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PATENT REQUEST: STANDARD PATENT

We, NITTETSU MINING CO., LTD, being the person(s) identified below as the Applicant, request the grant of a standard patent to the person identified below as the Nominated Person, for an invention described in the accompanying complete specification.

Full application details follow.

Applicant: NITTETSU MINING CO., LTD
Address: 3-2 Marunouchi 2-chome Chiyoda-ku Tokyo 100 Japan

Nominated Person: NITTETSU MINING CO., LTD
Address: 3-2 Marunouchi 2-chome Chiyoda-ku Tokyo 100 Japan

Invention Title: "Process for recovering sulfuric acid from metallic sulfate-containing exhaust sulfuric acid"

Name(s) of Actual Inventor(s): Yasuie Mikami; Nobuyoshi Iyatomi
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Attorney Code: RI

BASIC CONVENTION APPLICATION(S) DETAILS

<table>
<thead>
<tr>
<th>Application No.</th>
<th>Country</th>
<th>Country Code</th>
<th>Date of Application</th>
</tr>
</thead>
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<tr>
<td>3-293126</td>
<td>JAPAN</td>
<td>JP</td>
<td>8 November 1991</td>
</tr>
</tbody>
</table>

We are not an eligible person described in Section 33 - 36 of the Act.

Drawing number recommended to accompany the abstract 2

Dated this 4 day of November 1992

By: Registered Patent Attorney

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NOTICE OF ENTITLEMENT
(To be filed before acceptance)

I/We - Masanobu NAKAGAMI
of NITTETSU MINING CO., LTD.
3-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100, Japan

being "the applicant/"authorised by the applicant in respect of an application for
a patent for an invention entitled _______________________
filed under Application No. ______________________, state the following:-

Part 1 - Must be completed for all applications.
The person(s) nominated for the grant of the patent:

( ) *is/are the actual inventor(s)

[✓] has, for the following reasons, gained entitlement from the actual inventor(s):

The inventors are employees of the applicant and by virtue
of the contract of service to the applicant has assigned
their rights in the invention to the applicant.

Part 2 - Must be completed if the application is a Convention application.
The person(s) nominated for the grant of the patent *is/are:

[✓] the applicant(s) of the basic application(s) listed on the patent request form

[ ] entitled to rely on the basic application(s) listed on the patent request form
by reason of the following:

Part 3 - Must be completed if the application was made under the PCT and
claims priority.
The person(s) nominated for the grant of the patent *is/are:

[ ] the applicant(s) of the application(s) listed in the declaration under Article 8
of the PCT

or

[ ] entitled to rely on the application(s) listed in the declaration under Article 8
of the PCT by reason of the following:

(continued over)
1. A process for regenerating a spent sulfuric acid containing metal sulfates characterized in that divalent iron ions in the spent sulfuric acid is oxidized into trivalent iron ions, hydrochloric acid is added to such a liquid and then solvent extraction is carried out.

3. A process for regenerating a spent sulfuric acid containing metal sulfates comprising:
   a first step for oxidizing bivalent iron ions in a spent sulfuric acid into trivalent iron ions;
   a second step for adding hydrochloric acid to such a liquid so that a molar fraction of chorine ions in the liquid is adjusted to at least 4 times that of iron ions;
   a third step for subjecting solvent extraction of the liquid
to remove impure metal ions such as iron ions;
a fourth step for concentrating the solution after solvent extraction to sulfuric acid concentration of 60-75% by weight to recover hydrochloric acid;
a fifth step for separating metal sulfates deposited at this time; and
a sixth step for concentrating the separated solution again to sulfuric concentration of not less than 80% by weight.
Invention Title:

"Process for recovering sulfuric acid from metallic sulfate-containing exhaust sulfuric acid"

The following statement is a full description of this invention including the best method of performing it known to us:-
1. Field of the Invention:

This invention relates to a process for recycling a spent sulfuric acid, for example, exhausted from the stage of producing titanium dioxide, by regeneration.

