Chlorine/Bleach

Handling/Processing

Identification of Petitioned Substance

Chemical Names:
Calcium Hypochlorite
Sodium Hypochlorite
Chlorine Dioxide

Other Names:
Calcium hypochlorite and sodium hypochlorite also are known as bleach; synonyms are listed below in Table 1.

Trade Names:
Trade names are listed below in Table 1.

CAS Numbers:
Calcium Hypochlorite: 7778-54-3
Sodium Hypochlorite: 7681-52-9
Chlorine Dioxide: 10049-04-4

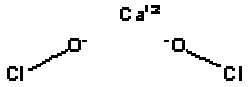
Other Codes:
Calcium Hypochlorite: 014701 (EPA/OPP Chemical Code)
Sodium Hypochlorite: 014703 (EPA/OPP Chemical Code); NH3486300 (RTEC number)

Characterization of Petitioned Substance

Composition of the Substance:

Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials not found in nature. Calcium hypochlorite and sodium hypochlorite are commonly known as bleach. The molecular formulas and structures of these compounds are shown below.[1]

Calcium Hypochlorite ($CaCl_2O_2$) **Sodium Hypochlorite** ($ClNaO$) **Chlorine Dioxide** (ClO_2)



Properties of the Substance:

Calcium hypochlorite is a white solid that readily decomposes in water, releasing oxygen and chlorine. Sodium hypochlorite is a colorless, transparent liquid (DCC, Undated) that is generally used dissolved in water at various concentrations. Sodium hypochlorite solutions are clear, greenish to yellow liquids. Calcium hypochlorite and sodium hypochlorite solutions both have an odor of chlorine.

[1] Source: www.chemfinder.com

Chlorine dioxide is a yellow-green to orange gas or liquid. Production of chlorine dioxide liquid uses acids and sodium chlorite solutions to generate the chlorine dioxide. To produce chlorine dioxide gas, hydrochloric acid (HCl) or chlorine is brought together with sodium chlorite.

Additional names and chemical properties of calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are listed below in Table 1.

Table 1. Synonyms and Chemical Properties of Calcium Hypochlorite, Sodium Hypochlorite, and Chlorine Dioxide[2]

	Calcium Hypochlorite	Sodium Hypochlorite	Chlorine Dioxide
Synonym	BK Powder; Calcium hypochloride; Calcium hypochlorite; Calcium hypochlorite, dry; Calcium oxychloride; Chloride of lime; Chlorinated lime; HTH; Hy-Chlor; Hypochlorous Acid, Calcium Salt; Lime chloride; Lo-Bax; Losantin; Mildew remover X-14; Perchloron; Pittchlor	Antiformin; B-K; bleach; Carrel-dakin solution; Chloros; Chlorox; Clorox; Dakin's solution; Hychlorite; Javelle water; Javex; Liquid bleach; Mera industries 2MOM3B; Milton; Modified dakin's solution; Piochlor; Showchlon; Sodium hypochlorite; Sodium hypochlorite, 13% active chlorine; Sodium oxychloride	Alcide; Anthium dioxcide; Chlorine(IV) oxide; Chlorine oxide; Chlorine peroxide; Chloroperoxide; Chloriperoxyl; Chloryl radical; Caswell No. 179A; Doxcide 50
Trade Names	Perchloron, Clorox™, Purex, CPE00345 Pro Pure Calcium Hypochlorite, Kem Tek SHOCK	Clorox™, Purex, Javel water	---
Molecular Weight	142.9848	74.44217	67.4518
Boiling Point (˚C)	---	40	-59
Melting Point (˚C)	100	18	11
Density	2.35 (25˚C)	1.209 (25˚C)	1.642 (0˚C)
Vapor Pressure (25˚C)	7.22E-13 mmHg	---	---
Water Solubility (25˚C)	2.14E+05 mg/L	---	3.01 g/L

Reaction products of calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are listed below in Table 2. The reaction products produced in water (highlighted) are those that are produced during the disinfection process.

