

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 November 2002 (14.11.2002)

PCT

(10) International Publication Number
WO 02/090268 A1

(51) International Patent Classification⁷: C02F 1/72, 1/58

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/US02/14122

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date: 2 May 2002 (02.05.2002)

Published:

(25) Filing Language: English

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(26) Publication Language: English

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(30) Priority Data:
09/850,549 7 May 2001 (07.05.2001) US

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WO 02/090268 A1

(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.

TITLEOrganoboron Waste Stream Treatment Using Hydrogen
Peroxide

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BACKGROUND OF THE INVENTION1. 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 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, 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⁺, NH₄⁺, 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 formula R₃B, R₂BOH, and RB(OH)₂ also are typical components of such waste streams. The R₄B⁻¹ compound requires a counter ion, M⁺. Typically M⁺ is Na⁺. The organic groups (R) of R₄B⁻¹M⁺ can be the same or different. R can be aryl or substituted aryl having 6 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 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 10 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 15 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. 20 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. 25 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 30 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^+ , 35 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 H₃BO₃, and diluting to 1000 ml total volume with de-ionized water.

Example 1

15 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 H₂O₂ was present. In this latter 20 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) 25 declined to about 700 ppm 4PBS after 120 minutes. For comparison, this experiment was repeated, except that 200 ppm H₂O₂ was present. In this latter case, the final 4PBS concentration was about 60 ppm.

Example 3

30 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 35 phenylisopropanol, phenol, and biphenyl, declined to about 1300 ppm 4PBS after 140 minutes. For comparison this experiment was repeated except that 200 ppm H₂O₂ 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^+ .

20 2. The process of claim 1 wherein the concentration of hydrogen peroxide is at least 200 ppm.

3. The process of claim 2 wherein the temperature is 200 to 250°C.

25 4. The process of claim 3 wherein $R_4B^{-1} M^+$ is sodium tetraphenylborate.

5. The process of claim 4 wherein the concentration of hydrogen peroxide is at least 2000 ppm.

INTERNATIONAL SEARCH REPORT

Inter Application No
PC1/US 02/14122A. 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 (AGHAZENALI 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.

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Date of the actual completion of the international search

Date of mailing of the international search report

20 September 2002

01/10/2002

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern'l Application No
PCT, US 02/14122

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5709841	A 20-01-1998	CA CN DE DE EP ES JP JP WO	2244948 A1 1211931 A 69704930 D1 69704930 T2 0881924 A1 2158500 T3 3285878 B2 11504262 T 9730759 A1	28-08-1997 24-03-1999 28-06-2001 28-03-2002 09-12-1998 01-09-2001 27-05-2002 20-04-1999 28-08-1997
US 5868945	A 09-02-1999	CA	2203201 A1	28-02-1998
US 5564105	A 08-10-1996	WO	9637442 A1	28-11-1996