REVISED ENVIRONMENTAL ASSESSMENT (EA) FOR CHLORINE DIOXIDE FOOD-CONTACT NOTIFICATION (FCN)

1. **Date**

November 13, 2006

2. **Name of Notifier**

Drew Industrial Division, Ashland Specialty Chemical Company, Ashland, Inc.

3. **Address**

c/o Lewis & Harrison, 122 C Street, NW, Suite 740, Washington, DC 20001

4. **Description of Proposed Action**

This FCN requests the use of the food-contact substance (FCS), chlorine dioxide, as an antimicrobial agent in the following applications:

- In the processing of red meat, red meat parts and organs as a spray and in the processing of red meat parts and organs as a dip.
- On processed, comminuted, or formed meat food products (except ready-to eat-meats and those meats precluded by the standards of 9 CFR Part 319) prior to packaging of food for commercial purposes.
- On raw agricultural commodities in the preparing, packaging or holding of food for commercial purposes.
- In water and ice that are used to rinse, wash, thaw, transport or store seafood.

All of above uses are currently regulated under 21 CFR §173.325 (*Acidified Sodium Chlorite Solutions*). Upon acid activation, as described in 21 CFR §173.325, acidified sodium chlorite solutions generate chlorine dioxide. As discussed in Section 6 of this EA, data developed by the notifier shows that the levels of chlorine dioxide and chlorite that occur following the use-instructions in 21 CFR §173.325 are equivalent to or greater than the levels of these substances that will result from the chlorine dioxide generation methods and uses proposed by this FCN. Consequently, this FCN will result in any or new or increased environmental risks.

5. Identification of Chemical Substances that are the Subject of the Proposed Action

a) Chemical Information for the Notified Chemical

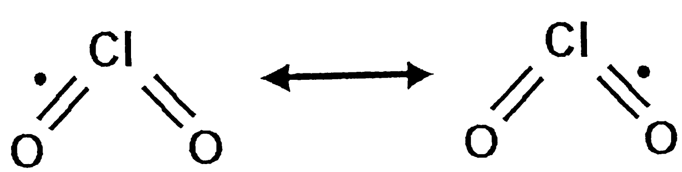
1. Chemical Name — Chlorine Dioxide

2. Synonyms — Chlorine Oxide, Chlorine (IV) Oxide

3. CAS Registry Number — 10049-04-4

4. Chemical Formula — ClO_2

5. Structure



6. Properties

Melting Point	-59°C
Boiling Point	11° C
Solubility (aqueous)	3.0 g/l at 25°C

b) Use Rates

The notifier is proposing that chlorine dioxide be applied as an aqueous solution to the food commodities listed in Section 4 of this EA, in an amount not to exceed 3 ppm residual chlorine dioxide. The precise amount of chlorine dioxide added will depend on the chemical demand of the process water and degree of microbial control desired. The notifier anticipates that the application rate will range from 5-10 ppm of chlorine dioxide.

c) Impurities

The impurities associated with chlorine dioxide will depend on the generation system (refer to Appendix 1). The electrochemical generation system produces small amounts (< 2%) of sodium hydroxide as an impurity. Therefore, at a maximum application rate of 10 ppm chlorine dioxide, the amount of sodium hydroxide associated with the chlorine dioxide treatment solution is < 200 ppb. The impurities associated with the other generation systems (gaseous chlorine-chlorite and acid-hypochlorite-chlorite) are unreacted chlorite, hypochlorous acid, chloride ion, sodium ion and chlorate ion. Based on a maximum application rate of 10 ppm chlorine dioxide, the levels of these impurities in the treatment solution are 800 ppb chlorite ion; 600 ppb of hypochlorous acid; 6 ppm of chloride ion; 400 ppb of sodium ion; and less than 50 ppb of chlorate ion.

6. Introduction of Substances into the Environment

a) Production of Chlorine Dioxide

Chlorine dioxide is manufactured on-site by reacting an aqueous solution of sodium chlorite (3.75%-25%) with either gaseous chlorine or a mixture of sodium hypochlorite and an acid. In addition, chlorine dioxide can be produced electrochemically. The different methods for generating chlorine dioxide are described in detail in Appendix 1.

