Our Ref: 488 17

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Section 29

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PATENT REQUEST : STANDARD PATENT

I/We, being the person/s identified below as the Applicant, request the grant of a patent to the person/s indicated below as the Nominated Person/s, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] [70] Applicant/s and Nominated Person/s:
Kronos Titan GmbH,
of Peschstrasse 5, D-51373 LEVERKUSEN, GERMANY

[54] Invention Title:
Process for clearing a technical iron chloride solution by selective precipitation

[72] Name/s of actual inventor/s: (optional)

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BASIC CONVENTION APPLICATION/S DETAILS:

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Basic Applicant/s: Kronos Titan-GbmH

DATED this THIRTIETH day of NOVEMBER 1993

Kronos Titan GmbH
By Patent Attorneys
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Fee: $ 195.00

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Section 29(1)
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NOTICE OF ENTITLEMENT

KRONOS TITAN GMBH of Peschstrasse 5, D-51373 Leverkusen, Germany being the applicant/Nominated Person in respect of the Application No. 52065/93 state the following:

The Nominated Person is entitled to the grant of the patent because the Nominated Person derives title to the invention from the inventors, ACHIM HARTMANN, DR DIETER SCHINKITZ and DR ULRICH ROTHE by assignment.

The Nominated Person is entitled to claim priority from the basic application listed on the patent request form because the Nominated Person made the basic application listed on the patent request form, and because the basic application is the first application made in a Convention country in respect of the invention.

Dated this 10th day of January, 1995

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a member of the firm of
DAVIES COLLISON CAVE
for and on behalf of
the applicant(s).

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-52065/93
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(54) Title
PROCESS FOR CLEARING A TECHNICAL IRON CHLORIDE SOLUTION BY SELECTIVE PRECIPITATION

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(56) Prior Art Documents
US 5271910
US 5248497

(57) Claim

1. Process for removing waste water-charging metal ions from an acidic solution essentially containing iron(II)chloride from cyclone dust dissolved in diluted acid salts from the production of titanium dioxide according to the chloride process by raising of the pH value and separation of the metal hydroxides which have formed, characterised in that the solution is first adjusted to a pH value between 0.3 and 0.8 with a first neutralisation agent and then the thus buffered solution is metered into a recipient vessel with a second neutralisation agent in water or purified iron(II)chloride solution such that the pH value therein is maintained at or above a value of 2.0 and the second neutralisation agent is difficult to dissolve and is present in excess with respect to the metal ions to be precipitated and charged with waste water.

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

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Invention Title: Process for clearing a technical iron chloride solution by selective precipitation

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

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PROCESS FOR PURIFYING A TECHNICAL IRON CHLORIDE SOLUTION BY SELECTIVE PRECIPITATION

The present invention relates to a process for removing waste water-charging metal ions from an acidic solution essentially containing iron(II)chloride from cyclone dust dissolved in diluted acid salts from the production of titanium dioxide according to the chloride process by raising of the pH value and separation of the metal hydroxides which have formed.

Iron(II)chloride solutions are used as precipitation and flocculants in waste water purification (Hydraulic information of Kronos Titan-GmbH, Ferrofloc®). Iron(II)chloride accumulates in large quantities during the production of titanium dioxide according to the chloride process. In this process a raw material, such as titanium slag or ilmenite, containing titanium and iron is chlorinated in the presence of coke as a reduction agent at temperatures around 100°C in a fluidized bed reactor. Apart from titanium chloride iron(II)chloride also forms therefrom. Along with the water-insoluble solids—essentially coke, unhydrolyzed titanium dioxide and silicium dioxide—as well as other metal chlorides, the iron(II)chloride is separated from the gas leaving the reactor in an externally coupled cyclone. The separated mixture is designated as cyclone dust. The costly reprocessing of the cyclone dust is described fro example in US 3 867 515.

Pasting of the cyclone dust in diluted acid salts and separating of the water-insoluble constituents produces a solution which contains primarily iron(II)chloride, in addition to aluminium chloride, manganese chloride, magnesium chloride, zirconium chloride and trace elements such as chromium, niobium and vanadium, as chlorides. If such an iron(II)chloride solution is to be used for waste water treatment and slurry conditioning, it must be considered that because of the unavoidable proportions of trace elements owing to the raw material composition, there are no constituents entering the waste water, which for their own part give rise to waste disposal problems. The 'charged' iron(II)chloride solution must be further purified prior to being added, that is, especially the chromium, niobium and vanadium ions have to be removed from the solution.

