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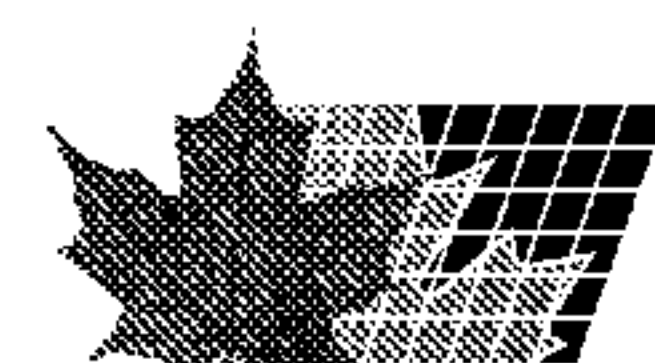
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(54) Titre : PROCESSUS DE GENERATION DE DIOXYDE DE CHLORE A BASE DE PEROXYDE D'HYDROGENE
(54) Title: HYDROGEN PEROXIDE-BASED CHLORINE DIOXIDE GENERATION PROCESS

(57) **Abrégé/Abstract:**

Chlorine dioxide is produced at high efficiency in a continuous process effected using hydrogen peroxide as the reducing agent in a single vessel generator-evaporator-crystallizer at the boiling point of the reaction medium under sub-atmospheric pressure. The reaction medium is maintained under steady state continuous operation with a residual chlorine concentration while having no residual hydrogen peroxide concentration in the reaction medium.



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(54) Title: HYDROGEN PEROXIDE-BASED CHLORINE DIOXIDE GENERATION PROCESS

(57) Abstract: Chlorine dioxide is produced at high efficiency in a continuous process effected using hydrogen peroxide as the reducing agent in a single vessel generator-evaporator-crystallizer at the boiling point of the reaction medium under sub-atmospheric pressure. The reaction medium is maintained under steady state continuous operation with a residual chlorine concentration while having no residual hydrogen peroxide concentration in the reaction medium.

TITLE OF INVENTIONHYDROGEN PEROXIDE-BASED CHLORINE DIOXIDE GENERATION PROCESSFIELD OF THE INVENTION

[0001] The present invention is concerned with the production of chlorine
5 dioxide by reduction of acidified chlorate ion solution, using hydrogen peroxide as
the reducing agent, and in particular with the production of substantially pure
chlorine dioxide where the reaction medium under steady-state conditions
contains a residual chlorine concentration.

BACKGROUND TO THE INVENTION

10 [0002] It is known to produce chlorine dioxide by reduction of an acidified
chlorate ion solution, using various reducing agents, such as chloride ions, sulfur
dioxide, methanol, hydrogen peroxide, etc. Such processes are typically carried
out continuously, preferably in a single vessel generator-evaporator-crystallizer. A
single-vessel process (SVP) involving the use of hydrogen peroxide as a reducing
15 agent is described in numerous patents and publications.

[0003] U.S. Patent No. 4,421,730 (Isa et al) discloses a hydrogen
peroxide-based chlorine dioxide generation process which requires the reduction
to be effected in the presence of chloride ions and a complex palladium (II)
catalyst in order to achieve commercially attractive production rates. According to
20 Isa, a residual concentration of hydrogen peroxide has to be maintained
continuously in the reaction medium under steady-state conditions in order to
minimize the product contamination with chlorine.

[0004] U.S. Patent Nos. 5,091,166 (Engstrom et al) and 5,091,167
(Engstrom et al) describe hydrogen peroxide based SVP type processes carried out
25 at two different acidity ranges. U.S. Patent No. 5,091,166 covers the acidity range
2 to 5N, whereas U.S. Patent No. 5,091,167 covers the acidity range 5 to 11N.
Both these patents constitute the basis of the commercial chlorine dioxide
generation process marketed under the trade name SVP-HPTM. According to the
literature describing the SVP-HPTM process, such an operation requires a residual
30 hydrogen peroxide concentration to be maintained continuously in the range of
0.01 to 0.1 M in order to overcome the kinetic limitations of the chlorine dioxide
generation reaction, as described, for example, in Burke et al, The Chemical

Engineering Journal, 60 (1995) 101-104, "Rate of reaction of chlorine dioxide and hydrogen peroxide"; Sokol "Peroxide-Based ClO₂ Process", presented in January 1993 at the 79th Annual Meeting of Canadian Pulp and Paper Association.

5 [0005] The SVP-HPTM process described in the two above-mentioned patents also is reported to suffer from an excessive foam formation leading to a decrease of chlorine dioxide yield when utilizing such process.

[0006] Canadian Patent No. 2,144,468 (Falgen et al) which shares a common assignee with the latter two above-mentioned U.S. patents, suggests a remedy to the excessive foaming problem by minimizing the steady-state
10 concentration of tin-based stabilizer of hydrogen peroxide in the reaction medium. However, the control of tin content in the reaction medium is not easily achievable. A specific recommendation stated in that patent, namely a reduction of the tin concentration in the hydrogen peroxide feed solution, may result in the destabilization of the feedstock, thus creating an unsafe situation.

15 [0007] U.S. Patent No. 5,366,714 (Bigauskas) proposes the premixing of hydrogen peroxide feed solution with at least one another feedstock (alkali metal chlorate or strong mineral acid) as a remedy to the excessive foaming problem experienced by the SVP-HP process. This introduces an additional step to the overall process which may not always be feasible or practical.

20 SUMMARY OF THE INVENTION

[0008] It has been surprisingly found that the above-described deficiencies of the prior art processes can be obviated or mitigated and a high efficiency and yield of chlorine dioxide production can be achieved by carrying out a subatmospheric, hydrogen peroxide-based chlorine dioxide generation process in
25 such a manner as to continuously maintain in the reaction medium, at steady-state, a residual chlorine concentration, while at the same time having no residual hydrogen peroxide concentration in said reaction medium.

