

PM04 10330-20

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SEP 23 1998

Mr. Algirdas G. Vilkas, Manager
Safety & Environmental Services
Praxair, Inc.
39 Old Ridgebury Road
Danbury, CT 06810-5113

Subject: Carbon Dioxide
EPA Registration No.: 10330-20
Your Submission of August 21, 1998

We have reviewed the labeling which you submitted on August 21, 1998.

The container labeling is basically acceptable, but the changes listed below must be made before labels are printed and released for shipment.

1. In the "AERATION" paragraph on the first page of the label, change "commercially" to "commercially".
2. On the second page, center heading "DIRECTIONS FOR USE", as our letter of July 21, 1998, had instructed.
3. Make the list of pests claimed under the second paragraph of the "GENERAL USE RESTRICTIONS:" read exactly as shown below.

This product is effective against the following types of insects which may occur in stored products or in structures which may be fumigated with this product:

1. **Beetles**, including the granary weevil, rice weevil, broadnosed grain weevil, lesser grain borer, larger grain borer, confused flour beetle, red flour beetle, American black flour beetle, khapra beetle, warehouse beetle, longheaded flour beetle, slender-horned flour beetle, larger black flour beetle, yellow mealworm, dark mealworm, black carpet beetle, rusty grain beetle, flat grain

beetle, saw-toothed grain beetle, merchant grain beetle, foreign grain beetle, corn sap beetle, cigarette beetle, drugstore beetle, cowpea weevil, bean weevil, pea weevil, broadbean weevil, coffee bean weevil, and cadelle;

2. **Psocoptera**, including the book louse;

3. **Moths**, including the Angoumois grain moth, Indian meal moth, almond moth, raisin moth, tobacco moth, Mediterranean flour moth, meal moth, rice moth, navel orangeworm, webbing clothes moth, casemaking clothes moth, and carpet moth.

- 4. In the first sentence of the fourth paragraph of the "GENERAL USE RESTRICTIONS:", change "40 F" to "40°F".
- 5. In item "b)" in the "PLACARDING" subsection of the "DIRECTIONS FOR USE" (third page of label), change "DANGER/PERLIGRO" to "DANGER/PELIGRO".
- 6. In the second sentence of the second paragraph of "PLACARDING", change "restricted-area entry interval" to "restricted-entry interval".
- 7. Left-justify the heading for the "FUMIGATION DIRECTIONS:" subsection of the "DIRECTIONS FOR USE" and shift the numbered paragraphs captioned "Storage Bins:" and "Trucks and Trailer:" to the left so that their numbers are on the left margin.
- 8. Center the heading

SPECIAL DIRECTIONS FOR SHIPBOARD, IN-TRANSIT SHIP OR SHIPHOLD FUMIGATION

and center its subheading "**IMPORTANT**". Left justify the paragraphs in this and remaining section.

- 9. In the last sentence of item "1." under "PRE-FUMIGATION PROCEDURES", change "master of the vessels" to "master of the vessel".
- 10. Delete the comma after "Never" from the fifth (and next-to-last) sentence of the paragraph entitled "PRE-FUMIGATION PROCEDURES:".

The proposed "Technical Bulletin" No. "TB-98-1" is generally acceptable, but the minor changes listed below must be made to it. Our comments assume that the information presented in the bulletin is factual. It is your responsibility as a registrant to make sure that no statements in the labeling for this product are false or misleading in any particular.

- 1. The same code number "TB-98-1" must appear on every page as the label refers to the bulletin by use of this code number.

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2. In the table on page 3, change the entry for "98% CO₂" and "8 Days" from "100.02" to "100.0%".
3. In the second sentence of "Field Studies and Tests", change "researches" to "researchers". Make the same change in the fourth sentence of this paragraph.
4. In the first sentence of the first paragraph of "Australian Studies", change "researches" to "researchers". Make the same change in the fourth sentence of this paragraph.
5. In the second (and last) sentence of the second paragraph of "Australian Studies", change "25, 000-ton" to "25.000-ton" (delete space).
6. Change the second sentence of the first paragraph of "U.S. Studies" to read:

Several companies have secured registrations for CO₂ fumigant products in the U.S.
7. In the second sentence of the last paragraph of "U.S. Studies", change "other, 6,000 bushels" to "other 6.000 bushels" (delete the first comma).
8. In fifth sentence under "Economics", change "low CO₂ and provide" to "low CO₂ and to provide". Delete "highly" from the next sentence.

Submit one copy of each element of final printed labeling (the label and the technical bulletin) before releasing the product for shipment.

