



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

June, 27, 2006

MEMORANDUM

SUBJECT: BioSide[®] HS15%-1. Evaluation of the Enviro Tech Chemical Services, Inc. Submission for Peroxyacetic Acid Wastewater EUP

FROM: Robert Quick, Chemist *Robert Quick*
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ID#: 6838-EUP-R-

DP BARCODE: D327984

DECISION NO.: 362514

PC CODE: Hydrogen Peroxide (000595)
Peroxyacetic Acid (063201)

CHEMICAL NAME: Peroxyacetic Acid (CAS# 79-21-0), Hydrogen Peroxide (CAS# 772-84-1)

MRID#: 466960-00, 466960-05, 466960-06

Background:

There are a large number of registered uses for hydrogen peroxide (HP) and peroxyacetic acid (PAA).

Hydrogen peroxide presently has the following EPA and FDA clearances:

1. 40 CFR 180.1197 exemption of the requirement of a tolerance in or on all food commodities at the rate of $\leq 1\%$ hydrogen peroxide per application on all growing and post-harvest crops.
2. 21 CFR 172.892 for modification of food starch to be added to human food items.
3. 21 CFR 178.1005 for sterilization of polymeric food surfaces. Sanitizing solution is not to contain more than 35% hydrogen peroxide.
4. 40 CFR 180.940 (a)(b)(c) as a sanitizing solution on food contact surfaces
5. 21 CFR 184.136 as GRAS when hydrogen peroxide meets Food Chemical Codex specifications to treat certain foods as a antimicrobial, bleaching agent, oxidizing and reducing agent. Residual hydrogen peroxide must be removed during processing of food.
6. 21 CFR 173.315 (a)(2) for use in washing or to assist in the lye peeling of fruits and vegetables that are not raw agricultural commodities. Used in combination with acetic acid. Not to exceed 59 ppm in wash water.
7. 40 CFR Part 180.1196 (b) for "Peroxyacetic Acid; exemption from the requirement of a tolerance" dated December 1, 2000. This Regulation permits use of sanitizing solutions containing a diluted end-use concentration of peroxyacetic acid up to 500 ppm on food processing equipment including aseptic equipment.
8. The Food & Drug Administration (FDA) has issued a Food Contact Substance Notification, FCN 000561, dated February 22, 2006. The intended use is part of "the process to treat food-contact surfaces to attain commercial sterility at least equivalent to that attainable by thermal processing for metal containers as provided in 21 C.F.R. Part 113". The Food Contact Substance is a mixture containing peroxyacetic acid, hydrogen peroxide, acetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) and water.

Peroxyacetic acid presently has the following EPA and FDA clearances:

1. 40 CFR 180.1196 as a direct application at up to 100 ppm per application to fruits, vegetables, tree nuts, cereal grains, herbs and spices.
2. 40 CFR 180.940(a)(b)(c) as a sanitizing solution on food contact surfaces
3. 21 CFR 173.315(a)(2) in washing or to assist in lye peeling of fruits and vegetables that are not raw agricultural commodities. Prepared by reacting acetic acid with hydrogen peroxide. Not to exceed 80 ppm in wash water.

A RED was issued for peroxy compounds in December 1993. The RED includes hydrogen peroxide and peroxyacetic acid.

Introduction:

This submission is for an Experimental Use Permit (EUP) for the use of the product, Biocide HS 15% (Antimicrobial Solution) for use as a combined sewer overflow (CSO) and stormwater disinfectant. The active ingredients are peroxyacetic acid and hydrogen peroxide. The product is proposed for use as a microbiocide/disinfectant for short-term CSO outfalls in the State of New Jersey.

