Carbon Dioxide
Handling/Processing

Identification of Petitioned Substance

Chemical Names:
carbon dioxide

Other Names:
carbonic acid gas
carbonic anhydride
dry ice

Trade Names:
carbon dioxide

CAS Number:
124-38-9

Other Codes:
FF6400000 (RTECS number)
016601 (EPA PC Code)
2046969 (EEC number)

Characterization of Petitioned Substance

Composition of the Substance:

Carbon dioxide is an inorganic compound composed of one carbon atom and two oxygen atoms, and its structure is presented in Figure 1. In nature, carbon dioxide occurs as a gas and comprises 0.03 percent of the Earth's atmosphere (Kirk-Othmer 2005). Carbon dioxide is utilized by plants during photosynthesis and is produced by respiration by animals and plants. It is an important component of the carbon cycle and is also a well known greenhouse gas.

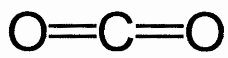

Figure 1. Chemical Structure of Carbon Dioxide

Properties of the Substance:

Carbon dioxide is a gas in the range of temperatures and pressures found in the Earth's environment. As a gas or liquid, carbon dioxide is colorless and odorless (Lewis 1993). Carbon dioxide does not exist as a liquid at atmospheric pressure; however, at -109.3 degrees Fahrenheit and atmospheric pressure (McMurry and Fay 1995), gaseous carbon dioxide becomes a white solid commonly known as dry ice (Lewis 1993). Although carbon dioxide is not very reactive at ordinary temperatures, in water it forms carbonic acid, a weak acid (Kirk-Othmer 2005).

Specific Uses of the Substance:

Carbon dioxide has many uses in manufacturing and in food production and handling. For example, it is used in chemical manufacturing (e.g., of aspirin), water softening, beverage carbonation, foundry-mold preparation, greenhouses, mining operations, oil well secondary recovery, health care, welding, extraction processes, and as a propellant in fire extinguishers and aerosol products (EPA 2004, Kirk-Othmer 2005).

In food production and processing, non-petitioned uses of carbon dioxide include use as a refrigerant (either in liquid or solid form) and in modified-atmosphere packaging to retard spoilage of meat or other packaged food (Kirk-Othmer 2005). Carbon dioxide is used in controlled and modified atmospheric storage of fruits and vegetables to increase storage life after harvest by decreasing respiration, reducing further growth, and reducing ethylene[1] production rates of fruits and vegetables or rendering fruits and vegetables less susceptible to ethylene's effects (Kader 1986).

[1] Ethylene is a naturally occurring ripening hormone of fruits.

The petition to amend the current listing of carbon dioxide on the National List from synthetic to non-synthetic (CCOF 2005) specifically proposes the following uses of carbon dioxide in organic handling and processing:

- Pest control/fumigant: For grains, herbs, and spices storage, carbon dioxide can be used to modify the atmosphere of storage bins thereby killing pests by suffocation and preventing additional pests.
- Ingredient for beverage carbonation: For carbonation of soda, fruit juice, and beer, carbon dioxide is pumped into the beverages. Addition of carbon dioxide also retards microbial breakdown of beverage ingredients.
- Extracting agent – production of natural flavors and extracts: Carbon dioxide in a supercritical state (i.e., the high temperature and pressure state where the gas and liquid phases are indistinguishable) is used to separate oleoresins, or spice extracts, from other plant components.
- Extracting agent – oil production: Carbon dioxide can help break up plant parts to enable oil to be extracted without using hexane for extraction and improve the antioxidant content of oil, allowing it to keep better.
- Slaughtering agent: For chicken processing, carbon dioxide is used to suffocate chickens.
- Processing aid – microbial control: For milk handling, carbon dioxide is dissolved in milk (post pasteurization) to inactivate microbial decomposition. The carbon dioxide keeps the microbes from obtaining oxygen.
- Processing aid – disinfectant: Alfalfa seeds can be soaked in high-pressure liquid carbon dioxide to kill seed borne pathogens.
- Propellant: For whipped cream, pressurized carbon dioxide aids ejection of food from aerosol can.
- Pest control: For fruit storage, pre-conditioning stone fruits in carbon dioxide helps them withstand controlled atmospheric storage.
- Extracting agent – coffee decaffeination: Carbon dioxide can be used to separate caffeine from coffee.