It is known that when the pH value of such a solution is raised above 1, the dissolved metal ions are precipitated as hydroxides according to their solubility products ; iron(II)ions

remain in solution up to a pH value of over 6. In this way a charged ('technical') iron(II)chloride solution could be theoretically converted to a pure iron(II)chloride solution by selective precipitation. Yet in practice this method is not expedient. If a neutralisation agent such as sodium hydroxide, calcium hydroxide, magnesium hydroxide, sodium carbonate or calcium carbonate is added to an acidic solution of cyclone dust, then metal hydroxide brines are formed which are extremely difficult to filter and cannot be deposited because of their gel-like structure.

Russian patent 676 559 describes the precipitation of metal hydroxides from a solution, containing undesired heavy metal ions other than iron, by addition of 8% sodium hydrogencarbonate solution at 20°C; when the pH value is raised to 4.5, the chromium especially is to be concentrated into filter cakes. Under the given precipitation conditions, the gel-like hydroxides cannot be filtered under justifiable expenditure. No details are given in this patent on the nature of the filter cake.

Another method for removing chromium from metal chloride solutions is described in US 4 765 908. Here, bentonites are added, in particular montmorillonite, at least one flocculant and alkali or earth alkali carbonates, together with zirconium catalysts and at least one polyelectrolyte, whereby the heavy metal ions are bonded absorptively and separation of the filter cake presents no difficulties. The filter residue can also be deposited. But because of the introduction of chemicals the process proves very costly; in addition, there is an abnormally large accumulation of slurry.

German patent P 41 30 808.5 proposes removal of the undesired ions from an iron(II)chloride solution produced from cyclone dust by selective crystallisation. The process described therein does result in the desired purification of the iron(II)chloride solution, yet the investment and operating costs for this procedure are very high.

The object of the present invention is to remove undesired metal ions, in particular chromium, niobium, zirconium and vanadium, from an iron(II)chloride solution, wherein quantities of a magnitude of 15 m^3/h have to be dealt with and the result of precipitation of the undesired metal ions as hydroxides is usually an extremely finely particled gel-like suspension, also wherein the metal hydroxides previously precipitated not by filtration are to be separated sufficiently quickly and completely, and the filter residue can be deposited in the previous form.

In accordance with the present invention, there is provided a process for removing

waste water-charging metal ions from an acidic solution essentially containing iron(II)chloride from cyclone dust dissolved in diluted acid salts from the production of titanium dioxide according to the chloride process by raising of the pH value and separation of the metal hydroxides which have formed, characterised in that the solution is first adjusted to a pH value between 0.3 and 0.8 with a first neutralisation agent and then the thus buffered solution is metered into a recipient vessel with a second neutralisation agent in water or purified iron(II)chloride solution such that the pH value therein is maintained at or above a value of 2.0 and the second neutralisation agent is difficult to dissolve and is present in excess with respect to the metal ions to be precipitated and charged with waste water.

The precipitation products produced according to the process of the present invention have very good filterability and the filter cake can be deposited.

Calcium carbonate has proved itself particularly advantageous as a second neutralisation agent. It is available in unlimited quantities and directly due to its difficult solubility in water or in an iron chloride solution, that is, through a type of natural buffer effect of the suspension in the recipient vessel, it appears to reach less spontaneous nucleation, thus preventing a gelling state. The solid formed by this neutralisation agent is essentially improved in its filterability. Nucleation also appears to be diminished with this process. The formation of iron(II)hydroxide is impossible because of the excessively low pH value in the recipient vessel. Neither is there any formation of iron(III)hydroxide as a result of the system-imminent carbon dioxide development (protective gas atmosphere), which effectively excludes oxidation with the atmospheric oxygen.

Whereas calcium carbonate is particularly preferred as second neutralisation agent, demonstrated by the desired buffer effect in suspension, neutralising by iron or iron compounds is preferred as first neutralisation agent for the neutralisation of the technical iron chloride solutions apart from earth alkali carbonate - preferences are still calcium carbonate or dolomite stone powder. The addition of iron increases the quantity of the desired end product, without bringing in by-products. With the addition of scrap iron as first neutralisation agent, no special measures have to be observed. With the introduction sinter, a mixed oxide of bivalent and trivalent iron, iron(III)ions do result which could be precipitated partially as iron(III)hydroxide when the solution is added to the second neutralisation agent and thus are lost along with the filter residue. Therefore, when the sinter is added as first neutralisation agent, before the buffered solution is added to the

recipient vessel with the second neutralisation agent, iron(III)ions have to be converted by means of scrap or another reduction agent into iron(II)ions.