Table 2: Reaction products of Calcium Hypochlorite, Sodium Hypochlorite, and Chlorine Dioxide

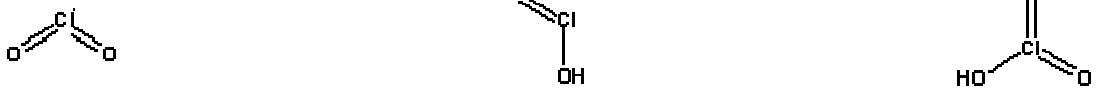
	Reaction Products Produced in Air	Reaction Products Produced in Water
Calcium Hypochlorite	Compounds commonly found in the air	Calcium, hypochlorite ions[3], and hypochlorous acid
Sodium Hypochlorite	Compounds commonly found in the air	Sodium, hypochlorite ions, and hypochlorous acid
Chlorine Dioxide	Chlorine gas and oxygen	Chlorite (50-70%) and chlorate ions

[2] Sources: www.chemfinder.com; ChemIDplus; Hazardous Substance Data Base; ATSDR

[3] An ion is an electrically charged atom or molecule.

As noted above in Table 2, chlorine dioxide forms chlorite ($ClHO_2$) and chlorate ($ClHO_3$) ions when added to water. Differences in the chemical structure of chlorine dioxide, chlorite, and chlorate are presented below.[4]

Chlorine Dioxide (ClO_2) **Chlorite** ($ClHO_2$) **Chlorate** ($ClHO_3$)



Specific Uses of the Substance:

Sodium and Calcium Hypochlorite

Sodium and calcium hypochlorite are chlorinated inorganic disinfectants used to control bacteria, fungi, and slime-forming algae that can cause diseases in people and animals (EPA, 1991, 1992). These disinfectants also are used in cleaning irrigation, drinking water, and other water and wastewater systems.

Chlorine Dioxide

Chlorine dioxide is an antimicrobial disinfectant and pesticide used to control harmful microorganisms including bacteria, viruses, and fungi on inanimate objects and surfaces primarily in indoor environments. It is used in cleaning water systems and disinfecting public drinking water supplies (ATSDR, 2004a). It also is used as a bleaching agent in paper and textile manufacturing, as a food disinfectant (e.g., for fruit, vegetables, meat, and poultry), for disinfecting food processing equipment, and treating medical wastes, among other uses (EPA, 2003a).

Approved Legal Uses of the Substance:

With regard to organic production, calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are currently approved for disinfecting and sanitizing livestock facilities and equipment and as algicides, disinfectants, and sanitizers (including irrigation system cleaning) in organic crop production. In addition, these chlorine materials are approved for disinfecting and sanitizing food contact surfaces in the production of processed products labeled as "organic" or "made with organic." Residual chlorine levels from all of these approved uses may not exceed the maximum residual disinfectant limit under the Safe Drinking Water Act (currently 4mg/L).

Additional legal approved uses of the substances are discussed below.

Sodium and Calcium Hypochlorite

Calcium hypochlorite and sodium hypochlorite are EPA-registered pesticides (OPP Nos. 014701 and 014703, respectively) that are used in controlling bacteria, fungi, and slime-forming algae (EPA, 1991, 1992). A Registration Standard for sodium and calcium hypochlorite was issued in February 1986 by EPA. EPA

[4] Source: www.chemfinder.com

concluded that no additional scientific data were needed to register or reregister products that contain 5.25 percent to 12.5 percent sodium hypochlorite or 65 percent to 70 percent calcium hypochlorite, as long as the products contain no other active ingredients, contain no inert ingredients other than water, and bear Toxicity Category I labeling (indicating the highest degree of acute toxicity) (EPA, 1991).

Calcium hypochlorite and sodium hypochlorite are both "indirect" food additives[5] approved by FDA (http://www.cfsan.fda.gov/~dms/opa-indt.html). Sodium hypochlorite is a generally recognized as safe (GRAS) substance (40 CFR 180.2), and calcium hypochlorite is exempt from the tolerance requirement under FFDCA section 408 (40 CFR 180.1054). Calcium hypochlorite and sodium hypochlorite may be used as a final sanitizing rinse on food processing equipment (21 CFR 178.1010); sodium hypochlorite may be used in washing and lye peeling of fruits and vegetables (21 CFR 173.315). These hypochlorites also can be used in postharvest, seed, or soil treatment on various fruit and vegetable crops (EPA, 1991).

Chlorine Dioxide

EPA has registered the liquid form of chlorine dioxide for use as a disinfectant and sanitizer. The Agency also has registered chlorine dioxide gas as a sterilant. According to EPA's website, chorine dioxide was due for pesticide reregistration in 2005.