All of these methods are well-established and have been previously reviewed by FDA. Accordingly, there are no extraordinary circumstances that apply to the manufacture of chlorine dioxide, as described herein.

b) Use Releases

Environmental releases from the use of chlorine dioxide may occur to both air and water. The released substances include chlorine dioxide, chlorite ion, chlorate ion, hypochlorous acid, sodium ion, and chloride ion. As discussed below, the releases of chlorine dioxide, chlorite and the sodium ion are anticipated to be less than those already approved under 21 CFR §173.325 (*Acidified Sodium Chlorite Solutions*).

The regulation under 21 CFR §173.325 allows acidified sodium chlorite solutions to be used in the processing of red meat, red meat parts and organs; on processed, comminuted and formed meat products and on raw agricultural commodities, by combining a sodium chlorite solution with any GRAS acid at levels sufficient to achieve a use-solution pH of 2.3 to 2.9 and a sodium chlorite concentration ranging from 500-1200 ppm. In addition, 21 CFR §173.325 allows the use of acidified sodium chlorite on seafood by mixing a sodium chlorite solution with any GRAS acid at levels to achieve a pH in the range of 2.5 to 2.9 and then by diluting this solution so that the sodium chlorite use-concentration ranges from 40-50 ppm.

A study conducted by the notifier (refer to Appendix 2) showed that an acidified sodium chlorite use-solution, made by combining a 1200 ppm solution of sodium chlorite with a GRAS acid at a level to achieve a use-solution pH of 2.3, resulted in chlorite levels up to 857 ppm and chlorine dioxide levels up to 47 ppm. A similar study was not conducted with the seafood use parameters; however, based on the study conducted with the 1200 ppm acidified sodium chlorite solution, the notifier estimates that, for the seafood use, the upper chlorite level is 35 ppm and the upper chlorine dioxide level is 4 ppm.

As indicated in Section 5 of this EA, the notifier is proposing a maximum residual level of 3 ppm chlorine dioxide. The application level to achieve this residual level will range from 5-10 ppm of chlorine dioxide. The chlorite levels associated with a 5-10 ppm use-solution of chlorine dioxide are approximately 800 ppb. Moreover, even when accounting for the conversion of chlorine dioxide into chlorite in process waste water the maximum chlorite level in process waste water (see below) is approximately 8 ppm. This is substantially below the chlorite levels the notifier found in the analytical study referenced above. Finally, the concentration of sodium ion in process water should be significantly higher under the existing 21 CFR §173.325 regulation compared to the subject FCN since the sodium chlorite level is much greater.

- <u>Air Releases</u>

Air releases of chlorine dioxide may occur during the use of this substance due to its known volatility. The notifier anticipates, at most, only insignificant air releases of the impurities and degradates associated with chlorine dioxide since these substances are relatively non-volatile.

Workplace exposures to chlorine dioxide are regulated by the Occupational Safety and Health Administration (OSHA), which has set a Permissible Exposure Limit or PEL for chlorine dioxide. If chlorine dioxide is used as intended, the notifier does not expect, at the maximum application rate proposed by this FCN, that the safe exposure limits will be exceeded including those established by NIOSH (Short-Term Exposure Limit or STEL of 0.3 ppm (0.9 mg/m^3) during any 15-minute period of a 10-hour workday) or the OSHA PEL of 0.1 ppm (0.3 mg/m^3) time-weighted average over an 8 hour shift[1]. In addition, the Material Safety Data Sheets (MSDS) for the precursor products used to produce chlorine dioxide identify the potential inhalation hazards associated with chlorine dioxide and provide inhalation limits for the workplace established by OSHA. Furthermore, workers handling chlorine dioxide are instructed to wear a respirator if exposure limits are exceeded.

- <u>Water Releases</u>

Potential water releases from the use of chlorine dioxide are chlorite ion, chlorate ion, sodium ion, hypochlorous acid and chloride ion. Releases to the aquatic environment are not expected for chlorine dioxide or hypochlorous acid since these substances should either be destroyed by the wastewater treatment system at the facility using chlorine dioxide or by the receiving POTW if the plant discharges its waste stream to a POTW. Releases for sodium and chloride ions have not been estimated since the levels of these releases, based on the concentrations for sodium and chloride ions in the treatment solution, are considered insignificant when compared to background environmental concentrations.