2. Description of the Prior Art:

Titanium dioxide has been used in a large quantity as a white pigment in paint industries and as a coloring material in various fields. As a process for producing titanium dioxide, a so-called "sulfate process" is most commonly known. In this process, ilmenite or titanium slag is milled into particles with particle sizes of not more than 200 mesh sieve pass, and then treated with concentrated sulfuric acid to give titanium sulfate solution. While adjusting the concentration by the addition of water or dilute sulfuric acid, scrap iron is added thereto in order to prevent the precipitation of iron ions contained as impurities, thereby reducing trivalent iron ions to bivalent.
iron ions, followed by allowing to cool to separate out ferrous sulfate. After removal of the separated substances, hydrolysis of the titanium sulfate solution gives titanium hydroxide, which is then filtered, washed, and finally calcinated to obtain titanium dioxide.

In these stages for producing titanium dioxide, a large quantity of spent sulfuric acid is chiefly exhausted in the stage of separation between the solid and liquid in titanium hydroxide. Conventionally, concerning the treatment process for the spent sulfuric acid, it was buried as gypsum or neutralized and then thrown out to the ocean. However, environmental problems have recently been being given a great deal of attention. Moreover, problems of securing a site to be filled up with the gypsum, and of requiring huge treating costs have been come up. How to deal with them is of important.

In order to deal with these problems, processes for recovering sulfuric acid from the spent sulfuric acid by separating of impurities from spent sulfuric acid have been suggested. For example, a process in which the spent sulfuric acid is concentrated as it is (Japanese Patent Publication Sho 46-5568, etc.) and a process in which the spent sulfuric acid is treated in combination of a vacuum
crystallization stage and a concentration stage are mentioned. Due to the deposition of a large quantity of metal sulfates, these processes are, however, problematic in that a desired highly concentrated sulfuric acid cannot be obtained.

More recently, Japanese Patent Laid-Open Hei 3-80103 and Hei 3-88718 disclose processes for removing impurities with solvent extraction method. Nevertheless, since a strongly acidic sulfuric acid solution is treated by means of a solvent extraction as it is in these processes, the actual efficiency for extracting iron ions is not so good as described in these patent applications. Moreover, the iron content thus recovered has low purity. Furthermore, these applications suggest the recovery of iron ions using methyl isobutyl ketone, but it is impossible to directly extract trivalent iron ion with such a neutral extracting agent as methyl isobutyl ketone, in which case the iron is extracted as a complex such as a chloride complex. Also, in the case where an acidic extracting agent is utilized in order to directly extract trivalent iron ions from the sulfuric acid solution, multi-stage extraction is necessarily involved due to its low extraction ratio.

SUMMARY OF THE INVENTION
An object of the present invention is to solve the above-mentioned problems and to provide a process for regenerating highly concentrated sulfuric acid from a spent sulfuric acid containing metal sulfates which is discharged in a large quantity, for example, from a spent liquid of acid washing or in the case of producing titanium dioxide by the sulfuric acid method.

Another object of the present invention is to attain the prevention of environmental pollution by effectively recovering a highly concentrated sulfuric acid from a spent sulfuric acid containing metal sulfates in a closed system.

Still another object of the present invention is to designate an available utilization of resource by recovering iron, titanium, etc. as by-products.

In order to solve these object, the present invention suggests the oxidization of bivalent iron ions in a spent sulfuric acid containing metal sulfates to trivalent iron ions followed by addition of hydrochloric acid to such a liquid and solvent extraction.

In particular, the regeneration of a spent sulfuric acid is suggested by the present invention, which
comprises a step for oxidizing bivalent iron ions in a spent sulfuric acid containing metal sulfates to trivalent iron ions; a step for adding hydrochloric acid to the liquid so that a molar fraction of chlorine ion in the liquid is adjusted to at least 4 times that of iron ions; a step for subjecting solvent extraction of the liquid to remove impure metal ions such as iron ions; a step for concentrating the solution after solvent extraction to a sulfuric acid concentration of 60-75% by weight to recover hydrochloric acid; a step for separating metal sulfates deposited at this time; and a step for concentrating the separated solution again to a sulfuric concentration of not less than 80% by weight.