[0009] The high purity of the gaseous chlorine dioxide product resulting from such process was found to be unexpected, having regard to the teaching of
30 the prior art. It was generally believed, in the prior art, that the presence of residual hydrogen peroxide in conjunction with the absence of residual chlorine in

the reaction medium at steady-state is a necessary condition required in order to obtain a gaseous chlorine dioxide product of high purity.

GENERAL DESCRIPTION OF THE INVENTION

[0010] Production of chlorine dioxide by reduction of chlorate ion, generally provided in the form of chloric acid, sodium chlorate or mixtures thereof, using hydrogen peroxide, is effected herein in a continuous process in a reaction zone in which an aqueous acid reaction medium, generally using sulfuric acid as the acid source, is maintained at its boiling point, generally about 25 to about 100°C, under a subatmospheric pressure, generally of about 50 to about 400 mm Hg. Chlorine dioxide is removed from the reaction zone in aqueous admixture with steam and is recovered as aqueous solution thereof.

[0011] The process is operated continuously by feeding the source of chlorate ion, hydrogen peroxide and acid at flow rates sufficient to maintain steady state conditions in the reaction medium. The chlorate ion source may be provided by an aqueous solution of alkali metal or alkaline earth metal chlorate, chloric acid or a combination thereof. Preferably sodium chlorate is used as a source of chlorate ions. Typically sodium chlorate at a concentration of about 300 to about 800 g/L is used as the source of chlorate ions. The hydrogen peroxide feed may be provided by a conventional commercial source of aqueous hydrogen peroxide solution, for example, having a concentration of about 50% w/v and the acid source may be provided by a sulfuric acid solution having a concentration of about 10 N to about 36 N. Premixing of at least two feedstocks also is possible.

[0012] A catalyst, such as palladium, may be added to improve the efficiency of chlorine dioxide generation. When such catalyst is added, the amount is generally in the range of about 5 to about 50 ppm (as Pd).

[0013] A residual concentration of chlorine in the reaction medium at steady-state should be maintained continuously during the production of chlorine dioxide at the level of between about 0.1 to about 0.5 g/L, preferably about 0.2 to about 0.4 g/L. The continuous presence of residual chlorine in the reaction medium must be accompanied by the simultaneous absence of residual hydrogen peroxide, in order for high purity chlorine dioxide to be produced. Under such

conditions, the purity of the resulting gaseous chlorine dioxide product is typically about 98% or higher, while at the same time foam formation is minimized.

[0014] The residual chlorine in the reaction medium can be maintained either by adding chlorine from an external source or by generating chlorine in-situ, for example, by oxidizing chloride ions, for example, added with the sodium chlorate feed solution.

EXAMPLE

[0015] This Example illustrates the process of the invention.

[0016] A commercial sub-atmospheric pressure 8 T/D chlorine dioxide generator operating according to ERCO R11™ process conditions of a reaction temperature of 77.0 to 77.4°C, subatmospheric pressure of 190 to 200 mmHg, reaction medium composition of 3.5 to 3.75 or H₂SO₄ and 2.3 to 2.6 M NaClO₃ in the presence of a palladium catalyst at a concentration of 30 ppm (as Pd) was monitored over a period of sixty hours. Chemical feeds to the process were a NaClO₃/NaCl solution with a composition of 705 to 710 g/L NaClO₃/9.0 to 9.2 g/L NaCl and a commercial 50% aqueous H₂O₂ solution with a concentration of 610 to 620 g/L. Sulfuric acid feed had a concentration of 30 N.

[0017] The chlorine dioxide production performance parameters of chemical efficiency and chlorine dioxide purity observed during the entire trial were consistently above a target value of 98%. There was no observed foam formation during the trial. During the trial, the concentration of dissolved chlorine and hydrogen peroxide in the reaction medium were periodically monitored. The dissolved chlorine content was found to be no less than 0.2317 g/L and up to 0.3965 g/L, as determined by analysis of the gases stripped off the liquor. Permanganate tests on the stripped generator liquor samples indicated a non-detectable level of H₂O₂ during the entire trial.

[0018] Considering the fast reaction of Cl₂ with H₂O₂, the presence of Cl₂ in the stripped off gases appeared to necessarily lead to the absence of hydrogen peroxide from the generator liquor. Specific support for this statement was provided through laboratory tests in which there was increased the hydrogen peroxide concentration in 3.5 N H₂SO₄ acidified water solutions initially containing 0.225 g/L of chlorine. The concentration of H₂O₂ measured after its

addition and stripping of residual Cl_2 gas, remained undetectable by the permanganate method until the initial concentration of added H_2O_2 exceeded 0.056 g/L. At that point, the Cl_2 concentration of the solution had dropped below 0.0833 g/L, far below the residual levels determined in the generator liquor samples referred to above.

SUMMARY OF DISCLOSURE

[0019] In summary of this disclosure, the present invention provides a novel procedure for preparing chlorine dioxide using hydrogen peroxide as the reducing agent. Modifications are possible within the scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A continuous process for the production of chlorine dioxide, which comprises:
continuous reducing using hydrogen peroxide chlorate ion in an aqueous acid reaction medium which is maintained at its boiling point under a subatmospheric pressure while maintaining in the reaction medium a residual chlorine concentration in said reaction medium of 0.1 to 0.5 g/L while having no residual hydrogen peroxide concentration in said reaction medium.
2. The method of claim 1 wherein said concentration of chlorine in the reaction medium is 0.2 to 0.4 g/L.