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SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Improved Process for the Removal of Cyanide from Wastewaters

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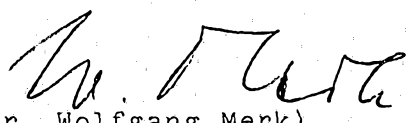
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do solemnly and sincerely declare as follows:-

1. I am/~~We are~~ authorised by Degussa Aktiengesellschaft, the applicant for the patent, to make this declaration on its behalf.
2. The basic application as defined by Section 141 of the Act was made in United States of America on 19 May 1989 by M. Quamrul Ahsan, Andrew Griffiths, Ernest Haug and Roy Norcross.
3. M. Quamrul Ahsan, Andrew Griffiths, Ernest Haug and Roy Norcross, of 85 West Prospect Street, Waldwick, New Jersey 07463; 343 Windsor Terrace, Ridgewood, New Jersey 07450; 91 Carol Street, #6, Ramsey, New Jersey 07446; and 44 Howard Avenue, Norwalk, Connecticut 06855, respectively and all in the United States of America are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The said applicant is the assignee of the invention from the actual inventors.
4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Frankfurt/Main this 12th day of June 19 90


(Dr. Wolfgang Merk)
Signature of Declarant

TO: THE COMMISSIONER OF PATENTS
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- (56) Prior Art Documents
US 3843516
US 3617567
US 3531405
- (57) Claim

1. A method for treating industrial wastewater containing cyanide for the conversion of cyanide toxic substances into non-toxic materials comprising contacting said wastewater with a source of hydrogen peroxide having a concentration between 35% and 90% by weight and phosphoric acid with a molar ratio between 0.05 and 0.3 moles of phosphoric acid per mole of hydrogen peroxide in a sufficient amount to oxidize said cyanide in the wastewater.

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FORM 10

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

Improved Process for the Removal of Cyanide from Wastewaters

The following statement is a full description of this invention, including the best method of performing it known to me/us

ABSTRACT OF THE DISCLOSURE

A process is disclosed for the detoxification of effluents containing cyanide by treating with a mixture of hydrogen peroxide and phosphoric acid.

IMPROVED PROCESS FOR THE REMOVAL OF CYANIDE FROM WASTEWATERS

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Background and Introduction

The present invention relates to a process for the detoxification of effluents containing cyanide and/or other oxidizable substances utilizing a mixture of hydrogen peroxide and phosphoric acid.

Wastewater from a variety of industrial processes pose a serious problem to the environment because of the presence of components in the wastewater that are harmful to the environment. Effluents from a variety of industrial processes often contain cyanide in various forms, such as simple cyanide and cyanide complexed with other toxic metals. The conversion of these toxic substances into non-toxic materials is of paramount importance before such wastewaters are discharged to the waterways in order to avoid serious damage to the environment, the aquatic life, and adverse impact on public health and safety.

A number of methods are currently available for the treatment of cyanide containing effluents. One of the best among the known methods for treating effluents containing cyanide and heavy metals, such as copper, zinc and nickel, involves the oxidation of cyanide contained in the wastewater with hydrogen peroxide. Heavy metals contained in such wastes are usually removed by precipitation as a part of the overall

process. The advantage of hydrogen peroxide over other chemical methods of cyanide destruction is that it adds no new substances to the environment except oxygen and water, unlike other processes which cause additional salt formation and the introduction of those salts into natural waterways.

5 In the case of effluents arising from ore-processing plants, the waste effluent often takes the form of so-called tailings pulp or slurry, wherein the proportion of solid may be 50% or even higher. In treatment of these pulps by hydrogen peroxide, a relatively large amount of hydrogen peroxide is sometimes required for treatment. In such cases, the economic viability of the detoxification process depends on reducing the consumption of treatment chemicals, especially hydrogen peroxide, as far as possible.

10 Several methods for reducing the amount of hydrogen peroxide are known. U.S. Patent 4,416,786 assigned to the same assignee as the present application, makes use of accurate measurement of oxidizing agent demand and the control of reagent dosage. U.S. Patent application 07/183,635, 15 assigned to the same assignee as the present application, involves the removal of magnetic materials before the treatment of pulp, since magnetic components have been found to cause catalytic decomposition of H_2O_2 and a corresponding increase in consumption.