The basic conception of the process for regenerating spent sulfuric acid containing metal sulfates according to the present invention is to effectively remove main impure metal ions, such as iron, titanium, and manganese, contained in the spent sulfuric acid and to concentrate the solution to regenerate it into a highly concentrated sulfuric acid.

In the impure metal ions, iron ions exist in a large amount as bivalent ions particularly. The removal of the bivalent iron ions is essential for effective
regeneration of the spent sulfuric acid. However, since the removal of the bivalent iron ions directly by solvent extraction treatment can be carried out only with great difficulty, the bivalent iron ions are first oxidized to the trivalent iron ions, and the trivalent iron ions are then removed by solvent extraction treatment. At this time, hydrochloric acid is added to the spent sulfuric acid to substitute the metal sulfates with chlorine ions, thereby giving an iron chloride complex, after which the solvent extraction is carried out. It has been found that such a procedure can extract more than 99% of iron ions, the extraction being more effective than the solvent extraction where the spent sulfuric acid is extracted as it is.

It has been also found that iron ions and titanium ions can be individually separated when a plurality of extracting agents are used in the solvent extraction treatment.

In the present invention, as the method for oxidizing the bivalent iron ions in the spent sulfuric acid, either a usual oxidation with chlorine or an oxidation by electrolysis may be used. Furthermore, an oxidation with air may also be utilized. In this oxidation step, for example, in the case of the oxidation with chlorine, the following reaction takes place by blowing a chlorine gas into the spent
sulfuric acid in a stoichiometric or excess amount relative to the divalent iron ions contained in the spent sulfuric acid, thereby oxidizing 99% or more of the bivalent iron ions with ease.

\[ 2\text{Fe}^{2+} + \text{Cl}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{Cl}^- \]

In the case of the oxidization with chlorine, the chlorine ions dissolved in the solution are recovered in a concentration step and then recycled.

To the spent sulfuric acid after the oxidization treatment is then added hydrochloric acid, followed by the solvent extraction treatment. In this case, the molar fraction of chlorine ions in the spent sulfuric acid is adjusted so as to be at least 4 times that of iron ions in the liquid. As shown in FIG. 1, it has been known that the extraction rate of trivalent iron ions in this solution is drastically decreased if the concentration of hydrochloric acid is less than 3 N (N = mol/L) and, therefore, the concentration of hydrochloric acid is desirably adjusted to be not less than 3 N.

The hydrochloric acid which has been added is recovered in the concentration step, and can be recycled.

The organic solvents which can be used for extracting impure metal ions such as trivalent iron ions from
the solution include acidic organophosphorus compounds, carboxylic acids, sulfonic acid, hydroxy oxime, oxine, beta-diketone, neutral phosphoric esters, phosphine oxide, ketones, alcohols, amines, and the like. These organic solvents can be used singly or in the mixture of them. In order to separate metal ions other than iron ions which are contained in a trace of amounts, it is very advantageous to jointly use several kinds of these solvents which may be used singly or in the mixture.

In this connection, benzene, chloroform, toluene, kerosine, n-hexane or the like may be utilized as a diluent to adjust the viscosity of the extracting agent. The choice of an appropriate diluent can improve the extracting ability of the organic solvent.

In carrying out this solvent extraction treatment, in order to separate trivalent iron ions and titanium ions respectively, the trivalent iron ions are first extracted from this solution with a ketone, an alcohol, a neutral phosphoric ester, or the like, and the titanium ions are then extracted with an acidic organophosphorus compound, a carboxylic acid, sulfonic acid, hydroxy oxime, or the like.

In order to preferentially extract the trivalent iron ions from the solution, for example, ketones are used to
carry out the extraction. In this case, methyl isobutyl ketone can particularly be used for the preferential extraction of the trivalent iron ions, but hardly extracts the titanium ions. Subsequently, acidic organophosphorus compounds are utilized to extract the titanium ions from the solution from which the trivalent iron ions have been extracted. In the acidic organophosphorus compounds, di(2-ethylhexyl) phosphoric ester is particularly desirable.