If calcium carbonate is used as the first neutralisation agent, the iron(II)chloride solution contains relatively high quantities of calcium chloride. Since this is often undesired, the calcium sulfate can be precipitated and separated from such a solution by addition of iron sulfate, whereby the concentration of iron(II)chloride increases accordingly.

The temperature of the suspension in the recipient vessel should preferably be 90°C. Under these conditions precipitation products are formed which can be separated especially advantageously and deposited.

It has proved beneficial to prolong the second partial neutralisation step. In this regard, metering of the solution neutralised with the first neutralisation agent into the recipient vessel should preferably be such that for every kilogram of calcium carbonate in the recipient vessel 25 to 331 buffered solution per hour should be added.

The invention is described hereinafter by way of examples.

A typical 'charged' iron(II)chloride solution of cyclone dust in diluted acid salts has the following composition:

Fe	8.8%	Ti	410 ppm
Mn	1.61%	Cr	1170 ppm
Mg	0.67%	V	2410 ppm
Ca	0.10%	Nb	580 ppm
HCl	2.6%	Zr	1140 ppm

The following four tests were performed with this technical iron(II) chloride.

Example 1

Buffering and precipitation with calcium carbonate (limestone powder) only.

1200 ml of the charged iron(II)chloride solution are heated at 70°C. 41.5 g limestone powder (ca. 97% $CaCO_3$, particle size less than 0.1 mm) are stirred in within 30 minutes. After the first neutralisation agent is added, the pH value is 0.78.

Of this solution 'neutralised' with the first neutralisation agent, 30 ml per minute are added to a limestone powder suspension (72 g limestone powder in 72 g water). After addition the pH value is in the recipient vessel is 2.8. The mixture is stirred for another 30 minutes and the pH value is raised to 3.4. The 70°C hot suspension is filtered. In all examples filtration is

carried out at 50 mbar using a suction filter with a diameter of 13 cm. The filtration procedure is set out in Table 1.

Table 1

Filtration quantity in ml	50	100	150	200	300	400	500	600
Filtration time in s	11	28	47	67	105	152	220	209

The filter cake is 100 mm thick and puncture-resistant. The clear filtrate has the following composition :

Fe	9.1%	Ti	9 ppm
Mn	1.7%	Cr	8 ppm
Mg	0.76%	V	3 ppm
Ca	3.2%	Nb	7 ppm
Al	25 ppm	Zr	5 ppm

The chromium iron ratio has improved from 0.0133 to 0.000088, and the vanadium iron ratio from 0.0274 to 0.000033. In a relatively short time (good filterability) a concentration of around 97% of the charging ions is achieved, whereby a puncture-resistant filter cake is produced from the precipitation products.

Example 2

Buffering of the charged iron chloride solution with rolled sinter and reduction of Fe^{3+}.

1200 ml of the charged (technical) iron(II)chloride solution mentioned initially are stirred with 25.5 g rolled sinter (FeO = 68%, Fe_2O_3 = 32%) for 1 hour at 80°C. Iron powder is added to reduce the Fe(III)ions and the mixture is stirred for a further 20 minutes at 80°C. The pH value is 0.75. This buffered solution is added to a recipient vessel at a metering rate of 30 ml/min.

It again contains 72 g limestone powder in 72 g water and has a temperature of 70°C. After 30 minutes of metering the pH value is 2.8. The mixture is stirred for another 30 minutes

and the pH value rises to 3.3. Filtration at 70°C is carried out in the suction filter under the same conditions as in Example 1. The filtration procedure is set out in Table 2.

Table 2

Filtration quantity in ml	50	100	150	200	300	400	500	600
Filtration time in s	14	31	57	87	165	276	415	540

The solution has the following composition :

Fe	10.30%	Ti	5 ppm
Mn	1.51%	Cr	6 ppm
Mg	0.74%	V	4 ppm
Ca	1.40%	Nb	4 ppm
Al	26 ppm	Zr	2 ppm

The chromium iron ratio has improved from 0.0133 to 0.000058, and the vanadium iron ratio from 0.0274 to 0.000039.

Example 3

Influence of the metering rate.

