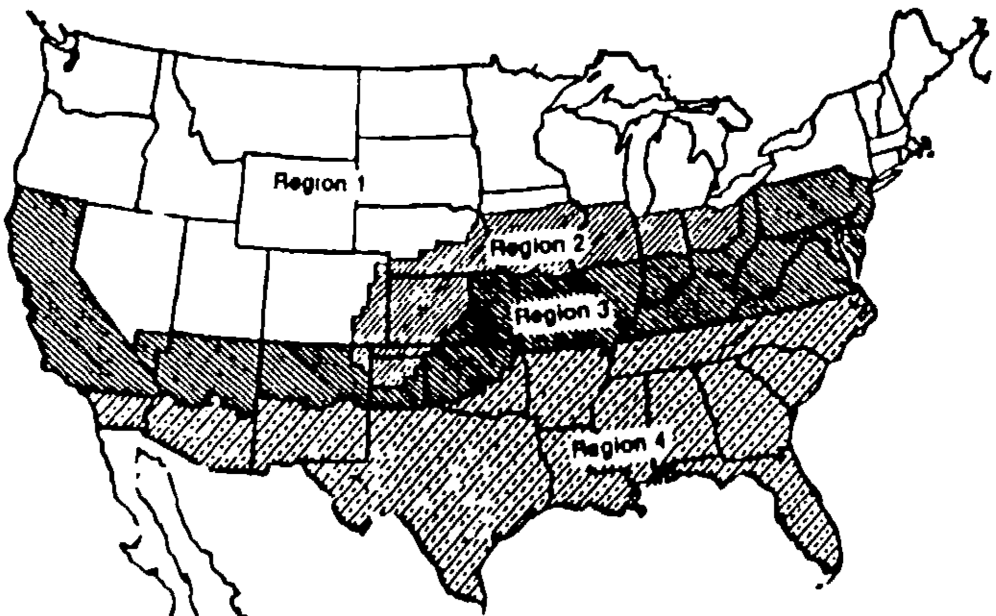

Figure 1—The map shows, by regions, the degree to which farm-stored grain in the United States is subject to insect attack: Region 1, little if any damage occurs to storage. Region 2, insects may be troublesome during the first season. Region 3, insects are troublesome every year. Region 4, insects are a serious problem throughout