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(21) International Application Number: PCT/GB98/00504 (22) International Filing Date: 18 February 1998 (18.02.98) (30) Priority Data: 9703662.8 21 February 1997 (21.02.97) GB (71) Applicant (for all designated States except US): TIOXIDE GROUP SERVICES LIMITED [GB/GB]; Lincoln House, 137-143 Hammersmith Road, London W14 0QL (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): NOBLE, Brian, Cameron [GB/GB]; 27 Rothbury Close, Ingleby Barwick, Cleveland TS17 0YR (GB). (74) Agent: MILLROSS, Christopher, Robert; Tioxide Group Services Limited, Patents Dept., Haverton Hill Road, Billingham, Cleveland TS23 1PS (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: TREATMENT OF A SOLUTION CONTAINING IRON SALTS		
(57) Abstract Soluble manganese salts present as contamination of a solution containing iron salts are removed by adding an oxidation agent capable of converting the soluble manganese salts to manganese dioxide and by adding manganese dioxide particles as seeding agent whereby any colloidal manganese dioxide is deposited on the seed particles.		

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Treatment of a Solution Containing Iron Salts

This invention relates to treatment of a mixture of iron and manganese salts so as to reduce the manganese content thereof and in particular to the treatment of iron salts produced in the production of titanium dioxide by the sulphate process.

In the sulphate process for the production of titanium dioxide, titaniferous raw material such as ilmenite is digested with sulphuric acid to form a solid mass which is treated with water and filtered to provide a solution containing mainly titanium sulphate, ferrous sulphate and ferric sulphate. The ferric ions are reduced to ferrous ions by the addition of iron, and the solution is cooled under vacuum to crystallise out the ferrous sulphate (commonly known as copperas) leaving a solution of titanium sulphate from which titanium dioxide may be precipitated by hydrolysis. Alternatively, the titanium dioxide may be precipitated first and the copperas crystallised out from the waste solution.

Clearly, the quantity of copperas relative to the quantity of titanium dioxide produced depends on the ratio of iron to titanium in the raw material. Typical figures are circa 1:1 for ilmenite (massive), 0.71:1 for ilmenite (sand) and 0.15 :1 for ilmenite (slag). In any case, it will be appreciated that copperas is produced in substantial amounts for which a use must be found as there are environmental problems involved in its disposal.

One use of copperas is as the base material from which a coagulant for treatment of water may be prepared. In one conventional method, the ferrous sulphate is oxidised to ferric sulphate by being dissolved in a mixture of sulphuric acid and nitric acid. On addition to water containing colloidal particles, the ferric sulphate hydrolyses to form an insoluble hydroxide which interacts with the colloidal particles causing them to coagulate. The coagulated particles can then be removed by settlement and/or filtration.

A further use of the by-product is for the production of iron oxide. However, the soluble manganese is not oxidised by the conventional methods. Although it is known that soluble manganese can be oxidised to insoluble manganese dioxide by the addition of a further oxidising agent such as peroxide or potassium permanganate, the manganese dioxide so produced is in very finely divided colloidal form which is difficult and expensive to remove, particularly on a commercial scale and hence the final ferric sulphate product still has sufficient manganese content to make it unacceptable for the above uses.

According to one aspect of the invention, there is provided a method of treating a solution containing iron salt(s) contaminated with soluble manganese salt(s) comprising adding to the solution an oxidising agent capable of converting said manganese salt(s) to manganese dioxide, characterised by the addition of manganese dioxide as seeding agent, whereby any colloidal

manganese dioxide is deposited on said seed particles, and by the separation of the manganese dioxide particles from the solution containing iron salt(s).

According to a preferred feature, the seeding agent is added before the additional oxidising agent. The seed particles desirably have an average particle size of at least 10 μm , but the preferred size is 30-50 μm .

In accordance with a further preferred feature, the seed particles are produced by reacting ferrous sulphate and potassium permanganate.

In order to reduce costs, the manganese dioxide particles separated from one batch of treated ferric sulphate solution can be recycled and used as the seed particles for a further batch of solution.

Treatment of copperas by the conventional method does not necessarily convert all the ferrous sulphate to ferric sulphate. Normally, this is disadvantageous. However, in accordance with a further preferred aspect of the invention, this residual ferrous sulphate can, by the addition of potassium permanganate, be used to produce the manganese dioxide seed particles. Of course, if too little ferrous sulphate is present to produce the required amount of seed particles, further ferrous sulphate may be added.

The oxidised agent may be any of the well known agents such as ozone, a peroxide, or a persulphate. Preferably, however, the oxidising agent is potassium permanganate which is added continuously over a period in the form of a saturated solution.

The method is effective when carried out at reflux temperature.