The trivalent iron ions extracted with methyl isobutyl ketone are stripped with water and recovered as the hydroxide thereof. After the recovery, iron oxides can be obtained by calcining. They can be used as coagulants or raw materials for ferrite. In the case of the back extraction of the trivalent iron ions, chlorine ions which are partially extracted together with the trivalent iron ions are also reversely extracted and are contained in the reversely extracted solution. The chlorine ions can be recovered as hydrochloric acid by adding sulfuric acid to the solution to carry out substitution followed by concentration.

The titanium ions extracted with di(2-ethylhexyl) phosphoric ester are stripped with a hydrofluoric acid solution or an alkaline solution such as sodium hydroxide, and are recovered as the hydroxide thereof, etc. After the
recovery, titanium oxide can be obtained by calcination. This can be used as a raw material for titanium.

In the present invention, the spent sulfuric acid from which impure metal ions such as iron ions have been removed is then recovered in two stages for concentration as a sulfuric acid having a concentration of not less than 80% by weight.

Iron ions, titanium ions, as well as scandium can be removed by the above-mentioned solvent extraction treatment, but the removal of manganese ions, aluminum, etc. is difficult. They remain in the solution in considerable amounts. They are deposited as the corresponding metal sulfates, after hydrochloric acid is recovered by concentration the solution to a concentrating of sulfuric acid of 60-75% by weight, by allowing the solution to cool. In this case, manganese is removed as manganese sulfate monohydrate. Other metal ions contained in the solution in a trace of amounts are simultaneously removed as the corresponding metal sulfates. Subsequently, the concentration of the solution from which the metal sulfates are removed gives highly concentrated sulfuric acid having a concentration of sulfuric acid of not less than 80% by weight.

In the first stage for concentration, almost all
of hydrochloric acid can be recovered, and the recovered hydrochloric acid can be reused in the step for solvent extraction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a drawing showing the relationship between the concentration of hydrochloric acid and extraction ratios of iron ions and titanium ions, using methyl isobutyl ketone; and

FIG. 2 is a flow chart showing the treating process of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, the working examples of the present invention will be described, but, the present invention is not, of course, restricted these examples.

EXAMPLE 1

Into 5 liters of an spent sulfuric acid having composition comprised of 360 g/ℓ of sulfuric acid, 1 g/ℓ of trivalent iron ions, 38 g/ℓ of divalent iron ions, 2.9 g/ℓ
of titanium, and 5.3 g/\text{Q} of manganese, which had been
exhausted in a stage for producing titanium oxide was fed a
chlorine gas in an amount 1.5 equivalents relative to the
bivalent iron ions together with air to oxidize the bivalent
iron ions to trivalent iron ions. This gave 5 liters of an
oxidized solution having composition comprised of 360 g/\text{Q} of
sulfuric acid, 39 g/\text{Q} of trivalent iron ions, 0.0 g/\text{Q} of
bivalent iron ions, 2.9 g/\text{Q} of titanium, 5.3 g/\text{Q} of
manganese and 25 g/\text{Q} of chlorine.

To this solution were added 2.5 liters of
concentrated hydrochloric acid to adjust the solution to be
about 4 N hydrochloric acid solution. This gave 7.5 liters
of a solution having composition comprised of 240 g/\text{Q} of
sulfuric acid, 26 g/\text{Q} of trivalent iron ions, 1.9 g/\text{Q} of
titanium, 3.5 g/\text{Q} of manganese, and 158 g/\text{Q} of chlorine.
Subsequently, this solution was brought into contact with 10
liters of methyl isobutyl ketone, whereby trivalent iron ions
were selectively extracted and removed. The resulting
solution was then brought into contact with 10 liters of 1
mol/\text{Q} solution of di(2-ethylhexyl) phosphoric acid in
kerosine, whereby titanium ions were extracted. These
solvent extraction treatments gave 7.5 liters of a solution
having composition comprised of 240 g/\text{Q} of sulfuric acid,
0.01 g/\text{\textgreek{g}} of trivalent iron ions, 0.03 g/\text{\textgreek{g}} of titanium, 3.5 g/\text{\textgreek{g}} of manganese, and 92 g/\text{\textgreek{g}} of chlorine.