This package contains: 1) an EUP label; 2) a Biocide HS 15% (Antimicrobial (Solution) master label accepted Jul 05 2005; a data package (MRID# 466960-06) entitled, "Decay Characteristics of Peroxyacetic Acid (PAA) and Hydrogen Peroxide (PERSAN_®, EPA #63838-2) in a Variety of Water Matrices"; 3) an analytical method entitled, "Validation of a New Method to Determine Peroxyacetic Acid (PAA) and Hydrogen Peroxide at Low Levels Used in the Treatment of Water and Wastewater"; 4) a letter dated September 30, 2005, from Mr. Michael Harvey, EnviroTech to Mr. Marshall Swindell AD, PM 33); 5) a copy of a letter dated Nov 26, 2002, from Mr. Marshall Swindell, AD PM 33 to Mr. Michael Harvey, Enviro Tech outlining data requirements; 6) a letter dated September 30, 2005, from Mr. Michael Harvey, Enviro Tech to the EPA OPP Document Processing Desk which is a supplement to EUP Form 8570-17. This letter discusses the EUP.

Conclusions and Recommendations:

1. The method appears to be satisfactorily validated for measuring residues of PAA and hydrogen peroxide (HP) in water for the proposed EUP.

If the registrant wants to use this method for the determination of HP and PAA as a test method, he should request that the colorimeter manufacturer reprogram a model of the colorimeter to measure HP and PAA.

2. No residue data for hydrogen peroxide (HP) and PAA for treated wastewater are submitted as requested at the pre-registration meeting described above. Presumably, these data will be generated as a part of the requested EUP. Residue data reflecting the maximum proposed application rate for the treatment of storm water overflow and from sewage treatment for both hydrogen peroxide and for peroxyacetic acid are needed.

3. It is important for the registrant to generate residue data for both HP and PAA reflecting the use of this product on both chemicals under both the storm water and the sewage uses. The registrant should also submit any other available data to the agency; e.g. copies of available HP – PAA treatment studies (European studies, Columbus Water Works Columbus, Georgia CSO study, Ohio EPA sanctioned PAA-wastewater disinfection studies, etc.

RASSB recommends that the registrant design the EUP program to reflect the shortest practical distance between the injection point for the product and the effluent discharge point for the collection of samples. This will provide the potential for the highest HP and PAA residues in the

discharge water.

During the analyses of samples collected and analyzed from the EUP program, the registrant should conduct a method validation recovery study for each group of analyses carried out.

4. Environmental fate data are submitted for HP and PAA in water and in soil.

a) No half life was calculated for HP in water in the model water study submitted because the HP level in none of the waters declined by any appreciable amount over the 96 hour period of the study.

b). The registrant has calculated half-life of PAA in the three waters at both the 1 ppm and the 20 ppm spike levels. The half life of PAA ranged from an interval of 12 minutes in seawater spiked at 20 ppm to 30 hours in moderately hard and very hard water spiked at the 20 ppm level.

The following informational are from supplemental data:

c) The pH of untreated soil was measured at 6.2 compared to the treated soil at 4.7.

d) Both PAA and HP are degraded from the saturated soil 20 minutes after contact.

These environmental data show that HP and PAA are stable in water under certain conditions. Residue data collected under conditions of actual use as requested in Conclusion 3 above will provide information on the decay rate for these residues.

Detailed Considerations

OPPTS GLN 860.1100 Chemical Identity

The active ingredients in the formulation are:

<u>Component(CAS No.)</u>	<u>Empirical Formula</u>	<u>Structural Formula</u>	<u>Formula Weight</u>
Hydrogen Peroxide (7722-84-1)	H ₂ O ₂	H-O-O-H	34
Peroxyacetic Acid (79-21-0)	C ₂ H ₄ O ₃ O	H ₃ -C-C-O-OH	75

The inert ingredients have various EPA and FDA clearances as both active and inert ingredients.

OPPTS GLN 860.1200 Proposed Use

The supplement to the EUP Form 8750-17 describes the scope of the EUP.

The requested duration of the EUP is one year. The EUP anticipates 24 storm events during the one year EUP during which treatment will take place. Treatment sites that will be treated will include but not be limited to rivers, canals, sloughs and marine estuaries.

The description of the treatment is; "The product will be added to the CSO effluent flow when a signal triggers the start of an over-flow event. The product will then be fed proportionally into the stream using a weir immediately downstream of the injection to insure adequate mixing. ----- The product will be injected as far upstream of the final discharge point as possible to allow a minimum of 5 minute, and preferably a 10 minute contact/residence time. We anticipate a 5-15 ppm concentration of PAA will be necessary."