However, it may be carried out at a temperature of 70 to 80°C, i.e. the temperature at which the copperas is dissolved in the sulphuric/nitric acids, so that the liquor can be taken straight from the reactor without any additional heating requirement.

The invention will be more readily understood from the following examples.

EXAMPLE 1

A manganese dioxide seeding agent was prepared by adding, over a period of 90 mins, a stoichiometric quantity (30 gpl) of potassium permanganate to 6L of analar ferrous sulphate (20 gpl Fe) under reflux. The solution was held at reflux for a further 60 mins and the resulting solid filtered out and washed with water. Measurement using a Malvern Mastersizer gave an average particle size of 43 μm .

EXAMPLE 2

Copperas obtained as a by-product in the preparation of titanium dioxide by the sulphate process was dissolved in a mixture of sulphuric and nitric acids to give a ferric sulphate liquor having a pH of 0.5. The iron and manganese content was measured. The liquor was then refluxed and 50 gpl of the seed of Example 1 added. A peristaltic pump was used to continuously add a stoichiometric amount of potassium permanganate over

a period of 90 minutes and the mixture was held at reflux for a further 30 minutes. A 25ml sample was taken every 30 minutes and filtered through a 0,45 μm filter under vacuum. The resulting filtrate was analysed for iron and manganese content. The filtered solid was washed with water and the particle size measured. The results are shown in Table 1

TABLE 1

Time (mins)	Mn content ($\mu\text{g/g}$)	Fe content (%)	Filter time (secs)	Particle size (μm)
0	1174	13.62	51	44.7
30	964	12.7	50	45.7
60	610	13	400	46.2
90	121	12.5	180	47.55
180	<10	12.6	140	47

EXAMPLE 3

Example 2 was repeated except that the seed particles were added in an amount of 75 gpl.

The results are shown in Table 2.

TABLE 2

Time (mins)	Mn content (μ g/g)	Fe content (%)	Filter time (secs)	Particle size (μ m)
0	1230	133.3	53	41.59
30	890	12.7	28	41.91
60	570	13	45	43.25
90	120	12.5	40	43.17
180	50	12.6	33	42.74

EXAMPLE 4

1 litre of the solution from Example 3 was placed in a measuring cylinder and left to settle. After 7 days a clear supernatant liquor was present which contained 21 μ g/g of manganese.

EXAMPLE 5

Example 3 was repeated except that an appropriate amount of the solids removed from the final solution was used as the seeding agent. Similar results were obtained.

EXAMPLE 6

The ferrous content of the solution resulting from the treatment of copperas with sulphuric and nitric acids was measured and, if necessary, further ferrous sulphate was added until there was sufficient to provide

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75 gpl of manganese dioxide seeding agent when a stoichiometric amount of potassium permanganate was added.

A further amount of potassium permanganate was then added as in Example 2. The final solution was allowed to settle. A clear supernatant liquor formed in less than 24 hours and contained 500 $\mu\text{g/g}$ manganese.

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CLAIMS

1. A method of treating a solution containing iron salts(s) contaminated with soluble manganese salt(s) comprising adding to the solution an oxidising agent capable of converting said manganese salt(s) to manganese dioxide, characterised by the addition of manganese dioxide as seeding agent, whereby any colloidal manganese dioxide is deposited on said seed particles, and by the separation of the manganese dioxide particles from the solution containing iron salt(s).
2. A method according to Claim 1, characterised in that the seeding agent is added before the addition of the oxidising agent.
3. A method according to Claim 1 or 2, characterised in that the seed particles have an average particle size of at least 10 μ m.
4. A method according to Claim 3 in which the seed particles have an average particle size of 30-50 μ m.
5. A method according to any preceding claim, characterised in that the seed particles are produced by reacting ferrous sulphate and potassium permanganate.

6. A method according to any preceding claim, characterised in that the manganese dioxide particles separated from the solution are recycled to form the seed particles.
7. A method according to any preceding claim characterised in that potassium permanganate and, if necessary, ferrous sulphate, are added to the solution to cause production of the seed particles.
8. A method according to any preceding claim, characterised in that the oxidising agent is potassium permanganate.
9. A method according to Claim 8, characterised in that the potassium permanganate is added continuously in the form of a saturated solution.
10. A method according to any preceding claim characterised in that the temperature of the solution is 70-80°C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/00504

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01G49/00 C01G49/14 C01G45/02

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 6 C01G

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 15 92 558 A (VARTA) 26 November 1970 see the whole document ---	1,8
A	US 4 067 789 A (HARRIS LEONARD ET AL) 10 January 1978 see column 2, line 38 - line 52; claim 1 ---	1
P, A	WO 97 34836 A (KEMIRA CHEMICALS OY ; JOKINEN SIMO (FI); AITTA EERO (FI)) 25 September 1997 see claims 1-3 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

International Application No

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