[1]See http://www.cdc.gov/niosh/npg/npgd0116.html

Maximum wastewater concentrations of chlorite and chlorate can be estimated using the following assumptions:

- The maximum application rate for chlorine dioxide is 10 ppm.
- Chlorine dioxide is completely converted to chlorite and chlorate in a 70:30 ratio[2]
- The maximum level of the chlorite impurity (unreacted chlorite) in the chlorine dioxide treatment solution is 0.8 ppm.

Therefore, the maximum concentration in wastewater is:

$$10 \text{ ppm} \times 0.70 + 0.8 \text{ ppm} = 7.8 \text{ ppm}$$

and the maximum concentration for chlorate is:

$$10 \text{ ppm} \times 0.30 = 3 \text{ ppm}$$

The estimated environmental concentrations (EEC's) for facilities that discharge directly into an aquatic body can then be calculated using the following assumptions:

- Approximately 50% of the total water discharged from a food-processing facility is treated with chlorine dioxide[3,4].
- The receiving stream dilution factor is 10 (see footnote 5 below)
- Chlorite removal and/or destruction by wastewater treatment at the food-processing facility is 99%[6].

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[2]The 70/30 ratio is based on data presented in a paper by Werdehoff and Singer that appeared in the September, 1987 issue of the Journal of the American Water Works Association. See Werdehoff, K.S., and P.C. Singer. *Chlorine Dioxide Effects on THMPP, TOXFP, and the Formation of Inorganic By-Products. Jour. AWWA.* September, 1987, pgs. 110-113. For additional information, refer to Food Additive Petitions (FAPs) Nos. 4A4408, 4A4414 and 0A4716.

[3]United States Asia Environmental Partnership; Civil Engineering Research Foundation. Clean Technologies in U.S. Industries: Focus on Food Processing, www.p2pays.org/ref/09/08853.htm

[4]Graham, M.D., Strasser, J., Mannapperuma, J.D. *Application of Ozonation and Membrane Treatment in Poultry Processing*; 400-02-023F; California Energy Commission: Sacramento, CA, 2002

[5]The stream dilution factor of 10 is based on a survey of poultry processing plants, which showed that 96% had a dilution factor of 20 or greater. Therefore, a dilution factor of 10 for all food-processing facilities should be considered a "worst-case" estimate. In this regard, it should be noted that EPA provided the notifier with a "7Q10" dilution factor of 24 for POTW's.

[6]Toxicological Profile for Chlorine Dioxide and Chlorite, Agency for Toxic Substances and Disease Registry, http://www.atsdr.cdc.gov/toxprofiles/tp160.pdf

Therefore, the maximum EEC for chlorite is:

(Concentration in chlorine dioxide treatment wastewater) (% of total plant water that is treated with chlorine dioxide) (1- % treatment removal/destruction efficiency) (1/stream dilution)

$$(7.8 \text{ ppm}) (0.50) (0.01) (0.10) = 0.0039 \text{ ppm or } 3.9 \text{ ppb}$$

and the maximum EEC for chlorate[7] is:

$$(3 \text{ ppm}) (0.50) (0.10) = 150 \text{ ppb}$$

Using the same assumptions, the chlorite and chlorate EEC's for facilities that send untreated wastewater to POTW's that then subsequently treat wastewater prior to aquatic discharge are expected to be lower than the EEC's presented above. This occurs since there is additional dilution factor that results from facility wastewater being a percentage or fraction of the total wastewater received by a POTW.

[7]The estimate for chlorate assumes no removal or destruction during wastewater treatment.

7. Environmental Fate of Emitted Substances

The environmental fate of chlorine dioxide is well-characterized in the published literature and has been covered in previous petitions submitted to FDA for chlorine dioxide and acidified sodium chlorite solutions, In brief, chlorine dioxide will rapidly be converted in the environment to chlorite and, to a minor extent, chlorate. Both chlorite and chlorate will react with organic matter to form chloride. In addition, unpublished data (refer to Appendix 3) available to the notifier shows that chlorite is susceptible to photodegradation in the environment.

8. Environmental Effects of Released Substances

An extensive amount of ecotoxicity data has been compiled on sodium chlorite and sodium chlorate. Only limited data is available on chlorine dioxide since, as indicated above, chlorine dioxide is very short-lived in the environment.