The trivalent iron ions extracted with methyl isobutyl ketone were reversely extracted with 10 liters of water to obtain an aqueous solution having composition comprised of 19 g/\text{\textgreek{g}} of iron and 49 g/\text{\textgreek{g}} of chlorine, and recovered as hydroxide. After the recovery, about 270 g of iron was recovered as iron (III) oxide (\text{Fe}_2\text{O}_3) by calcination. The recovery was about 97%.

The titanium ions extracted with 1 mol/\text{\textgreek{g}} solution of di(2-ethylhexyl) phosphoric acid in kerosine were reversely extracted with 10 liters of an aqueous 2 mol/\text{\textgreek{g}} of sodium hydroxide solution, and the formed hydroxide was recovered, after which it was calcined to recover about 23 g of titanium (IV) oxide. The recovery was about 95%.

The solution which had been treated with solvent extraction was concentrated at about 120°C and at 74 mmHg to sulfuric acid concentration of about 70% by weight to recover about 5.9 liters of hydrochloric acid (116 g/\text{\textgreek{g}} as chlorine). The concentrated solution was allowed to cool, and about 70 g of deposited metal sulfates (chiefly manganese sulfate monohydrate) were separated. Thereafter, the solution was concentrated at about 180°C and at 10 mmHg to recover 1.1
liters of about 82 wt% strength sulfuric acid solution having composition comprised of 1510 g/ℓ of sulfuric acid, 0.00 g/ℓ of trivalent iron ions, 0.04 g/ℓ of titanium, 3.5 g/ℓ of manganese and 0.02 g/ℓ or less of chlorine. The recovery of sulfuric acid was about 92%.

EXAMPLE 2

7 liters of an spent sulfuric acid having composition comprised of 450 g/ℓ of sulfuric acid, 1 g/ℓ of trivalent iron ions, 42 g/ℓ of divalent iron ions, 5.3 g/ℓ of titanium, and 5.2 g/ℓ of manganese were electrolytically oxidized to oxidize bivalent iron ions contained in the solution to trivalent iron ions. Subsequently, 3 liters of concentrated hydrochloric acid were added into it to adjust the solution to be about 3 N solution, thereby obtaining 10 liters of a solution having composition comprised of 315 g/ℓ of sulfuric acid, 30 g/ℓ of trivalent iron ions, 0.0 g/ℓ of divalent iron ions, 3.7 g/ℓ of titanium, 3.6 g/ℓ of manganese, and 128 g/ℓ of chlorine.

Subsequently, this solution was brought into contact with 20 liters of methyl isobutyl ketone, whereby trivalent iron ions were selectively extracted and removed. The resulting solution was then brought into contact with 20
liters of 1 mol/Q solution of di(2-ethylhexyl) phosphoric acid ester in kerosine, whereby titanium ions were extracted. These solvent extraction treatments gave 10 liters of solution having composition comprised of 315 g/Q of sulfuric acid, 0.00 g/Q of trivalent iron ions, 0.03 g/Q of titanium, 3.6 g/Q of manganese, and 50 g/Q of chlorine.

The trivalent iron ions extracted with methyl isobutyl ketone were reversely extracted with 30 liters of water to obtain an aqueous solution having composition comprised of 10 g/Q of iron and 26 g/Q of chlorine, and recovered as hydroxide. After the recovery, about 420 g of iron was recovered as iron (III) oxide (Fe₂O₃) by calcination. The recovery was about 98%.

The titanium ions extracted with 1 mol/Q solution of di(2-ethylhexyl) phosphoric acid ester in kerosine were reversely extracted with 20 liters of an aqueous 2 mol/Q of sodium hydroxide solution, and the formed hydroxide was recovered, after which it was calcined to recover about 60 g of titanium (IV) oxide. The recovery was about 97%.