Sincerely yours,



William W. Jacobs, Ph. D.
Insecticide-Rodenticide Branch
Registration Division (7505C)

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CARBON DIOXIDE

CAS: 124-38-9

Active Ingredient: Carbon Dioxide 99.8%
Inert Ingredient : 0.2%

KEEP OUT OF REACH OF CHILDREN

WARNING

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

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 a physician immediately.

SEP 23 1998
Under the Federal Insecticide, Fungicide, and Rodenticide Act
Registration No. 10330-20

WARNING: May be fatal if inhaled. Do not breathe vapor. Can increase respiration and heart rate. May cause nervous system damage. May cause dizziness and drowsiness. For handling activities in enclosed areas during fumigation, use either a supplied-air respirator with MSHA/NIOSH approval number TC-19C or self-contained breathing apparatus (SCBA) with MSHA/NIOSH approval number TC13-F.

AERATION: After fumigation, aerate treated areas until level of CO₂, as measured by commercially available analyzers such as the Gow -Mac Model 20-600 or the Nova 420, is below 5000 ppm.

RE-ENTRY (Below 5000 ppm CO₂): If CO₂ levels are below 5000 ppm, persons may re-enter the treated area without respiratory protection.

RE-ENTRY (5000-30,000 ppm CO₂): If CO₂ levels are between 5000 and 30,000 ppm, persons may re-enter the treated area without respiratory protection for 15 minutes or less. For periods longer than 15 minutes, persons must wear the respiratory protection device specified above under WARNING.

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

The USDA has set a limit of 0.5% (5000 ppm) maximum CO₂ concentration in the work areas.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with the labeling.

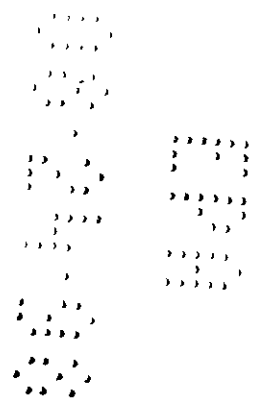
GENERAL USE RESTRICTIONS: This product is used to fumigate storages, trucks, trailers, sealed railroad cars and ships. The following may be treated - all raw and processed agricultural products such as: corn, including popcorn, barley, oats, rice, (milled and or enriched), sorghum, wheat, rye, and other 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, mammal skins, stuffed animals, herbarium, specimens, rare books and wood products such as carvings.

This product is effective against the following types of insects which may occur in stored products or in structures which may be fumigated with this product:

1. **Beetles**, including the granary weevil and rice weevil, broadnosed grain weevil, lesser grain borer, larger grain borer, confused flour beetle, red flour beetle, and American black flour beetle, khapra beetle and warehouse beetle, longheaded flour beetle slender-horned flour beetle, larger black flour beetle, yellow mealworm and dark mealworm, black carpet beetle, rusty grain beetle and flat grain beetle, saw toothed grain beetle and merchant grain beetle, foreign grain beetle, corn sap beetle, cigarette beetle, drugstore beetle, cowpea weevil, bean weevil, pea weevil and broadbean weevil coffee bean weevil and cadelle;
2. **Psocoptera**, including the book louse;
3. **Moths**, including the grain moth, Indian meal moth, almond moth and raisin moth, tobacco moth and Mediterranean flour moth, meal moth, rice moth navel orangeworm, webbing clothes moth, casemaking clothes moth, and carpet moth.

Dosages rates vary from 60% atmosphere to 100% atmosphere. Treatment times vary from 2 days to 4 days. See our Bulletin TB-98-1 for details on treatment specifics.

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 as 60% CO2 as possible.



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TRAINING: All persons working with this product should be knowledgeable of the hazards of this chemical, and trained in the use of the 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 the 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 the area being fumigated).

PLCARDING STATEMENTS: 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 least 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) The 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 points of entry to the treated area. They must remain posted during the application and throughout the restricted-area entry interval until the concentration of carbon dioxide is below 5000 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:

- 1. **Storage Bins:** Purge bin to 60% atmosphere. We recommend a two-day treatment for killing adult insects and a four-day treatment for killing all life stages. For specific flow rates to use, contact a qualified fumigation engineer.
- 2. **Trucks and Trailer:** Treat as indicated above for Storage Bins. Do not move trucks or trailers during treatment. They must be aerated before treatment is allowed.

SPECIAL DIRECTIONS FOR SHIPBOARD, IN-TRANSIT SHIP OR SHIPHOLD FUMIGATION

IMPORTANT

Shipboard, in-transit ship or shiphold fumigation is also governed by US Coast Guard Regulations. Refer to and comply with these regulations prior to fumigation.

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emergency conditions. If necessary to enter fumigated area, appropriate personnel protection equipment must be used. Never, enter fumigated area 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 the hold prior to discharge, test spaces directly above the 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 for the fumigant means a gas mask or respirator that is jointly approved by the Mining Enforcement and Safety Administration and the National Institute of Occupational Safety and Health. See text in "**WARNING:**" paragraph under "**HAZARDS TO HUMANS AND DOMESTIC ANIMALS**" on the front panel for the specific type of approved respiratory device to use.