The ecotoxicity data on sodium chlorite is presented in a document that the U.S. Environmental Protection Agency (USEPA) recently issued as part of the reregistration review of sodium chlorite and chlorine dioxide. The ecotoxicity data on sodium chlorite (and sodium chlorate and chlorine dioxide) is summarized in Table 1 below. The data shows that technical chlorite is slightly to practically non-toxic to freshwater fish on an acute basis, with 96-hr. acute LC_{50}'s ranging from 50 to 420 ppm. Technical chlorite is slightly toxic to estuarine/marine fish; the 96-hr LC_{50} in the sheepshead minnow is 75 ppm. Technical chlorite is moderately to very highly toxic to freshwater invertebrates, with 48-hr. LC_{50}'s ranging from 27 ppb to 146 ppb. Technical chlorite is slightly to highly toxic to estuarine/marine invertebrates, with 96-hr EC_{50}'s ranging from 0.576 to 21.4 ppm. In terms of avian toxicity, technical chlorite is moderately toxic to birds on an acute oral basis, with acute oral LD_{50}'s ranging from 382 to 660 mg/kg and slightly to practically non-toxic to birds on an acute dietary basis, with dietary LC_{50}'s ranging from 2031 ppm to >10,000 ppm. The available data on technical chlorate shows that this substance is practically non-toxic, on an acute basis, to freshwater and marine fish and invertebrates and avians. The limited data on chlorine dioxide indicates that chlorine dioxide is highly toxic to freshwater and marine fish.

[8] *Chlorine Dioxide - Environmental Hazard and Risk Assessment*, USEPA, July 13, 2006. This document is in Appendix 4).

TABLE 1
Summary of Ecotoxicity Data for Chlorine Dioxide, Chlorite and Chlorate

Organism	Test	ClO_2	ClO_2^-	ClO_3^-
Bluegill sunfish	LC_{50} (96 hr.)	150 ppb	208-420 ppm	>1000 ppm
Rainbow trout	LC_{50} (96 hr.)		50.6-360ppm	>1000 ppm
Daphnia magna	EC_{50} (48 hr.)		27-161 ppb	>1000 ppm
Mysid shrimp	LC_{50} (96 hr.)		576 ppb	>1000 ppm
Eastern Oyster	EC_{50} (96 hr.)		21 ppm	>1000 ppm
Sheepshead minnow	LC_{50} (96 hr.)	Juvenile 20 ppb Adult: 170 ppb	75 ppm	>1000 ppm
Rat	LD_{50} (acute oral)		260 mg/kg	> 5000 mg/kg
Mallard duck	LD_{50} (acute oral)		382-660 mg/kg	> 2500 mg/kg
Mallard duck	LC_{50} (acute dietary)		> 5600 ppm	> 5000 ppm
Bobwhite quail	LC_{50} (acute dietary)		2031 - 10,000 ppm	>5000 ppm

An evaluation of the ecotoxicity data on chlorite was conducted by a research group associated with the University of Maryland. The group proposed an acute ecological risk criteria (ERC) or water quality criteria (WQC) of 0.135 ppm for the chlorite ion (see Appendix 5). This value takes into account the large different in chlorite toxicity between fish and aquatic invertebrates. USEPA's Office of Water essentially concurred with this proposal (see Appendix 6).

Based on the EEC's derived in Section 6 of this EA and the ERG for chlorite noted above and the results of the ecotoxicity studies conducted with chlorate, the notifier does not anticipate any adverse environmental effects from the use of chlorine dioxide pursuant to this FCN since the EEC's are significantly below concentrations that are considered toxic to non-target organisms.

9. Mitigation Measures

Mitigation measures need not be considered since no potential adverse effects are expected to occur.

10. Alternatives to Proposed Action

Alternatives to the proposed action need not be considered because no potential adverse effects are expected to occur.

11. List of Preparers

This EA was prepared by Eliot Harrison of Lewis & Harrison. Mr. Harrison's background is in biology and chemistry and he has several years of experience preparing technical and regulatory submissions on chemicals.

12. Certification

The undersigned official certifies that the information presented is true, accurate and complete to the best knowledge of Ashland, Inc.

Name: Eliot Harrison

Title: Agent for Drew Industrial Division, Ashland Specialty Chemical Company

Signature:

Date: November 13, 2006