However, in all of the above processes the consumption of hydrogen peroxide may be too high in many cases involving detoxification of cyanide (simple and metal complexed) in pulps or slurries that contain considerable amounts of solids.

- 5 There is, therefore, a need for a process which enables detoxification of cyanide containing effluents, especially a pulp or a slurry containing high amounts of solids, with economically viable amounts of hydrogen peroxide.

Summary of the Invention

- 10 According to a broad form of this invention, there is provided a method for treating industrial wastewater containing cyanide for the conversion of cyanide toxic substances into non-toxic materials comprising contacting said wastewater with a source of hydrogen peroxide having a concentration between 35% and 90% by weight and phosphoric acid
15 with a molar ratio between 0.05 and 0.3 moles of phosphoric acid per mole of hydrogen peroxide in a sufficient amount to oxidize said cyanide in the wastewater.

- 20 The present invention pertains to a method of treating cyanide contained in wastewater with particularly high levels of solid in the stream. The process involves mixing hydrogen peroxide, in the form of an aqueous solution of a concentration which is between 35% and 90%, preferably at least 50%, and phosphoric acid in the form of a concentrated industrial solution and adding this mixture to the clear wastewater or waste pulp/slurry containing solids.

- 25 A wide range of molar ratios between hydrogen peroxide and phosphoric acid may be used. According to the present invention, $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2$ molar ratio between 1:60 and 1:3 have been investigated resulting in a substantial reduction in the consumption of hydrogen peroxide when compared to using hydrogen peroxide alone.



Detailed Description of the Invention

The present invention pertains to the preparation of an oxidizing agent by mixing hydrogen peroxide at a concentration between 35% and 90%, preferably between 45% and 75%, by weight and phosphoric acid at a concentration of between 30% and 97%, preferably between 80% and 90%, in proportions that correspond to between 0.01 and 0.3 moles of phosphoric acid per mole of hydrogen peroxide, and preferably between 0.05 and 0.1 moles of phosphoric acid per mole of hydrogen peroxide, and includes but is not confined to the use of this mixture to oxidize contaminants in wastewater.

One embodiment of the present invention is carried out with the following steps for continuous treatment of wastewater containing cyanide and other contaminants arising from an ore-processing operation:

1. The effluent from an ore processing operation typically containing one or more heavy metals and cyanide, which may be a pulp or a slurry with up to 60% solid content, is allowed to flow through one or more detoxification tanks, each equipped with a propeller-type stirrer to agitate the effluent. The tanks are chosen in size and number to provide sufficient reaction time for the oxidation of contaminants which is typically between 5 minutes and 2 hours.

2. Aqueous hydrogen peroxide, at a concentration of between 35% and 90%, preferably between 45% and 75% by weight,

and phosphoric acid, at a concentration between 50% and 90%, preferably between 80% and 85% by weight, are mixed together before introduction to and contact with the waste effluent. This mixing of reactants can be accomplished in a number of ways.

For example: (a) the reagent may be premixed in a fixed ratio and the mixture is pumped directly into the detoxification tank at a set flow rate and (b) the reagents may be mixed immediately before introduction to and contact with the waste effluent. According to this mode of mixing, the hydrogen peroxide and phosphoric acid can be dosed in fixed proportions into a relatively small vessel with agitator, located at a point near the surface of the effluent in the first detoxification tank. As more liquid is pumped or allowed to flow into the small vessel, the mixture overflows into the detoxification tank.

Lime slurry or sodium hydroxide solution (preferably sodium hydroxide) is added to the effluent in order to maintain the pH between 9 and 12, preferably between 9.5 and 11.5. After oxidation of the cyanide and other oxidizable pollutants have been satisfactorily completed, further steps may be carried out in order to further purify the effluent. Such steps include, but are not limited to, the addition of copper (II) salts to precipitate ferrocyanide ions, or iron (III) salts to precipitate arsenic.

The reaction between the oxidizing mixture of H_3PO_4 and H_2O_2 with the cyanide may be accelerated by the addition of a catalyst, such as a soluble copper (II) salt, especially copper (II) sulfate pentahydrate, in an amount which yields a concentration of dissolved copper ion in the effluent between 5 and 500 parts per million.