STORAGE AND DISPOSAL

STORAGE: Do not contaminate water, food or feed by storage or disposal. Store in bulk CO₂ vessels which are permanent installations or in approved CO₂ cylinders.

Store cylinders under lock and key in a dry, cool, well-ventilated area. Post the area 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 as dropping, bumping, dragging or slicing.

Do not use rope slings, hooks, tongs, or similar-devices to unload cylinders. Transport cylinders using hand truck or fork lift truck to which the cylinders 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 PROCEDURES:

Evacuate immediate area of leak. Use respiratory device for entry into affected area to correct problem. See **WARNING:** paragraph under **HAZARDS TO HUMANS AND DOMESTIC ANIMALS** on the front panel for the specific type of approved respiratory device to use.

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LEAKING OR DAMAGED CYLINDERS:

Move leaking or damaged cylinder outdoors or to an isolated location, observing strict safety precautions. When completely empty, return to manufacturer if instructed or dispose of leaking 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 CO2 vessels are generally moved empty and depressurized. The usual method to dispose of excess CO2 is to dilute with air by venting. Care must be exercised to prevent accumulations of high concentrations of vented CO2 gas in an enclosed or low lying area. This is usually accomplished by very slow venting of the CO2 to avoid a local asphyxiation hazard.

CONTAINER DISPOSAL:

Bulk CO2 vessels should be removed and disposed of only by qualified CO2 service personnel.

Return empty CO2 cylinders for reuse and disposal.

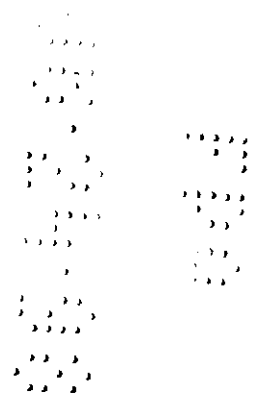
When cylinder is empty, close valve, screw safety cap onto valve outlet and replace protection bonnet before returning to shipper. Only registrant is authorized to refill cylinders. Do not use cylinders for any other purpose. Follow registrant's instruction for return of empty or partially empty cylinders.

DOT Shipping Name: Carbon Dioxide UN 1013

EPA Reg. No. 10330-20

Obtain material safety data sheet P-4574 from Praxair.

Praxair Danbury, CT 0680-5113



Technical Bulletin

CO₂ Grain Fumigation Marketing Program

(Supersedes Liquid Carbonic XB-84-2)

SEP 23 1998
10330-20

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, thus the condition tends to maintain higher quality over extended storage periods. In pre-industrial times, hermetic storage was probably the only means of keeping large quantities of grain free from insect attack for significant periods 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 used. Today active but primitive hermetic storages are reported in operation in India, and underground storages are still used in Yemen, Somalia, Sudan and Egypt. Modern concrete hermetic storage bins have been built in Cyprus and Kenya for corn storage, primarily for protection against famine. The potential of hermetic storage remains viable because it eliminates the need to use grain protectants and fumigants and also help maintain product quality over extended storage periods.

Hermetic storage could also be of value when large crops and carryover produce a grain surplus, but it is not a reasonable alternative for most current and projected storage needs in the U.S. In most instances, to implement this method, we would have to construct new storage facilities and alter existing ones.

The use of modified atmospheres offers a more practical method of storage. It does not leave chemical residue as do conventional fumigants and protectants. And although a need for some sealing is likely, extensive modification of existing storage facilities is not usually required. Instead, all that is necessary is to change the existing atmosphere in the storage structure by purging it with CO₂, which is lethal to insects.

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CO₂ Grain Fumigation Marketing Program

(Supersedes Liquid Carbonic XB-84-2)

CO₂ 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 USDA., has done extensive work in this area over the past 15 years. Many of his studies involved only one life stage, usually the adult, of one or a few species. (Keep in mind that the adult is generally the easiest life stage to kill.) Also, many researches have used mixtures of CO₂, oxygen (O₂), and nitrogen (N₂). From this data (Table 1), we can see that increasing the N₂ concentration from 97 to 100% greatly increases mortality as does increasing the CO₂ concentration from 37 to 60%. Increasing the CO₂ concentration to 99%, however, produces less mortality than obtained at 60%. Laboratory studies such as this suggest that CO₂ is more effective than N₂, and there is probably no need to increase the CO₂ concentration above 60% when purging. Also, the table indicates longer exposures may be required to obtain complete control of this species.