<u>Approved Legal Uses of the Substance:</u>
Carbon dioxide is approved by EPA for pesticide use as a fumigant, insecticide, and rodenticide (EPA PC Code 016601) (Orme and Kegley 2006). The U.S. Food and Drug Administration (FDA) includes carbon dioxide on its list of food substances affirmed to be "Generally Recognized as Safe" (GRAS). Title 21, §184.1240 of the Code of Federal Regulations[2] (CFR) states that carbon dioxide is to be used at levels not to exceed current good manufacturing processes and at purity suitable for its intended use. FDA also lists carbon dioxide in regulations for salad dressing, indicating that salad dressings and mayonnaise may be packed in atmospheres in which the air is replaced in whole or part by carbon dioxide (see 21 CFR §169.150, 169.140, 169.115).

<u>Action of the Substance</u>:
The action of carbon dioxide varies for each of the petitioned uses, each of which is described below:

- In the application as a pest control in grain storage (and herb/spice storage), carbon dioxide acts to stimulate insect respiration while displacing needed oxygen. Fumigation of grain with high levels of carbon dioxide (>60 percent) can rapidly kill pests, while long-term lower levels of carbon dioxide (10 to 30 percent) can be maintained to kept insects away (White et al. 1990). For effective carbon dioxide fumigation, storage structures need to be gas-tight or carbon dioxide needs to be continuously added (Mann et al. 1999).
- In carbonated beverages, carbon dioxide acts to add a pungent taste, acidic bite, and fizz. It is also a preservative against yeast, mold, and bacteria. Carbon dioxide is added under pressure either to the water or syrup and water mixture in manufacturing of the beverages (Kirk-Othmer 2005).
- As an extracting agent, supercritical carbon dioxide (i.e., carbon dioxide in the high temperature and pressure state where the gas and liquid phases are indistinguishable) has a high diffusivity and high solvent strength (Turner 2006). Extraction is performed by pumping supercritical carbon dioxide through a vessel filled with the item to be extracted. The supercritical carbon dioxide is then

[2] See http://www.access.gpo.gov/cgi-bin/cfrassemble.cgi?title=200421.

depressurized and the extracted component collected (Turner 2006). The temperature and pressure of the supercritical carbon dioxide is modified depending on the compound to be extracted whether is it natural flavors and extracts, oil, or caffeine (Dziezak 1986).

- For chicken processing, carbon dioxide atmospheres are used as a slaughtering agent, because chickens cannot breathe in an atmosphere with increased carbon dioxide (CCOF 2005). In one study, 45 percent atmospheric carbon dioxide was mentioned as a level used for chicken processing (Raj 1998).
- For milk handling, carbon dioxide can be added post-pasteurization to slow microbial growth and increase the shelf life of the milk. The addition of carbon dioxide acts to increase the lag time of bacteria, lower bacteria growth rates, and lengthen the time for the microorganisms to reach stationary growth (Hotchkiss et al. 1999).
- In treatment of alfalfa seeds for sprout production, supercritical carbon dioxide is used to kill microorganisms on the seeds. The likely mode of action is that the carbon dioxide extracts intracellular substances from the microbial cells or from membranes (Mazzoni et al. 2001). In a laboratory study, Mazzoni et al. (2001) found that there was no negative impact on seed germination due to carbon dioxide treatment.
- As a propellant, carbon dioxide is added under pressure to an aerosol container with a product (e.g., whipped cream). When the valve of the container is opened, the propellant and the product are expelled as a mixture (Kirk-Othmer 2005).
- For fruit storage, the petitioned use of carbon dioxide is for pest control. Ahmadi et al. (1999) reported the carbon dioxide atmosphere may prevent spore production and the spread of decay from infected to healthy fruit. The tolerance of different types of fruit to carbon dioxide level and length of exposure varies greatly, which is why the petitioned use of carbon dioxide for stone fruits (i.e., containing large hard seeds, or pits) is as a pre-conditioning method (CCOF 2005). Many stone fruits cannot tolerate elevated concentrations of carbon dioxide for extended storage periods, but shorter periods are possible for pest control (Ahmadi et al. 1999).

Status

International

Carbon dioxide is allowed for use under all international organic standards that were researched. These are the following:

The **Canadian General Standards Board** lists carbon dioxide for use in organic agriculture for certain applications (http://www.pwgsc.gc.ca/cgsb/on_the_net/032_0310/standard-e.html). Specifically, it is found in three places:

- Permitted Substances List (PSL) for Crop Production, Pest Management, Section A.3.1.2: Controlled-atmosphere storage is listed as an approved method for pest management.
- Permitted Substances List (PSL) for Crop Production, Post Harvest Substances, Section A.4.1: Controlled-atmosphere storage, carbon dioxide, oxygen, or nitrogen are listed as for post-harvest.
- Permitted Substances List (PSL) for Processing, Non-organic Additives for Organic Food Products, Section C.1.2: Carbon dioxide is listed.