In another embodiment of the present invention, the detoxification may be carried out in a batch mode. Such a method is suitable in cases where smaller quantities of cyanide containing effluent are produced as, for example, from steel hardening shops or electroplating operations.

Experimental Details

Preparation of Reagent

Several batches of mixtures of phosphoric acid (87% aqueous solution) and hydrogen peroxide (50% aqueous solution) were prepared by adding calculated volumes of both these reagents to a flask and stirring for 10-15 minutes. The mixing was carried out at ambient temperature. Table 1 shows the volumes of these reagents used and corresponding molar ratios of H_3PO_4 and H_2O_2 .

Detoxification Test

Each detoxification test was performed on 1 kg of pulp sample in a polyethylene container equipped with a

stirrer for continuous stirring. A definite volume of the mixtures (as described above) was introduced into the pulp and stirred for 20 minutes. All experiments were carried out at room temperature and the pH of the pulp was carefully monitored during the period of reaction. A portion of the sample was then removed, filtered and the residual cyanide content was determined using a spectrophometric method known as Picric acid method for cyanide analysis.

The invention is illustrated by the following examples.

Examples:

An ore processing effluent generated from a gold bearing ore from Alaska was treated according to the present invention and by hydrogen peroxide alone. The effluent was in the form of a slurry containing 50% solids by weight. The effluent contained 1150 ppm of cyanide in the form of free cyanide and cyanide complexes of zinc and copper. Table 2 contains a summary of the examples described here.

In Example 1, 1 kg of the above effluent was treated with 45.0 ml of 50% H_2O_2 alone and the final treated effluent contained a cyanide concentration of 13.5 ppm. In Example 2, 1 kg of the same effluent was treated with 14 ml of mixture G (Table 1), containing 10.0 ml of 50% H_2O_2 and 4.0 ml of 85% H_3PO_4 . The treated effluent in Example 2 contained a cyanide

concentration of only 1.3 ppm of cyanide. The mixture G (Table 1), therefore, resulted in a decrease of H_2O_2 consumption by 78%, at the same time producing a much better quality effluent (only 1.3 ppm CN compared to 13.5 ppm CN).

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Examples 3 through 16 describe tests that were performed on an effluent sample in the form of a pulp with 50% solids received from a gold mine in British Columbia, Canada. The effluent contained 664 ppm of cyanide in the form of free cyanide and cyanide complexes of zinc and copper. Mixtures prepared with various molar ratios as summarized in Table 1, were used in different amounts as shown in Table 2. Corresponding residual cyanide contents, after 20 minutes reaction time, are also listed in Table 2. All the examples show that mixtures of 85% H_3PO_4 and 50% H_2O_2 are more efficient in cyanide removal than when equivalent amounts of H_2O_2 alone are used.

Examples 3, 4 and 5 show the results of treating 1 kg of pulp with 3.5 ml, 5.0 ml, and 5.7 ml of 50% H_2O_2 alone, respectively, resulting in residual cyanide concentrations of 477 ppm, 476 ppm and 451 ppm, respectively. The best result was achieved by using 5.7 ml of 50% H_2O_2 alone; resulting in a residual cyanide concentration of 451 ppm, equivalent to 32% cyanide removal. In Example 8, a mixture of H_3PO_4 and H_2O_2 with molar ratio of 1:60 (mixture B, Table 1) is used to treat the same sample of pulp. By using 5.82 ml of the mixture,

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which contains 5.70 ml of 50% H_2O_2 and 0.12 ml 85% H_3PO_4 , resulted in a residual cyanide value of 320 ppm, which is equivalent to 52% destruction of cyanide from the above sample. Examples 6 and 7 show the results of using the same mixture B, but different amounts per kg of pulp.

Examples 12, 13 and 14 show the results of using a mixture of H_3PO_4 and H_2O_2 with 1:24 molar ratio (mixture E, Table 1). In Example 14, using 5.99 ml of the mixture E, containing 5.7 ml of 50% H_2O_2 and 0.29 ml H_3PO_4 , resulted in a residual cyanide value of 6.8 ppm, which is equivalent to 99% cyanide removal compared to 32% removal when 5.7 ml of 50% H_2O_2 alone is used according to Example 5.