Table 1 — Mean Number of Adult Insects Emerging from Wheat Infested with 1- to 5-week-old immatures and exposed for 1 to 4 days to indicated atmosphere at 80°F (26.7°C).

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 CO₂ for stored product insect control. Some obvious advantages of using CO₂ are,

- Lower costs
- Less stringent sealing requirements
- Faster insect mortality
- Less influence on performance caused by slight fluctuations in concentrates.

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Temperature Affects CO₂ Control

The effect of temperature on the length of time necessary to obtain good control with CO₂ is as important as it is with any conventional fumigants. Grain temperature should be above 70°F (21.1°C) during the treatment with CO₂. What happens at lower temperatures can be seen in Table 2. Here it can be seen that it takes 3 to 6 days for the 60% CO₂ atmosphere to give complete kill and that the cold air is no longer so effective in reducing emergence.

TABLE 2 — Percent Reduction in Emergence when Immature Rice Weevils Were Exposed to CO₂ at Two Different Temperatures for 8 Days.

Atmosphere	Reduction in Emergence			
	1 Day	3 Days	6 Days	8 Days
35°F (1.67°C)				
98% CO ₂	99.8%	100.0%	100.0%	100.02
60% CO ₂	95.6%	94.4%	98.8%	98.8%
60°F (15.56°C)				
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 CO₂ atmospheres in grain storage until 1970. It was then that USDA at Columbus, GA researches attained and maintained a 35% CO₂ concentration for 2, 4, and 7 day periods in an upright concrete silo containing 68,000 bushels of in-shell peanuts. This lack of interest was undoubtedly due to the success of conventional fumigants and grain protectants. Later in 1973, at the terminal elevators in North Charleston, SC, 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. In this test, a CO₂ concentration of about 60% was successfully sustained for 96 hours. The success of this test is shown in Table 3: CO₂ fumigation reduced all species of insects by more than 99% and decreased kernel damage by 99%.

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TABLE 3 — Average number of insects per sample and damage to 28,000 bu of corn treated with a 60% CO₂ atmosphere at the terminal elevator in North Charleston, SC. Samples collected before and after a 4-day treatment of the corn with CO₂.)

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 CO₂ in 1976. In the first test, gaseous CO₂ was released at 3 points into the base of a welded metal bin containing 7000 tons of wheat. The pressure of the CO₂ 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 CO₂. They have also studied sealing extensively as CO₂ costs are much higher in Australia than in the United States.

By 1984, all 10 terminal elevators in the State of Victoria were sealed and modified for CO₂ use. At the same time in Western Australia, the cooperative Bulk Handling, LTD, planned to have in the near future 25 horizontal grain storage units with an average 25, 000-ton capacity as well as many of their vertical steel and concrete storages sealed for CO₂.

U. S. Studies

Interest in using CO₂ to protect grain against insect infestation has increased in the U.S. but not to the extent it has in Australia. Several large CO₂ producers, including Liquid Carbonic, have applied to the EPA for labels for CO₂ and Airco has already obtained one. In the 1980's, the USDA cooperated in pilot tests with Liquid Carbonic and Airco in treating grain storage facilities ranging from terminal elevators to on-farm storage with CO₂.

The publication written by Dr. Jay (1980) details the actual techniques involved in using CO₂ in upright concrete silos and describes field tests using these methods of application. Three methods are discussed for purging the atmosphere of a silo with CO₂: 1) applying the CO₂ into the top of

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a full bin, 2) applying CO₂ into the bottom of a full bin, and 3) adding CO₂ to the grain stream as the silo is filled.

In a test conducted at a large Texas terminal elevator, CO₂ was supplied on site from a 5-ton vessel equipped with vaporizers to an upright concrete silo containing approximately 40,000 bushels of wheat. A 96-hour treatment of infested wheat reduced emergence by 100% when samples were examined after 7 days. By 30 days after treatment, percent reduction decreased to 99.5%; at 60 days, to 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. CO₂ concentrations of 52 to 82% 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. A 99.9% control was observed in all grain samples from the 6,000 bushel bin. Temperatures of the grain ranged from 82 to 92°F (27.8 to 33.3°C).

Economics

The economics of using CO₂ versus other fumigants have been monitored but not adequately investigated. Several factors contribute to the cost of CO₂ treatments. Next to labor, which is variable, the most important factor is the cost of the CO₂. Another factor is, of course, the mechanics involved in applying it. For example, reports and testing have indicated that it may be necessary to recirculate the CO₂ to prevent persistent regions of low CO₂ and provide an even concentration throughout the storage area. With all costs considered, however, we know that CO₂ is highly competitive with conventional fumigants. Cost comparisons run by Continental Grain in Texas showed that the cost for liquid fumigant (methyl bromide) was 0.7¢/bushel compared to 0.76¢/bushel for CO₂.