CODEX Alimentarius Commission, which implements the Joint FAO/WHO Food Standards Programme, lists carbon dioxide in the Codex Alimentarius collection of food standards (ftp://ftp.fao.org/docrep/fao/005/Y2772e/Y2772e.pdf). Specifically, it is listed in the following areas:

- Principles of Organic Production Section C on Handling, Storage, Transportation, Processing and Packaging for pest management. Controlled atmosphere, including carbon dioxide, can be used as pest control in storage or transport containers and areas.
- On the Permitted Substances for the Production of Organic Foods lists, carbon dioxide is listed in four places:

- Substance for Plant Pest and Disease with the requirement that it must be recognized by certification body or authority.
- Ingredients of Non Agricultural Origin Referred to in Section 3 of These Guidelines: Food additives, including carriers, for plant products.
- Ingredients of Non Agricultural Origin Referred to in Section 3 of These Guidelines: For processing livestock and bee products.
- Processing Aids Which May Be Used for the Preparation of Products of Agricultural Origin Referred to in Section 3 of These Guidelines: for Plant Products.

European Economic Community (EEC) Council Regulation 2092/91 lists carbon dioxide as a processing aid that may be used for processing of ingredients of agricultural origin from organic production (Section B) referred to in Article 5(3)(d) and Article 5(5a)(e) (http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991R2092_do_001.pdf).

International Federation of Organic Agriculture Movements lists carbon dioxide as an approved extraction method for all ingredients (organic and non-organic) (CCOF 2006).

Japanese Agricultural Standard of Organic Agricultural Products lists (http://www.ams.usda.gov/nop/NOP/TradeIssues/JAS.html), carbon dioxide as allowed for use in storage facilities as carbon dioxide powder, and as a substance for processing.

Evaluation Questions for Substances to be used in Organic Handling

Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical process? (From 7 U.S.C. § 6502 (21).)

Carbon dioxide is available from natural sources and as a byproduct of various artificial sources. Major sources for commercial carbon dioxide include the following (Kirk-Othmer 2005):

- production of ammonia and hydrogen;
- combustion of carbonaceous fuels;
- controlled fermentation;
- lime-kiln operation;
- chemical synthesis such as production of sulfuric acid, phosphoric acid, and ethylene oxide; and
- natural carbon dioxide gas wells.

Most of these processes, except gas wells, can be considered manufacturing processes. All of the processes require purification of the carbon dioxide before use in the food industry.

In ammonia and hydrogen plants, carbon dioxide is created when methane or other hydrocarbons are converted to carbon dioxide and hydrogen ($CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$) (Kirk-Othmer 2005). Methane is exposed to steam in order to crack the methane molecules (CCOF 2005). The carbon dioxide resulting from this reaction is dried to remove water and distilled in a column under pressure to remove impurities including hydrocarbons and hydrogen (CCOF 2005). At ammonia plants, the hydrogen is produced in the presence of a controlled amount of air to produce the necessary ratio of hydrogen to nitrogen required to synthesize ammonia (Kirk-Othmer 2005).

Combustion of coke, coal, fuel oil, or natural gas produces carbon dioxide as a byproduct. Although the process is similar to the process in ammonia plants, air is not needed as a source of nitrogen because ammonia is not produced (Kirk-Othmer 2005).

Carbon dioxide is also produced as a byproduct when natural substances such as molasses, corn, wheat, and potatoes are fermented for the production of ethanol and other alcohols. Although fermentation is a natural process, its rate is artificially increased in commercial fermentation processes (see Evaluation

Question #2). In addition, the carbon dioxide must be purified by activated-carbon absorption or chemical purification processes (Kirk-Othmer 2005).

Lime kiln operations use calcium carbonate (limestone) to neutralize acids that exist within waste streams from industrial processing (Johnson Matthey Catalysts 2006). This acid-base reaction produces gas by-products containing 40 percent carbon dioxide, which can be separated from dust and further cleaned by scrubbers and recovered by absorption (Kirk-Othmer 2005). According to the petitioner (CCOF 2005), some plants that produce chemical products such as sulfuric acid, phosphoric acid, and ethylene oxide also purify and sell the carbon dioxide that is a byproduct of those reactions.

Although natural gas wells containing high percentages of carbon dioxide are a natural source of carbon dioxide, physical and chemical processes must be used to recover the carbon dioxide from the natural gas. These processes include passing the carbon dioxide bearing gases counter-current to a solution that removes carbon dioxide by absorption and retains it until it is desorbed in separate equipment. Alkali carbonate and ethanolamine solutions are the most frequently used absorbing mediums (Kirk-Othmer 2005).

Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources? (From 7 U.S.C. § 6502 (21).)

Among the sources of carbon dioxide discussed in Evaluation Question #1, only one (natural gas wells) involves the extraction of carbon dioxide from a natural source. Physical and chemical processes are used to extract the carbon dioxide from the natural gas. These processes do not chemically change the carbon dioxide and no further chemical formulation or manufacturing processes are required.

Evaluation Question #3: Is the petitioned substance created by naturally occurring biological processes? (From 7 U.S.C. § 6502 (21).)

Among the sources of carbon dioxide discussed in Evaluation Question #1, only fermentation to produce ethanol and carbon dioxide is a naturally occurring biological process. However, the fermentation process is artificially initiated, controlled, and accelerated. For example, the fermentation process is enhanced by mechanical grinding the corn kernel or grain, addition of enzymes and ammonia for pH control and nutrient, and the addition of cultured yeast in a sealed fermentation chamber (RFA 2005).

Evaluation Question #4: Is there a natural source of the petitioned substance? (From 7 CFR § 205.600 (b) (1).)

The natural source of carbon dioxide is underground wells, as described by the petitioner (CCOF 2005). These sources are limited by location, but in some parts of the U.S. concentrations of carbon dioxide in underground gases can range up to 90 or almost 100 percent carbon dioxide (Johnson Matthey Catalysts 2006). In the United States, carbon dioxide wells exist in several states, including Colorado, Mississippi, New Mexico, Utah, Wyoming (Johnson Matthey Catalysts 2006), and Washington (Kirk-Othmer 2005). This natural source is one of many sources listed by the petitioner; however, it cannot be the sole source of carbon dioxide because of the limited locations where it is available. Transporting pressurized gas for long distances is not always feasible according to the petitioner, especially in the relatively small quantities needed for organic food processing (CCOF 2005). In addition, it still is necessary to purify carbon dioxide from underground wells by one of the absorption processes described in Evaluation Question #1.

Evaluation Question #5: Is there an organic agricultural product that could be substituted for the petitioned substance? (From 7 CFR § 205.600 (b) (1).)

Substitutes for carbon dioxide that are organic are limited, and there were no agricultural products identified that can be used as substitutes for carbon dioxide. However, a few other gases and water were identified as possible substitutes for some of the processes. In most cases, the substitutes include pesticides, insecticides, and other chemicals.

For grain storage pest control, besides synthetic chemical fumigants, nitrogen is listed as a possible pest control gas. According to studies summarized by White et al. (1990), nitrogen is not as efficient as carbon dioxide because it does not stimulate insect respiration as it displaces oxygen. According to the petitioner, for carbonation of beer, recycled carbon dioxide from fermentation processes could be used (CCOF 2005).

The petitioner lists decapitation as a substitute for chicken processing (CCOF 2005); however, animal welfare issues have been raised regarding electrical shocks that are often used before decapitation of chickens (Raj 1998). A similar method of suffocation using either a 90 percent argon and air mixture, or a 60 percent argon, 30 percent carbon dioxide, and air combination was tested by Raj (1998), and found effective for killing chickens. Argon, which comprises 0.93 percent of air, is produced commercially as a byproduct of distillation processes that separate air in order to produce hydrogen or nitrogen (Kirk-Othmer 2005). Although argon is derived from natural sources, it is not included as an agricultural or natural product on the National List. The extent of processing and purification in production of argon is similar to that required in production of carbon dioxide.

Substitutes for propellants include hydrocarbons and other compressed gases such as nitrogen and nitrous oxide (Kirk-Othmer 2005). None of these qualify as agricultural products; however, nitrogen, like argon, is available commercially as a distilled product of air (Kirk-Othmer 2005). The only natural solvent for coffee decaffeination besides carbon dioxide is water. It is not as effective as carbon dioxide, and more flavor and color compounds are removed along with the caffeine in a water extraction than carbon dioxide extraction (Dziezak 1986).

No natural substitutes were identified for the remaining petitioned uses (extraction, milk handling, seed treatment, and fruit storage). Oleoresin and oil extraction alternatives include solvents such as hexane and dichloromethane (Palmer and Ting 1995). Although there is current research on methods to improve the shelf-life of milk, carbon dioxide currently appears to be the most tested method for post-pasteurization microbial control in use (DMI 1998). For alfalfa seed treatment, soaking the seeds in calcium hypochlorite is a non-natural alternative (Mazzoni et al. 2001). Besides careful handling and sanitation, non-natural synthetic fungicides and insecticides were the only alternatives to modified atmospheric storage for fruits uncovered in the literature (Ahmadi et al. 1999).