Chlorine dioxide is added to drinking water as a disinfectant in some municipal water-treatment systems in the United States. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (chlorine dioxide's oxidation product) (EPA, 2002).

According to FDA, chlorine dioxide is a direct food additive permitted in food for human consumption when it used in an amount not to exceed 3 ppm residual chlorine dioxide as an antimicrobial agent in water used in poultry processing and to wash fruits and vegetables (21 CFR 173.300).

Action of the Substance:

In water and soil, sodium and calcium hypochlorite separate into sodium, calcium, hypochlorite ions, and hydrochlorous acid molecules. Hypochlorous acid molecules are neutral and small in size. As a result, when hypochlorous acid molecules exist in equilibrium with the hypochlorite ions, they easily diffuse through the cell walls of bacteria. This changes the oxidation-reduction potential of the cell and inactivates triosephosphate dehydrogenase, an enzyme which is essential for the digestion of glucose. Inactivation of this enzyme effectively destroys the microorganism's ability to function.

Chlorine dioxide kills microorganisms directly by disrupting transport of nutrients across the cell wall.

Status

International:

Canada - Canadian General Standards Board - http://www.pwgsc.gc.ca/cgsb/032_310/32.310epat.pdf

Bleach (not exceeding 10 percent) is permitted in packaging and sanitation. Additionally, it is an acceptable agent for cleaning equipment when used in the production and processing of maple syrup.

European Economic Community (EEC) Council Regulation 2092/91 –
http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991R2092_do_001.pdf

[5] Indirect food additives are substances used in food-contact articles, and include adhesives and components of coatings (21 CFR Part 175), paper and paperboard components (21 CFR Part 176), polymers (21 CFR Part 177), and adjuvants and production aids (21 CFR Part 178).

Sodium hypochlorite (e.g., as liquid bleach) is authorized for the clearing and disinfecting of livestock buildings and installations.

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))

Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are manufactured by chemical processes. The chemical manufacturing processes for calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are described below.

Calcium Hypochlorite[6]

Calcium hypochlorite is produced by passing chlorine gas over slaked lime.[7] It is then separated from the coproduct, calcium chloride, and air dried or vacuumed.

Sodium Hypochlorite[8]

Generally, sodium hypochlorite is produced by reacting chlorine with a solution of sodium hydroxide (NaOH, also called lye or caustic soda). This method is used for most commercial productions of sodium hypochlorite. A more active, but less stable formulation of sodium hypochlorite can be produced by chlorinating a solution of soda ash (Na_2CO_3).

Chlorine Dioxide[9]

To form chlorine dioxide, sodium chlorate ($NaClO_3$) and sulfuric acid (H_2SO_4) are reacted with sulfur dioxide (SO_2), or chloric acid is reacted with methanol (CH_3OH) (HSDB, 2005). Alternatively, chlorine dioxide can be formed with chlorine (Cl_2) and sodium chlorite; sodium hypochlorite with hydrochloric acid; potassium chlorate with sulfuric acid; or by passing nitrogen dioxide through a column of sodium chlorate.

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).)

No. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are manufactured by a chemical process. They are not extracted from naturally occurring sources.

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

No. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are not found in nature.

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

No. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are manufactured by a chemical process.

[6] Source: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
[7] Slaked lime is calcium hydroxide, a colorless crystal or white powder created when lime (calcium oxide) is reacted with water.
[8] Source: http://www.oxy.com/OXYCHEM/Products/sodium_hypochlorite/sodium_hypochlorite.htm
[9] Source: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB; Simpson et al., Unknown Date

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

Citric acid or other acids (e.g., acetic acids, ascorbic acid, citric acid, and vinegar) could be substituted for bleach materials. Natural acids eliminate the growth of pathogens because many pathogens cannot grow at pH levels below 4.5. Additionally, natural acids may possess bactericidal capabilities by: reducing the pH; disrupting the membrane transport, permeability, and/or anion accumulation; or reducing internal cellular pH by the dissociation of hydrogen ions from the acid (Parish et al., 2003). Many types of produce, especially fruit, naturally possess significant concentrations of organic acids such as acetic, benzoic, citric, malic, sorbic, and succinic acids. Citric acid is used as a drip irrigation cleaner, equipment cleaner, chelating agent, and pH adjuster. Citric acid is biodegradable and considered environmentally safe. According to the NOP Regulations (205.605(a)), nonorganic citric acid used as an ingredient in or on processed products labeled as "organic" or "made with organic" must be produced by microbial fermentation of carbohydrate substrates.

