Memorandum

Date: March 17, 2004

From: Division of Petition Review
Chemistry Review Group

Subject: FAP 4A4751 (MATS #1151. M2.0 & 2.1): Vulcan chemicals. Chlorine dioxide produced by electrochemical generation for use as an antimicrobial agent in water contacting poultry, processed fruits, and vegetables. Submissions dated 10/1/03 and 1/16/04.

To: Division of Petition Review, HFS-265
Regulatory Group I
Attention: Paul DeLeo, Ph.D.

Vulcan Chemicals has submitted a petition requesting that 21 CFR 173.300 (Chlorine dioxide) be amended to allow an alternative method of manufacture for the subject additive, chlorine dioxide (ClO_2). Currently, ClO_2 is regulated under §173.300 for use as an antimicrobial agent in water used in poultry processing and in the washing of processed fruits and vegetables in an amount not to exceed 3 ppm (mg/kg) residual ClO_2. Under §173.300, ClO_2 can be generated from either the reaction of (1) an aqueous solution of sodium chlorite with either chlorine gas or a mixture of sodium hypochlorite and hydrochloric acid; or (2) an aqueous solution of sodium chlorate with hydrogen peroxide and sulfuric acid. In either case, the generator effluent contains at least 90% (by weight) of ClO_2 with respect to all chlorine species. The subject petition proposes to expand the regulation under §173.300 in order to allow the electrochemical (electrolytic) generation of ClO_2 from sodium chlorite.

Identity

The identity of the additive is provided on p. 00004 and p. 000014.

Name	Synonyms	CAS Reg.No.	Formula	Molecular Weight	Melting Point (°C)	Boiling Point (°C)	Solubility (at 25°C & 34.5 mmHg) *
Chlorine dioxide	Chlorine oxide Chlorine (IV) oxide	10049-04-4	ClO_2	67.45 g/mole	-59	11	3.01 g/l

We have no questions on the identity of the subject additive.

Manufacturing Process and Specifications

The petitioner has stated that ClO_2 is produced by an electrochemical process, which is described on pp. 000004-5 and in Appendix II (pp. 000020-22). The major difference between the proposed and regulated process of ClO_2 generation is that the petitioned process is accomplished by electrolysis rather than chemical activation. In the electrochemical cell process, ClO_2 is generated from an aqueous solution of sodium chlorite ($NaClO_2$) according to the following half-cell reactions:

* Solvent not stated, presumed to be water

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Anode: $2Na^+ + 2\ ClO_2^- \rightarrow 2Na^+ + 2\ ClO_2 + 2e^-$
Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Combining these reactions, ClO_2 is formed at the anode while sodium hydroxide (NaOH) is formed at the cathode. Therefore, the stoichiometric chemical equation of the electrochemical reaction used to produce ClO_2 is as follows:

$$2\ NaClO_2 + 2H_2O \xrightarrow[\text{Electricity}]{} 2\ ClO_2 + 2\ NaOH + H_2$$

According to the petition, two typical methods of electrochemical generation technologies, "direct oxidation" and "fixed bed oxidation" are commercially available (p. 000005). In the direct oxidation process, $NaClO_2$ is passed directly over the anode of a direct current cell, oxidized to ClO_2, and further purified through a hydrophobic membrane (i.e., ERCO Model R101 generator) or a stripper column (i.e., PureStrip Model P-30E generator). In the fixed bed oxidation process, the complete conversion of $NaClO_2$ to ClO_2 occurs in a packed bed of catalyst in the presence of direct current (i.e., Halox Model H2000 generator). Both types of electrochemical generation systems continuously generate ClO_2 from a 25% $NaClO_2$ aqueous solution (as a single precursor chemical) that is recycled through an electrolyte cell, and also co-produce an effluent stream of NaOH and H_2 gas resulting from the electrolytic reaction at the cathode. The H_2 gas is either dissolved in the effluent or vented to air. The petitioner states that neither of these reaction by-products are present in the generated ClO_2.

In your letter dated on 11/26/03, the petitioner was requested to provide a statement as to which petitioned process would be used to generate the ClO_2 under the amended §173.300, and also provide product data sheets for the generators under the typical operating conditions. In the submission dated 1/16/04, the petitioner stated that the current petition is intended to cover all types of commercially available electrochemical ClO_2 generation equipment. The petitioner has also provided the requested information regarding typical operating conditions, including specifications for the 25% $NaClO_2$ (precursor chemical), and product yields for 3 commercial electrochemical ClO_2 generators: PureStrip Model P-30E (PureLine Treatment systems, LLC), Halox Model H2000 Chlorine Dioxide (ClO_2) Generator (Halox Technologies, Inc.), ERCO Model R101 Generator (ERCO Worldwide).

Additionally, the petitioner has provided data that summarizes the ClO_2 production rate, concentration, and purity (including by-products) for 3 commercial generators (p. 000023, and submission dated 1/16/04). The ClO_2 concentration typically produced in commercial generators ranges from 540 ppm-1200 ppm. All generators produce effluent containing ClO_2 with purity greater than 94%, which is accordance with the current regulation that specifies a minimum 90% ClO_2. Accordingly, depending on the generation system, the effluent can contain small quantities of chlorine, chlorite (ClO_2^-), and chlorate (ClO_3^-) under the typical operating conditions (p. 000023, and submission dated 1/16/04). Thus, no new impurities are introduced by the petitioned method for generating ClO_2 relative to the regulated methods. The relevant information is presented in Table 2.