Evaluation Question #6: Are there adverse effects on the environment from the petitioned substance's manufacture, use, or disposal? (From 7 CFR § 205.600 (b) (2).)

The production of carbon dioxide is a byproduct of processes that have adverse effects on the environment via air pollution, solid waste streams, and drilling underground wells. However, because carbon dioxide is simply a byproduct of these reactions, these effects would be occurring regardless of carbon dioxide production. Carbon dioxide is a greenhouse gas and use of carbon dioxide for organic food production will result in a delayed release to the atmosphere in some cases. However, for all of the petitioned uses, ultimately the carbon dioxide will still be released after use in organic handling/processing.

Evaluation Question #7: Does the petitioned substance have an adverse effect on human health as defined by applicable Federal regulations? (From 7 CFR § 205.600 (b) (3).)

Carbon dioxide exists at about 0.03 percent in air. Up to 0.5 percent is considered not harmful to humans, but higher concentrations of carbon dioxide can be harmful (Kirk-Othmer 2005). Adverse reactions from inhalation include dizziness, headache, elevated blood pressure, tachycardia (elevated heart rate), and the risk of unconsciousness or death. The petitioned uses that involve modifying the atmosphere (i.e., insect control in grains, herb, spices, and fruit storage and chicken slaughtering) require a percentage of carbon dioxide that would be harmful to humans (ranges between 10 and >60 percent). However, modified atmosphere food storage is frequently contained in sealed bins (White et al. 1990) and chicken slaughtering can be performed in chicken storage containers (Raj 1998). It is not expected that workers will have prolonged contact to these high levels of carbon dioxide.

In addition, frostbite may occur on contact with the liquid or solid forms (Orme and Kegley 2006). Although none of the petitioned uses of carbon dioxide would utilize the solid form, treatment of alfalfa seeds would use the liquid form and extraction processes would use the supercritical state, which has some properties of the liquid.

Evaluation Question #8: Is the nutritional quality of the food maintained when the petitioned substance is used? (From 7 CFR § 205.600 (b) (3).)

No information was found indicating that carbon dioxide depletes essential nutrients or energy yielding substances from food products when used as petitioned. Studies have shown that elevated carbon dioxide storage does not effect grain seed germination and quality (White et al. 1990).

Evaluation Question #9: Is the petitioned substance to be used primarily as a preservative? (From 7 CFR § 205.600 (b) (4).)

As discussed previously, carbon dioxide decreases microbial growth rates by limiting the availability of oxygen. Thus, in multiple applications carbon dioxide could act as a preservative. Carbon dioxide is added to pasteurized milk to extend shelf-life (Hotchkiss et al. 1999), essentially acting as a preservative. In carbonated beverages it has a secondary effect of acting as a preservative against yeast, mold, and bacteria (Kirk-Othmer 2005). The petitioned uses of carbon dioxide that do not involve this preservative benefit of carbon dioxide are use as an extracting agent and chicken processing.

Evaluation Question #10: Is the petitioned substance to be used primarily to recreate or improve flavors, colors, textures, or nutritive values lost in processing (except when required by law, e.g., vitamin D in milk)? (From 7 CFR § 205.600 (b) (4).)

The petitioned uses of carbon dioxide do not include those that are primarily to recreate or improve flavors, colors, textures, or nutritive values lost in processing.

Evaluation Question #11: Is the petitioned substance generally recognized as safe (GRAS) when used according to FDA's good manufacturing practices? (From 7 CFR § 205.600 (b) (5).)

Carbon dioxide is included on the FDA's list of affirmed GRAS substances (21 CFR, Part 184, Subpart 1240).

Evaluation Question #12: Does the petitioned substance contain residues of heavy metals or other contaminants in excess of FDA tolerances? (From 7 CFR § 205.600 (b) (5).)

No evidence was found indicating that carbon dioxide used for food handling and processing has residues exceeding FDA's Action Levels. In the use of carbon dioxide for grain storage pest control, White et al. (1990) noted that carbon dioxide leaves no chemical residues on food, which is considered to be a benefit of its use as an extraction agent, in addition to its high purity (Palmer and Ting 1995).

Steps taken to purify carbon dioxide for food processes include use of activated carbon absorbers or the Reich chemical process. The Reich process uses a potassium dichromate washer for the oxidation of organic impurities and removal of hydrogen sulfide, concentrated sulfuric acid for dehydration and dichromate removal, and dry solid ash tower for removal of residual oxidized material (Kirk-Othman 2005).

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