The process is as in Example 2, however the metering rate of the charged solution into the calcium carbonate suspension is raised to 50 ml/min. After addition the pH value is 2.2 and after 30 minutes stirring it is 3.2. As seen from Table 3, filterability has not deteriorated, however the concentration of chromium has dropped to 0.00018 and that of vanadium to 0.0027.

Table 3

Filtration quantity in ml	50	100	150	200	300	400	500	600
Filtration time in s	12	27	52	83	160	268	401	521

The solution has the following composition :

Fe	10.28%	Ti	13 ppm
Mn	1.5%	Cr	19 ppm
Mg	0.74%	V	277 ppm
Ca	1.37%	Nb	46 ppm
Al	32 ppm	Zr	9 ppm

Example 4

Conventional neutralization as comparative example.

1200 g acidic charged $FeCl_2$ solution are heated at 80°C and neutralized with rolled sinter, as in Example 2, and trivalent iron ions were reduced with iron. This solution (pH = 0.78, 70°C) is now (partially) neutralized in 30 minutes by addition of 72 g solid limestone powder. After this addition the pH value has risen to 2.7, increasing to a value of 3.0 after a further 30 minutes of stirring. The 70°C warm suspension is filtered as described above. Table 4 shows the filterability, now essentially deteriorated.

Table 4

Filtration quantity in ml	20	40	60	80	100	250	200
Filtration time in s	8	22	62	180	240	650	1520

Filtration comes to a relatively early standstill. The ca. 3 mm thick filter cake comprises a gel-like, semi-fluid mass. The filtrate has the following composition :

	Fe	10.41%	Ti	15 ppm
5	Mn	1.51%	Cr	39 ppm
	Mg	0.74%	V	64 ppm
	Ca	1.38%	Nb	51 ppm
	Al	195 ppm	Zr	12 ppm

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The concentration is also correspondingly small - to 0.00037 for Cr/Fe and to 0.00061 for V/Fe.

The Claims defining the invention are as follows:

1. Process for removing waste water-charging metal ions from an acidic solution essentially containing iron(II)chloride from cyclone dust dissolved in diluted acid salts from the production of titanium dioxide according to the chloride process by raising of the pH value and separation of the metal hydroxides which have formed, characterised in that the solution is first adjusted to a pH value between 0.3 and 0.8 with a first neutralisation agent and then the thus buffered solution is metered into a recipient vessel with a second neutralisation agent in water or purified iron(II)chloride solution such that the pH value therein is maintained at or above a value of 2.0 and the second neutralisation agent is difficult to dissolve and is present in excess with respect to the metal ions to be precipitated and charged with waste water.

2. Process as claimed in Claim 1, characterised in that the second neutralisation agent is an earth alkali carbonate.

3. Process as claimed in claim 2, wherein the second neutralisation agent comprises calcium carbonate or dolomite stone powder.

4. Process as claimed in Claim 1 or 2, characterised in that the quantity of the second neutralisation agent is 1.05 to 1.4 times the metal ions to be stoichiometrically precipitated and containing waste water.

5. Process as claimed in any one of Claims 1 to 4, characterised in that the first neutralisation agent is an earth alkali carbonate or scrap iron.

6. Process as claimed in Claims 1 to 4, characterised in that the first neutralisation agent is iron sinter and by addition of a reduction agent, before the solution is added to the recipient vessel, the iron(III)ions are reduced.

7. Process as claimed in claim 6, wherein the reduction agent comprises iron.

8. Process as claimed in any one of Claims 1 to 6, characterised in that the temperature of the suspension in the recipient vessel is 90°C.

9. Process as claimed in any one of Claims 1 to 8, characterised in that the metering rate of the buffered solution into a calcium carbonate suspension is 25 l/h to 33 l/h, relative to 1 kg calcium carbonate in the recipient vessel.

DATED this 11th day of January, 1995

KRONOS TITAN GMBH
By Its Patent Attorneys
DAVIES COLLISON CAVE

AUSTRALIAN L.S.

ABSTRACT

A 'technical' acidic iron chloride solution formed from cyclone dust is neutralized with a first neutralization agent and metered into a recipient vessel with a second neutralization agent. All ions to be removed, especially chromium, vanadium, zirconium and niobium, are precipitated as hydroxides with good filterability and can be separated industrially by filtration under economic conditions. The filter cake can be deposited. Calcium carbonate is the preferred neutralization agent. Buffering can also occur preferably with iron or iron sinter (with reduction of the Fe(III) ions prior to the second neutralization step).