Examples 15 and 16 show the results of using a mixture of H_3PO_4 and H_2O_2 with 1:20 molar ratio (mixture F, Table 1). Example 16 shows that using 5.293 ml of this mixture which contains 5.0 ml of 50% H_2O_2 and 0.293 ml of 85% H_3PO_4 results in 100% removal of cyanide, compared to 32% removal when 5.7 ml of 50% H_2O_2 alone is used, according to Example 5.

All of the above examples show dramatic improvement in cyanide removal by using mixtures of H_3PO_4 and H_2O_2 over that obtained by using H_2O_2 alone.

Examples 17 through 30 show the results of testwork on a pulp sample from a mine in Nevada. This pulp consisted of 50% solids and contained 356.0 ppm of cyanide in the form

of simple cyanide and cyanide complexed with copper and zinc. Examples 17 through 21 show the results of treating 1 kg of pulp with various amounts of 50% H_2O_2 alone. Residual cyanide analyses show very little cyanide removal even with a large excess of H_2O_2 .

Examples 22, 23 and 24 shows the results of using a mixture of H_3PO_4 and H_2O_2 with molar ratio of 1:60. Example 22 shows virtually complete removal of cyanide with a residual concentration of cyanide less than 0.1 ppm, while in Example 17 using an equivalent amount (15.69 ml) of 50% H_2O_2 alone, only about 15% of the cyanide is removed. Similar dramatic improvements in cyanide detoxification are shown in Examples 25 through 30.

Table 1

Synthesis of phosphoric acid and hydrogen peroxide mixtures at various molar ratios.

Designation	Volume of Reagents (ml)		Calculated molar ratios of H_3PO_4 and H_2O_2 in the mixtures
	85% H_3PO_4	50% H_2O_2	
Mixture A	0.0	100.0	0:1
Mixture B	2.0	100.0	1:60
Mixture C	3.0	100.0	1:40
Mixture D	4.0	100.0	1:30
Mixture E	5.0	100.0	1:24
Mixture F	6.0	100.0	1:20
Mixture G	40.1	100.0	1:3

TABLE 2

Consumption of reagents and results of treatment of effluent samples with hydrogen peroxide alone and with various mixtures of phosphoric acid and hydrogen peroxide

Examples	Molar ratio of H_3PO_4 and H_2O_2	Total volume of mixture used/kg of pulp (ml)	Volume of 85% H_3PO_4 in the mixture /kg pulp (ml)	Volume of 50% H_2O_2 in the mixture /kg of pulp (ml)	Concen- tration of residual cyanide (ppm)
Example 1	0:1	45.0	0.00	45.0	13.5
Example 2	1:3	14.0	4.0	10.0	1.3
Example 3	0:1	3.50	0.00	3.50	477.0
Example 4	0:1	5.00	0.00	5.00	476.0
Example 5	0:1	5.70	0.00	5.70	451.0
Example 6	1:60	3.57	0.07	3.50	399.0
Example 7	1:60	5.10	0.10	5.00	347.0
Example 8	1:60	5.82	0.12	5.70	320.0
Example 9	1:30	3.64	0.14	3.50	237.0
Example 10	1:30	5.20	0.20	5.00	156.0
Example 11	1:30	5.93	0.23	5.70	148.0
Example 12	1:24	3.68	0.18	3.50	198.0
Example 13	1:24	5.25	0.25	5.00	139.0
Example 14	1:24	5.99	0.29	5.70	6.8
Example 15	1:20	3.71	0.21	3.50	162.0
Example 16	1:20	5.29	0.29	5.00	< 0.1
Example 17	0:1	15.69	0.00	15.69	302.0
Example 18	0:1	15.00	0.00	15.00	350.0
Example 19	0:1	13.00	0.00	13.00	350.0
Example 20	0:1	9.00	0.00	9.00	350.0
Example 21	0:1	7.00	0.00	7.00	350.0
Example 22	1:60	16.00	0.31	15.69	< 0.1
Example 23	1:60	15.30	0.30	15.00	78.4
Example 24	1:60	7.14	0.14	7.00	161.0