The registrant plans to take samples just prior to the PAA injection, immediately after injection of the product and again just prior to final discharge. This will serve as a "baseline" for the decay curve for that particular CSO site. The registrant notes on page 2 of this supplement to Form 8570-17 that the sample taken immediately after injection will be analyzed only for PAA.

RASSB requests that all samples taken be analyzed for both HP and PAA.

The proposed label for the EUP does not contain any of the above information. The label proposed use is on "Combined Sewer Overflow (CSO) and Stormwater". The label directions have three parts; Mixing, Contact Time and Flow, Dosing.

The Mixing of the product is to be instantly and mixed to assure complete and intimate contact with the water being treated. The Contact Time and Flow requires a minimum contact time of 5 minutes and longer contact times of 10 to 15 minutes are recommended. The product should be injected as far upstream from the discharge point as possible for efficacy purposes. The Dosing is to be from 5-20 ppm PAA residuals in the treated water.

RASSB recommends that the registrant design the EUP program to reflect the shortest practical distance between the injection point for the product and the effluent discharge point for the collection of samples. This will provide the potential for the highest HP and PAA residues in the discharge water.

OPPTS GLN 860.1340 Residue Analytical Method

MRID# 466960-05. An analytical method entitled, "Validation of a New Method to Determine Peroxyacetic Acid (PAA) and Hydrogen Peroxide at Low Levels Used in the Treatment of Water and Wastewater", has been submitted.

Page 3 of the method states that the method study does not meet the GLP requirements of 40 CFR Part 160 in that no formal protocol was written prior to commencement of the validation testing. It further states that standard toxicological and laboratory procedures were used in accordance with OPPTS and AOAC guidelines. The registrant states that the analytical method is

based on the EPA-accepted "DPD (N,N-diethyl-p-phenylenediamine) colorimetric method for measuring total chlorine in drinking water and wastewater" and has been validated and accepted by the EPA (page 10 of this study). The registrant states that, "The present method relies on the ability of peroxyacetic acid (PAA) to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion into iodine that reacts with a color reagent (DPD), which turns the solution to a shade of pink, the intensity of which is proportional to the concentration of PAA. The colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the results in terms of ppm as Cl_2 ". The registrant has determined that hydrogen peroxide does not interfere with the measurement of PAA provided that the analysis is completed within 30 seconds of introducing the DPD reagent.

In order for hydrogen peroxide to be measured, it must be activated by addition of ammonium molybdate and given time to react with the iodide to produce iodine. When the DPD reagent is added to the solution, the pink color that is measured by the colorimeter is a measure of both PAA and hydrogen peroxide, both expressed as ppm chlorine. The hydrogen peroxide level is determined by subtracting the PAA residue level from the total PPA and hydrogen peroxide value. This difference is the hydrogen peroxide residue level.

The conversion factor for calculating hydrogen peroxide residue from the chlorine residue is 0.479 (M.W. $H_2O_2 \div$ M.W. chlorine).

Because the colorimeter is programmed to measure chlorine and not peroxyacetic acid, the ppm number for chlorine is converted into ppm peroxyacetic acid by multiplying by a factor of 1.07 (M.W. of PAA/M.W. of Cl_2). If the registrant wants to use this method for the determination of PAA, he should request that the colorimeter manufacturer reprogram a model of the colorimeter to measure PAA.

The DPD method was validated using solutions of PAA at nominal concentrations of 0.05-2.0 ppm PAA and solutions containing 0.07-2.87 ppm hydrogen peroxide. Recoveries for PAA ranged from 95.4-102.0% and for hydrogen peroxide ranged from 89.0-185.7%. All except one HP recovery value was in the range of 89.0-120.7%.

The method appears to be satisfactorily validated for measuring residues of PAA and hydrogen peroxide in water for the proposed EUP. If the registrant wants to use this method for the determination of HP and PAA as a test method, he should request that the colorimeter manufacturer reprogram a model of the colorimeter to measure HP and PAA.