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).)

Sodium and Calcium Hypochlorite

There is no information available from EPA or FDA to suggest that environmental contamination results from the proper manufacture, use, or disposal of calcium hypochlorite or sodium hypochlorite. Calcium hypochlorite and sodium hypochlorite are registered pesticides, implying that there is a potential for misuse or improper disposal. However, these compounds are highly reactive and are broken down by sunlight to compounds commonly found in the air. In water and soil, sodium and calcium hypochlorite separate into sodium, calcium, hypochlorite ions, and hypochlorous acid molecules. Calcium hypochlorite and sodium hypochlorite are not bioaccumulative.

Although sodium and calcium hypochlorite are low in toxicity to avian wildlife, they are highly toxic to freshwater fish and invertebrates. Discharges of hypochlorite-containing wastes from facilities (i.e., point sources) are regulated through issuance of site-specific wastewater discharge permits intended to ensure that the amount of hypochlorites discharged will not pose a significant adverse effect to wildlife (EPA, 1991). Additionally, current NOSB approval is conditioned on residual chlorine levels in the water not exceeding the limit set by the Safe Drinking Water Act (4 mg/L).

When released to water or soil, one of the reaction products of sodium and calcium hypochlorite is hypochlorite ions. When mixed with organic materials (e.g., dirt), hypochlorite produces trihalomethanes (THMs)[10], which are carcinogenic (http://www.epa.gov/safewater/hfacts.html). Currently, the maximum contaminant level (MCL) for total THMs is 0.080 mg/L (http://www.epa.gov/safewater/hfacts.html).

Sodium hypochlorite has the potential to raise soil pH and add sodium to the soil. Sodium hypochlorite may also be phytotoxic; an experimental application of sodium hypochlorite directly to the leaves of eight species of foliage plants caused severe necrosis, chlorosis, and leaf abscission following a single application (HSDB, 2005).

Chlorine Dioxide

Information on chlorine dioxide available from EPA and FDA does not indicate that environmental contamination results from its proper manufacture, use, or disposal. However, during the "activation" of chlorine dioxide (i.e., activating dilute aqueous solutions of sodium chlorite with an acid to produce chlorine dioxide), the release of gas to the air or "off gassing" can be a safety hazard to users.

[10] Trihalomethanes (THMs) are a group of four chemicals (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) that are formed along with other disinfection reaction products when chlorine or other disinfectants used to control microbial contaminants in drinking water react with naturally occurring organic and inorganic matter in water.

According to ATSDR (2004b), chlorine dioxide has not been found at any of the 1,647 current or former National Priorities List (NPL) sites that are targeted by EPA for long-term federal clean-up activities.

No information was found in the literature on concentrations of chlorine dioxide in air, sediments, or soil. In sediments and soil, concentrations of chlorine dioxide are expected to be small or not detectable due to its high reactivity (ATSDR, 2004b).

Chlorine dioxide contamination in water is difficult to identify because it is intentionally added to drinking water as a disinfectant in some municipal water-treatment systems. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (EPA, 2002). Levels of chlorite ion were sampled from drinking water distribution systems of publicly owned treatment works (POTW) facilities that utilized chlorine dioxide in the United States as part of the Information Collection Rule (ICR) in 1998; approximately 16 percent had levels of chlorite ion over the MCL of 1 mg/L (ATSDR, 2004b).

Chlorine dioxide is a very reactive compound and breaks down quickly in the environment (ATSDR, 2004a). In air, sunlight rapidly causes chlorine dioxide to break down into chlorine gas and oxygen. When used as a disinfecting agent, however, the product of chlorine dioxide is primarily chlorite. Although chlorite in water may move into groundwater, reactions with soil and sediments may reduce the amount of chlorite reaching groundwater. The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Toxic reaction products are not known to occur when chlorite is mixed with organic materials. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (EPA, 2002).

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).)