	Example 25	1:40	13.39	0.39	13.00	0.1
	Example 26	1:40	9.27	0.27	9.00	3.4
	Example 27	1:40	7.21	0.21	7.00	161.0
5	Example 28	1:24	13.64	0.64	13.00	0.1
	Example 29	1:24	9.45	0.45	9.00	5.0
	Example 30	1:24	7.35	0.35	7.00	105.0

10 In some cases, the presence of phosphate in wastewater is a case for environmental concern. We expect that much of the phosphate arising from the use of phosphoric acid in the present process will be removed during and after the process by precipitation with calcium and ferric ions. In the event that a large excess of residual phosphate is present in the treated effluent, this excess phosphate can be removed by precipitation as calcium phosphate by the addition of lime slurry. Phosphate can be removed even more effectively by the addition of ferric ion (ferrifloc e.g. $F_2(SO_4)_3$) which will precipitate the phosphate as ferric phosphate.

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Further variations and modifications of the foregoing will be apparent to those skilled in the art and are intended to be encompassed by the claims appended hereto.

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The claims defining the invention are as follows:

1. A method for treating industrial wastewater containing cyanide for the conversion of cyanide toxic substances into non-toxic materials comprising contacting said wastewater with a source of hydrogen peroxide
5 having a concentration between 35% and 90% by weight and phosphoric acid with a molar ratio between 0.05 and 0.3 moles of phosphoric acid per mole of hydrogen peroxide in a sufficient amount to oxidize said cyanide in the wastewater.
2. A method according to claim 1 wherein the hydrogen peroxide is
10 mixed with phosphoric acid and the mixture is pumped directly into the cyanide containing wastewater at a desired flow rate.
3. The method according to claim 1 wherein the hydrogen peroxide and the phosphoric acid are mixed immediately before introduction to and contact with the wastewater.
- 15 4. The method according to any one of claims 1 to 3 wherein the phosphoric acid is at a concentration between 30 and 97%.
5. The method according to claim 4 wherein the concentration of phosphoric acid is between 80 and 90%.
6. The method according to any one of claims 2 to 5 wherein the
20 concentration of hydrogen peroxide is at least 50%.
7. The method according to any one of claims 1 to 6 wherein the ratio of phosphoric acid to hydrogen peroxide is between 1 : 60 and 1 : 3.
8. The method according to claim 7 wherein the proportions correspond to 0.01 and 0.3 moles of phosphoric acid per mole of hydrogen
25 peroxide.
9. The method according to claim 8 wherein the ratio is between 0.05 and 0.01 moles of phosphoric acid per mole of hydrogen peroxide.
10. The method according to any one of claims 1 to 9 wherein the cyanide containing wastewater contains up to 60% solids content.
- 30 11. The method according to any one of claims 1 to 10 wherein the wastewater flows through a plurality of detoxification tanks, each tank being equipped with a propeller-type stirrer to agitate the wastewater effluent, the reaction time for the oxidation of the cyanide containing contaminants being sufficient to accomplish essentially complete
35 oxidation.
12. The method according to claim 11 wherein the duration of the reaction is from 5 minutes to 2 hours.



13. The method according to any one of claims 1 to 12 wherein an alkaline material is added to the wastewater effluent in order to control the pH of the effluent solution between 9 and 12.

14. The method according to any one of claims 1 to 13 wherein the
5 oxidizing reaction of the cyanide is accelerated by the addition of a catalyst.

15. The method according to claim 14 wherein the catalyst is a soluble copper (II salt).

16. The method according to claim 15 wherein the catalyst is
10 copper (II) sulfate pentahydrate.

17. The method according to any one of claims 1 to 16 wherein any excess phosphate from the phosphoric acid is removed by treating with calcium hydroxide for precipitation.

18. The method according to any one of claims 1 to 16 wherein any
15 excess phosphate for the phosphoric acid is removed by adding ferric ion to precipitate the phosphate as ferric phosphate.

19. A method for treating industrial wastewater containing cyanide for the conversion of cyanide toxic substances into non-toxic materials which method is substantially as herein described with reference to any
20 one of the Examples.

20. Effluent whenever treated by the method of any one of claims 1 to 19.

DATED this SEVENTEENTH day of FEBRUARY 1992

Degussa Aktiengesellschaft

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



LMM/1311v