During the analyses of samples collected and analyzed from the EUP program, the registrant should conduct a method validation recovery study for each group of analyses carried out.

OPPTS GLN 860.1500 Residue Data and Environmental Fate 161 GLN Series

The proposed use is for treatment of wastewater. In a pre-registration meeting with the

registrant, the Agency requested environmental fate data including:

1. Information on the dissipation rate of HP and PAA in the presence of wastewater effluent.
2. Provide scientific data literature or other information to indicate the likely dissipation rate of HP and PAA in the wastewater process.
3. Submit copies of available HP – PAA treatment studies (European studies, Columbus Water Works Columbus, Georgia CSO study, Ohio EPA sanctioned PAA-wastewater disinfection studies, etc.
4. If the registrant is unable to resolve the degradation rate of HP and PAA in disinfected wastewater effluent and of actual residue data on the residue levels in the treated water, then dissipation data will need to be generated to support this use and will need to include:
 - a. Pilot plant or actual field trials to show the degradation rate of HP and PAA in treated wastewater effluents and the residue levels of HP and PAA in these effluents.
 - b. The studies will need to represent the maximum HP and PAA application rates for all wastewater effluent treatment uses that are proposed on the labels.
 - c. The studies should include sites in which the treated effluent water holding or contact time represents the shortest real-world intervals that the treated effluent water will be held before being released into receiving water bodies.
 - d. The residue data should reflect the analysis of the treated wastewater for HP and PAA, acetic acid and any other degradates that may be present and of toxicological interest as a result of the HP-PAA treatment. The analytical method must be validated at these levels by fortifying untreated samples with the analytes of interest at this level.

No residue data for treated wastewater were submitted as requested at the pre-registration meeting described above. Presumably, these data will be generated as a part of the requested EUP. Residue data reflecting the maximum proposed application rate for the treatment of storm water overflow and from sewage treatment for both hydrogen peroxide and for peroxyacetic acid are needed.

Information on the decay of peroxyacetic acid and hydrogen peroxide in water are reported in a study entitled, "Decay Kinetics of Peroxyacetic acid (PAA) and Hydrogen Peroxide (Persan[®], EPA #63838-2) in a Variety of Water Matrices", MRID# 466960-06. The study author was Jonathan Howard, P.h.D., Enviro Tech Chemical Services, Inc., Modesto CA 95358. The study completion date was 20 August 2003. The study does not meet the requirements of 40 CFR 160, Good Laboratory Practices in that no formal protocol was written prior to commencement of laboratory work. The waters used in the decay study did

not appear to represent sewage water. The water used would presumably represent a worst case for sewage water vs stormwater.

Three different water sources were used in the experiment. Dosage levels for both PAA and HP in water were 1 and 20 ppm. The waters used were: a moderately hard EPA water, a very hard EPA water and seawater. The pH, conductivity, total alkalinity, and total hardness were determined for the waters. The decay of the HP and the PAA were monitored for 96 hours. All analytical measurements for PAA were terminated when the PAA concentration reached the detection limit of the analytical method.

The analytical method utilized was the method described above, "Determination of Peracetic Acid (PAA) and Hydrogen Peroxide (H_2O_2) in Water".

The results of the study are submitted in the form of graphs which are plotted as time vs analyte level in terms of ppm in the water.

The study results show that:

1. For the low 1 ppm dose of PAA in seawater, the PAA level was nearly depleted after about 4 hours (level ~ 0.05 ppm). For the low level dose of PAA in moderately and very hard waters, PAA levels after spiking with 1 ppm PAA were on the order of 0.6 ppm after 300-350 minutes.
2. For long-term monitoring of 1 ppm PAA in all three waters, the PAA level in sea water had declined to less than 0.1 ppm after ~ 4 hours. In the hard waters, PAA had declined to less than 0.1 ppm at approximately 40 hours.
3. For short term monitoring of the 20 ppm PAA in seawater, the PAA level in seawater declined to ~ 0.05 ppm after about 120 minutes. In the hard waters, PAA levels were much more stable and were ~15-16 ppm after 250 minutes.
4. For the long term monitoring of PAA, the PAA level in sea water had declined to less than 0.1 ppm in less than 4 hours. In the moderately hard water, PAA had declined to ~ 5 ppm at approximately 100 hours. The decline of PAA in very hard water was rapid after 40 hours; the registrant attributes this to a contaminant in the study sample.
5. For HP, there was little decline of HP residues in any of the three waters at either the 1 ppm or the 20 ppm spike levels. This was true for all time periods out to and including the 96 hour time interval.
6. The registrant has calculated half-life of PAA in the three waters at both the 1 ppm and the 20 ppm spike levels. The half life of PAA ranged from an interval of 12 minutes in seawater spiked at 20 ppm to 30 hours in moderately hard and very hard water spiked at the 20 ppm level.

7. No half life was calculated for HP in water because the HP level in none of the waters declined by any appreciable amount over the 96 hour period of the study.

The persistence and half lives reported and calculated above are not in agreement with what EPA has previously assumed for the persistence and rapid decay of both PAA and HP in our earlier reviews for these chemicals. Both chemicals are more persistent in water than the Agency had previously believed.

It is important for the registrant to generate residue data reflecting the use of this product on both chemicals under both the storm water and the sewage uses. The registrant should also submit any other available data to the agency, e.g. (European studies, Columbus Water Works Columbus, Georgia CSO study, Ohio EPA sanctioned PAA-wastewater disinfection studies, etc.

Information on the decomposition of peroxyacetic acid and hydrogen peroxide in soil are reported in a study entitled, "The Environmental Fate and Impact of Perasan™ and Perasan™ 'A' (Equilibrium mix of Peroxyacetic Acid and Hydrogen Peroxide) in Soil", no MRID#. The study author was Jonathan Howard, P.h.D., Enviro Tech Chemical Services, Inc., Modesto CA 95358. The study completion date was 31 December, 2003. The study does not have a GLP page. Perasan contains 15% PAA and 22% HP. Perasan 'A' contains 5.6% PAA and 27% HP.

The study consists of soaking a sandy loam soil from Central valley, CA, with a solution of Perasan containing 1027 ppm of PAA and 1468 ppm of HP.

The registrant states that peroxygen-based compounds in various agricultural applications. This study was performed to assess the the environmental fate and impact of Perasan in soil. **Because the does not have GLP page and no mention is made about the conduct of the study, RASSB considers this study to be only supplemental information.**

The soil was saturated with a solution of Perasan 15 containing 1027 ppm of PAA and 1468 ppm of HP. The decay rates of both chemicals were followed. Another sample of the same soil was then saturated with a 1.5% solution of Perasan 5.6

The pH and the conductivity of the treated soils were monitored for several hours and compared with an untreated soil sample. The pH and the conductivity were monitored for 9 days.

Analyses of the Perasan 5.6-treated saturated soil were conducted with a calibrated pH-conductivity probe (Hanna Instruments HI 9812 pH-EC-TDS meter).

Analyses of the Perasan -15-treated saturated soil samples were taken for analysis of PAA and HP utilizing the DPD method, (previously described in this memo).

The registrant reports the following results for the Perasan 5.6-treated soil:

1. The pH of untreated soil was measured at 6.2 compared to the treated soil at 4.7.
2. The soil conductivity was $1900 \mu\text{Scm}^{-1}$ for the saturated soil compared to a conductivity of $750 \mu\text{Scm}^{-1}$ for untreated soil (a siemen is a moh and is 1/ohms, Also note that moh is ohm spelled backward.).
3. Both the pH and the conductivity return to the same values as untreated soils after 9 days.

The registrant attributes this change to the degradation of the acetate ion. RASSB concurs with this conclusion.

4. Both PAA and HP are degraded from the saturated soil 20 minutes after contact.
5. Two-thirds of the PAA was degraded one minute after contact and after 13 minutes, only 0.33 ppm PPA remained of the 1027 ppm dose.

RASSB considers these soil data as only supplemental data.