Calcium Hypochlorite or Sodium Hypochlorite

Potential human health effects due to calcium hypochlorite or sodium hypochlorite use as a disinfectant for food contact surfaces occur dermally or via inhalation. Contact with strong hypochlorite solutions may cause burning pain, inflammation, and blisters to the skin. Mild bleach solutions may cause mild and transitory irritation when they come in contact with the eye, while more concentrated solutions may cause severe injuries. Long-term exposure to low levels of hypochlorite can cause dermal irritation. Inhalation of chlorine gas released from concentrated hypochlorite solutions may cause nasal irritation, sore throat, and coughing (ATSDR, 2002).

Chlorine Dioxide

Inhalation and dermal exposure are the main routes of concern for human exposure when chlorine dioxide is used as a disinfectant for food contact surfaces. Chlorine dioxide is a severe respiratory and eye irritant. According to the Occupational Safety and Health Administration (OSHA), inhalation can produce coughing, wheezing, respiratory distress, and congestion in the lungs. Irritating effects in humans were intense at concentration levels of 5 ppm. OSHA has set a limit of 0.1 parts of chlorine dioxide or chlorite per million parts of air (0.1 ppm) in the workplace during an 8-hour shift, 40-hour workweek (http://www.osha.gov/SLTC/healthguidelines/chlorinedioxide/recognition.html).

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

There was no information found indicating that the nutritional quality of food is not maintained when using bleach materials.

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

No. The approved use of chlorine materials is as a disinfectant for food contact surfaces.

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).)

No. The approved use of chlorine materials is as a disinfectant for food contact surfaces.

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).)

Calcium hypochlorite and sodium hypochlorite are both "indirect" food additives[11] approved by FDA (http://www.cfsan.fda.gov/~dms/opa-indt.html). Sodium hypochlorite is a generally recognized as safe (GRAS) substance (40 CFR 180.2), and calcium hypochlorite is exempt from the tolerance requirement under FFDCA section 408 (40 CFR 180.1054).

According to FDA, chlorine dioxide is a direct food additive permitted in food for human consumption when it used as an antimicrobial agent in water used in poultry processing and to wash fruits and vegetables in an amount not to exceed 3 ppm residual chlorine dioxide (21 CFR 173.300).

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. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide do not contain residues of heavy metal or other contaminants in excess of FDA tolerances.

References:

ATSDR. 2002. ToxFAQs™ for Calcium Hypochlorite/Sodium Hypochlorite Available at: http://www.atsdr.cdc.gov/tfacts184.html.

ATSDR. 2004a. ToxFAQs™ for Chlorine Dioxide and Chlorite. Available at: http://www.atsdr.cdc.gov/tfacts160.html.

ATSDR. 2004b. Toxicological Profile for Chlorine Dioxide and Chlorite. Available at: http://www.atsdr.cdc.gov/toxprofiles/tp160.html.

DCC. Undated. Available at: http://www.dcchem.co.kr/english/product/p_basic/p_basic11.htm.

EPA. 1991. R.E.D. Facts. Sodium and Calcium Hypochlorite Salts. Available at: http://www.epa.gov/oppsrrd1/REDs/factsheets/0029fact.pdf.

EPA. 1992. Reregistration Eligibility Document Sodium and Calcium Hypochlorite Salts. Available at: http://www.epa.gov/oppsrrd1/REDs/old_reds/case0029.pdf.

EPA. 2002. List of Drinking Water Contaminants & MCLs. Available at: http://www.epa.gov/safewater/mcl.html.

[11] Indirect food additives are substances used in food-contact articles, and include adhesives and components of coatings (21 CFR Part 175), paper and paperboard components (21 CFR Part 176), polymers (21 CFR Part 177), and adjuvants and production aids (21 CFR Part 178).

EPA. 2003. Pesticides: Topical & Chemical Fact Sheets. Chlorine Dioxide. Available at: http://www.epa.gov/pesticides/factsheets/chemicals/chlorinedioxidefactsheet.htm.

HSDB. 2005. Available at: http://toxnet.nlm.nih.gov/.

Parish M.E., L.R. Beuchat, T.V. Suslow, L.J. Harris, E.H. Garrett, J.N. Farber, F.F. Busta. 2003. Chapter V Methods to reduce/eliminate pathogens from fresh and fresh-cut produce. Comprehensive Reviews in Food Science and Food Safety 2(Supplement):161-173. Available at: http://members.ift.org/NR/rdonlyres/975AF206-DBD7-4E5E-8871-3EE6119850E8/0/crfsfssupn1p161173.pdf.