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(54) Title: ORGANOBORON WASTE STREAM TREATMENT USING HYDROGEN PEROXIDE

(57) Abstract: A process for the treatment of aqueous waste streams having a pH of 5 to 11 and containing organoboron compounds of the formula  $R_4B^{-1}M^{+}$  with hydrogen peroxide in order to convert such organoboron compounds to boric acid and organic compounds.



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**TITLE**

Organoboron Waste Stream Treatment Using Hydrogen  
Peroxide

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**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to the treatment of  
10 aqueous waste streams containing organoboron compounds  
in order to convert the organoboron compounds to boric  
acid and organic compounds. In particular, this  
invention relates to the hydrolysis of phenylated boron  
compounds to boric acid and benzene.

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**2. Description of Related Art**

Organoboron compounds, such as triphenylborane,  
are suitable for use as promoters in the hydrocyanation  
of butadiene. Arylboron compounds used in  
20 hydrocyanation reactions can be prepared by the process  
described in U.S. Patents 4,046,815 and 4,076,756. The  
preparation of such compounds can produce an aqueous  
waste stream that contains various amounts of  
organoboron compounds. For environmental reasons, it  
25 is desirable to reduce the level of organoboron  
compounds in such streams.

U. S. Patent 5,709,841 discloses a process in  
which aqueous waste streams containing organoboron  
compounds of the formula  $R_3B$ ,  $R_4B^{-1}$ , and  $R_2BOH$  are  
30 treated to hydrolyze the compounds to boric acid and  
the corresponding hydrocarbons. The process involves  
treatment of the waste streams to adjust the pH of the  
stream to a value between 5 and 9 and elevating the  
temperature to at least 150° C, at a pressure  
35 sufficiently high to prevent substantial evaporation of  
the aqueous solution. This process may not be  
sufficient for complete  $R_4B^{-1}$  hydrolysis within a  
reasonable period of time.

U.S. Patent 4,840,765 discloses a process for acid  
40 hydrolysis of 4PBS (sodium tetraphenylborate) contained

in nuclear waste. The hydrolysis is performed in the presence of a copper(II) cation catalyst and formic acid.

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#### BRIEF SUMMARY OF THE INVENTION

The present invention is a process for treating an aqueous waste stream containing an organoboron compound of the formula  $R_4B^{-1}M^+$ , comprising adjusting the pH of  
10 said stream to a value between 5 and 11, and contacting said stream with hydrogen peroxide at a temperature of at least 150° C;

wherein:

R is selected from the group consisting of phenyl,  
15 ortho-tolyl, para-tolyl, naphthyl, para-methoxyphenyl, para-aminophenyl and biphenyl, and wherein R is optionally substituted with Br or Cl, and  
 $M^+$  is selected from the group consisting of  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $Li^+$ ,  $H^+$ , and  $Cs^+$ .

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#### DETAILED DESCRIPTION OF THE INVENTION

Aqueous waste streams containing  $R_4B^{-1}M^+$  may result from preparing triphenylboron by the method described in U.S. Patent 4,046,815. Organoboron compounds of the  
25 formula  $R_3B$ ,  $R_2BOH$ , and  $RB(OH)_2$  also are typical components of such waste streams. The  $R_4B^{-1}$  compound requires a counter ion,  $M^+$ . Typically  $M^+$  is  $Na^+$ . The organic groups (R) of  $R_4B^{-1}M^+$  can be the same or different. R can be aryl or substituted aryl having 6  
30 to 12 carbon atoms. Examples of such R groups are phenyl, orthotolyl, paratolyl, naphthyl, para-methoxyphenyl, para-aminophenyl, biphenyl, chlorophenyl, and bromophenyl. Such waste streams will usually contain, in addition to the organoboron  
35 compound(s), (1) alkali metal halides, (2) lower alkyl alcohols (ie, those with 1 to 6 carbon atoms), and (3) boric acid.

The aforementioned waste streams containing the organoboron compounds can be treated to hydrolyze the

organoboron compounds to boric acid and an organic compound, and then subjected to a distillation to remove the resulting organic compound (benzene, for example, in the case of phenylated boron compounds). The resulting product is then amenable to biotreatment. It is important that substantially all of the organoboron content is hydrolyzed prior to biotreatment. Compounds of the formula  $R_4B^{-1}M^{+}$  (sodium tetraphenylborate, for example) are particularly difficult to hydrolyze. Sodium tetraphenylborate can inhibit wastewater biotreatment systems.

The addition of hydrogen peroxide to the hydrolysis reaction increases the extent of hydrolysis of the  $R_4B^{-1}$  compounds. This makes the hydrolysis product more amenable to bio-processing.