Table 2. ClO_2 composition from 3 commercial generators

Parameters	PureStrip P-30E	ERCO R101	Halox H2000
ClO_2 Purity	>99%	98.4 ± 0.3%	>93.75%
Chlorine in ClO_2	<0.5%	0.3-0.7%	0
Impurity	Not observed	ClO_2^-: 1.0%; ClO_3^-:0.3%	ClO_2^-: 3.7%; ClO_3^-:2.8%

We have no questions on the method of manufacture.

Proposed Use and Technical Effects

The petitioner has incorporated by reference all pertinent information on ClO_2 contained in FAP 4A 4408 and FAP 4A4415. ClO_2 is currently permitted for use as an antimicrobial agent in water used in poultry processing (FAP 4A 4408) and in washing processed fruits and vegetables (FAP 4A4415) in an amount not to exceed 3 ppm residual ClO_2 (§173.300). The petitioner has stated that they are not proposing any changes in the currently-regulated use, use levels, and technical effect of ClO_2.

Since the ClO_2 produced by the petitioned process has the same chemical identity and proposed use as the ClO_2 produced by the currently-regulated methods, we concur that the ClO_2 produced by the petitioned process would have the same technical effect as the ClO_2 produced by the currently-regulated methods. We have no questions.

Analytical Method for ClO_2

The current regulation cites the 18th Edition of the Method 4500-ClO_2 E, entitled, "Standard Methods for the Examination of Water and Wastewater (1992)" or an equivalent method. The petitioner has proposed to update the analytical method to the most recent edition (20th Ed., 1998; p. 000019). We have confirmed that the updated method is identical to the method cited in the regulation, and concur with updating the citation in the regulation. We have no questions on the analytical method.

Residues in Food

The petitioner notes that since the ClO_2 produced by the electrochemical generation method has the same identity, use and functional effect as the ClO_2 produced by the currently-regulated processes, the use of ClO_2 produced by the petitioned process would not result in any new residues in the diet. The petitioner further notes that principal reaction products of ClO_2 are chlorite (ClO_2^-), chlorate (ClO_3^-), and chloride (Cl^-), and that ClO_2^-, ClO_3^- and ClO_2 are unstable in the presence of organic substances (such as those in foods), and will degrade to chloride (Cl^-) over time. The petitioner has incorporated by reference information in FAPs 4A4415 and 4A4408 to address issues related to ClO_2 and chlorinated by-products in food, as well as the impact of ClO_2 on the nutritional quality of food (p. 000009). We concur with the petitioner's assessment.

The only residue at issue from the use of ClO_2 is chlorite (ClO_2^-). The petitioner has incorporated by reference pertinent information in FAP 4A4408 on residual ClO_2^-. In your letter dated on 11/26/03, the petitioner was requested to clarify the stated residual level of < 2.6 ppm of ClO_2^- on food (based on the use of ClO_2 on poultry). In the submission dated 1/16/04, the petitioner has responded that the estimate was adopted from a previous petition regarding the chemical generation of ClO_2 from ClO_3^- (FAP 0A4716). According to the previous chemistry memorandum dated 3/26/94[1], the correct residual level of ClO_2^- is 1.1 ppm. However, the petitioner has stated that residual ClO_2^- will be diminished to zero as a result of further reduction to Cl^- at sufficiently acidic pH (p. 000009). We concur with the petitioner's assessment with regard to residual ClO_2^- on food. We have no further questions.

[1] Chemistry memorandum, FAP 4A 4408, dated 3/26/1994, Z. Olempska-Beer to R. Martin

Exposure

The petitioner has not provided an exposure estimate, relying on previous determinations that no residual of ClO_2 or its by-products are present in food when consumed. According to previous chemistry memoranda,[2,3] residual ClO_2 or its by-products(e.g., ClO_2^-, and ClO_3^-) will be washed off (fruits and vegetables) or decomposed prior to or during cooking (poultry and meats). Thus, no measurable residues of ClO_2 and its reduction products will be present in food treated according to the use conditions specified in §173.300 when consumed. As discussed above, the electrochemically generated ClO_2 would substitute for the already-regulated ClO_2. Thus, we concur that there would be no exposure to ClO_2 or any of its by-products (ClO_2^-, ClO_3^-, Cl^-) from the petitioned process for generating ClO_2. We have no questions on the exposure estimate.

Proposed Regulation

The petitioner has provided wording (Appendix I) for the amendment of 21 CFR 173.300 to provide for the use of ClO_2. The petitioner proposes to revise the wording of paragraph (a) by enumerating the currently-regulated process as (1) and (2), respectively, and adding "(3) electrolysis of an aqueous solution of sodium chlorite." Paragraph (a) would also be revised to include the updated method in the "20th Ed., 1998" instead of the currently-listed "18th Ed., 1992."
The language proposed for regulation is acceptable.

Summary

In summary, ClO_2 generated by electrochemical (electrolytic) generation is considered to be of the same purity as ClO_2 generated by currently-regulated methods (§173.300). Since the ClO_2 produced by the proposed method would substitute for ClO_2 produced by the already-regulated methods, there would be no change in the exposure to ClO_2 or any of its by-products if this petition is regulated.

We have no further questions.

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HFS-265: HSLee: 418-3006:FAP4751memo.doc
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[2] Chemistry memorandum, FAP 4A 4408, dated 10/31/1994, Z. Olempska-Beer to R. Martin
[3] Chemistry memorandum, FAP 0A 4716, dated 10/27/2003, M. DiNovi to R. Martin