The solution which had been treated with solvent extraction was concentrated at about 110°C and at 74 mmHg to a sulfuric acid concentration of about 65% by weight to recover about 6.9 liters of hydrochloric acid (72 g/Q as
chlorine). The concentrated solution was allowed to cool, and about 94 g of deposited metal sulfates (chiefly manganese sulfate monohydrate) were separated. Thereafter, the solution was concentrated at about 180 °C and at 10 mmHg to recover 2.0 liters of about 81 wt% strength sulfuric acid solution having composition comprised of 1490 g/L of sulfuric acid, 0.1 g/L of titanium, 3.2 g/L of manganese and 0.02 g/L or less of chlorine. The recovery of sulfuric acid was about 95%.

In addition to the above-mentioned examples, Table 1 shows the conditions of extraction rate of trivalent iron ions varied by the addition of hydrochloric acid. In the table, the volumetric ratio of the organic phase to the aqueous phase was 1:1, and all diluents except for methyl isobutyl ketone were diluted with kerosine. The conditions were the same as those of Example 2.
Table 1

Extraction Rate of Trivalent Iron Ions

<table>
<thead>
<tr>
<th>Concentration of Extracting Agent</th>
<th>Aqueous Phase Only</th>
<th>Oxidization + HCl Addition (Oxidizin Liq.:Conc.HCl = 1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc.</td>
<td>&lt;1%</td>
<td>99%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>Tributyl phosphate</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>2-Ethylhexyl 2-ethylhexylphosphonic acid (Trade Name:PC88A)</td>
<td>17%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>di (2-ethylhexyl) phosphoric acid (Trade Name:DP8R)</td>
<td>14%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>bis (2,4,4-trimethylpentyl) phosphinic acid (Trade Name:CYANEX 272)</td>
<td>11%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>Tertiary Amine (Trade Name:Alamine 336)</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>Hydroxy oxime (Trade Name:LIX63-70)</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>20 vol%</td>
<td>β-diketone (Trade Name:LIX54)</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for regenerating a spent sulfuric acid containing metal sulfates characterized in that divalent iron ions in the spent sulfic acid is oxidized into trivalent iron ions, hydrochloric acid is added to such a liquid and then solvent extraction is carried out.

2. The process according to Claim 1, characterized in that said solvent extraction is carried out as to trivalent iron ions and titanium ions individually.

3. A process for regenerating a spent sulfuric acid containing metal sulfates comprising:
   a first step for oxidizing bivalent iron ions in a spent sulfuric acid into trivalent iron ions;
   a second step for adding hydrochloric acid to such a liquid so that a molar fraction of chorine ions in the liquid is adjusted to at least 4 times that of iron ions;
   a third step for subjecting solvent extraction of the liquid to remove impure metal ions such as iron ions;
   a fourth step for concentrating the solution after solvent extraction to sulfuric acid concentration of 60-75% by weight to recover hydrochloric acid;
   a fifth step for separating metal sulfates deposited at this
time; and

a sixth step for concentrating the separated solution again
to sulfuric concentration of not less than 80% by weight.

4. The process according to Claim 3, characterized in

that said solvent extraction is carried out as to trivalent
iron ions and titanium ions individually.

DATED THIS 4th DAY OF NOVEMBER 1992
NITTETSU MINING CO., LTD
PATENT ATTORNEYS FOR THE APPLICANT
F B RICE & CO
FIG. 1

- Fe
- Ti

EXTRACTION RATE OF METAL IONS

HCL CONCENTRATION IN EXHAUST SULFURIC ACID (N)
FIG. 2

EXHAUST H₂SO₄

OXIDIZATION WITH CHLORINE

HCl ADDITION

SOLVENT EXTRACTION — STRIPPED

SOLVENT EXTRACTION — STRIPPED pH ADJUSTMENT

RECOVERY — CONCENTRATION OF Cl₂

SULFATES — FILTRATION

CONCENTRATION

HIGHLY CONCENTRATED H₂SO₄