Hydrogen peroxide is preferred over other oxygen sources because of its high solubility which allows 200 ppm or greater levels to be used in the process. Preferably, the concentration of hydrogen peroxide is at least 200 ppm. More preferably, the concentration is greater than 2000 ppm.

The hydrolysis reaction can be performed at a pH of 5 to 11. The temperature should be at least 150°C. Preferably, the temperature is 200 to 250°C. The preferred pressure of the hydrolysis is 150 to 4000 psig (1.14 to 27.7 MPa). Preferably, the pressure is chosen to minimize vaporization of the aqueous solution.

Optionally, a metal catalyst may be used to promote the hydrolysis of  $R_4B^{-1}$  compounds. However, due to potential bio-toxicity issues, it is preferred that no such catalyst be used.

The present process is amenable to the aforementioned  $R_4B^{-1}M^{+}$  compounds in which  $M^{+}$  is  $K^{+}$ ,  $NH_4^{+}$ ,  $Li^{+}$ ,  $H^{+}$ , and  $Cs^{+}$ . It is also applicable to organoboron compounds in which the R groups are substituted with Br or Cl.

### EXAMPLES

Examples 1 to 3 were carried out in 10 ml, 316 stainless steel, mini-bomb reactors heated by a 200°C sand bath. Ten reactors, charged with 6 ml each of identical 4PBS (sodium tetraphenylborate) solutions, were simultaneously placed in the 200°C bath and then removed intermittently at predetermined times. In all runs, solution pH was maintained at about 9.3 using a buffer solution made by mixing 882 ml of 0.1N NaOH solution with 9.27g H<sub>3</sub>BO<sub>3</sub>, and diluting to 1000 ml total volume with de-ionized water.

#### Example 1

A solution containing 2000 ppm sodium tetraphenylborate (4PBS) in pH 9.3 buffer solution declined to about 600 ppm 4PBS after 120 minutes holdup time. For comparison, this experiment was repeated, except that 200 ppm H<sub>2</sub>O<sub>2</sub> was present. In this latter case, the final 4PBS concentration was about 3 ppm.

#### Example 2

A solution containing 2000 ppm 4PBS in pH 9.3 buffer solution (with 1 mL second phase benzene added) declined to about 700 ppm 4PBS after 120 minutes. For comparison, this experiment was repeated, except that 200 ppm H<sub>2</sub>O<sub>2</sub> was present. In this latter case, the final 4PBS concentration was about 60 ppm.

#### Example 3

A solution containing 2000 ppm 4PBS in pH 9.3 buffer solution with 1 ml of second phase organics containing about 90% benzene plus cyclohexane, about 6-12% isopropanol, and about 1% other organics such as phenylisopropanol, phenol, and biphenyl, declined to about 1300 ppm 4PBS after 140 minutes. For comparison this experiment was repeated except that 200 ppm H<sub>2</sub>O<sub>2</sub> was present. In this latter case, the final 4PBS concentration was about 10 ppm.

What is claimed is:

- 5 1. A process for treating an aqueous waste stream  
containing an organoboron compound of the formula  $R_4B^{-1}$   
 $M^+$ , comprising adjusting the pH of said stream to a  
value between 5 and 11, and contacting said stream with  
hydrogen peroxide at a temperature of at least 150° C;  
10 wherein:  
R is selected from the group consisting of phenyl,  
ortho-tolyl, para-tolyl, naphthyl, para-methoxyphenyl,  
para-aminophenyl and biphenyl, and wherein R is  
optionally substituted with Br or Cl, and  
15  $M^+$  is selected from the group consisting of  $Na^+$ ,  $K^+$ ,  
 $NH_4^+$ ,  $Li^+$ ,  $H^+$ , and  $Cs^+$ .
2. The process of claim 1 wherein the concentration  
of hydrogen peroxide is at least 200 ppm.  
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3. The process of claim 2 wherein the temperature is  
200 to 250°C.
4. The process of claim 3 wherein  $R_4B^{-1} M^+$  is sodium  
25 tetraphenylborate.
5. The process of claim 4 wherein the concentration  
of hydrogen peroxide is at least 2000 ppm.

## INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C02F1/72 C02F1/58

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 709 841 A (REIMER RONALD ANTHONY) 20 January 1998 (1998-01-20) cited in the application claims ---	1
A	US 5 868 945 A (AGHAZEYNALI HOSSEIN ET AL) 9 February 1999 (1999-02-09) claims; examples ---	1
A	US 5 564 105 A (GRANT DAVID C ET AL) 8 October 1996 (1996-10-08) claims -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

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