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REDUCTION OF RESIDUAL CHLORIDE IN IRON OXIDES

This invention relates to a process for the reduction of residual chloride present in regenerated iron oxides.

During the last twenty years, the regenerated iron oxides (RIO) produced from hydrochloric acid waste liquid generated from steel pickling have been recognized as an important source of raw material for preparing products containing iron oxides such as iron-oxide based catalysts and high-grade ferrites. The raw material cost savings associated with the substitution of a low cost, regenerated iron oxide for most of the conventional commercial sources of iron oxides are substantial.

One drawback of utilizing regenerated iron oxides from hydrochloric acid waste liquids generated from steel pickling is that the ferric oxides inevitably contain chloride ions, typically in the range of about 0.1 to 0.5% measured as grams of chloride per 100 grams of regenerated iron oxide. In the field of ethylbenzene dehydrogenation catalysts, it is known that the small amounts of residual chloride present in all regenerated iron oxides affect catalyst performance adversely. For the ferrite producers, the chloride ion present in the regenerated iron oxide is not only corrosive to the ferrite manufacturing installations but also injurious to the quality of the ferrite produced.

Reducing the chloride-ion content in regenerated iron oxides by an economical procedure, without significantly changing the ferric oxide quality is believed to be one of the most critical issues for the development of regenerated iron oxides as commercially useful raw materials.

Japanese patent application J59,050,031, published September 13, 1992, discloses a method for purifying iron oxide from waste hydrochloric acid pickling solution containing ferric chloride by treatment with ferrous sulfate, ferric sulfate or ammonium sulfate solution. The iron oxide purified by this prior art method

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still contains a substantial amount of chloride. Moreover, it is time consuming to dissolve these salts in water. Furthermore, the raw material costs for these sulfate salts are relatively high.

5 Suganuma, et al. in 4th International Conference on Ferrites, Advances in Ceramics, Vol. 15, 81-85 (1986), reported a method for removing chloride ions from hematite powders by heating the ferric oxide in air with the addition of sulphur dioxide and/or moisture. However, sulphur oxide is a toxic gas which is unhealthy and environmentally undesirable.

10 Thus, there remains a need for a commercial process which will substantially reduce the chloride contents in regenerated iron oxides (RIO) at a low cost without significantly changing the quality of the iron oxides.

15 The present invention relates to a process for removing chloride from a chloride-containing iron oxide, which process comprises the steps of:

- (a) mixing the chloride-containing iron oxide with a solution comprising H_2SO_4 to form a mixture; and
- (b) separating the iron oxide from the mixture formed in step (a),
20 optionally followed by drying and calcining. The purified regenerated iron oxides are particular suitable for making iron oxide-based catalysts such as ethylbenzene dehydrogenation catalyst and high-grade ferrites.

25 The iron oxides to be treated by the process of the present invention in its broadest aspect are selected from any iron oxides of mineral or synthetic origin which contain either trace or substantial amounts of chloride. Various methods for the obtaining of iron oxides from scrap steel, steel scaling liquors, or iron chloride as industrial waste product have been described in U.S.
30 Patent No. 4,935,219. The iron oxides obtained from some of these methods inevitably contain residual chlorides originating from the chloride-containing reagents or raw materials present during the process of generating the iron oxides.

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As a preferred embodiment, the iron oxides treated in the instant invention are the regenerated iron oxides (RIO) produced from hydrochloric acid waste liquids generated from steel pickling. During the process of producing the regenerated iron oxides, hydrochloric acid pickling wastes are sprayed into a roaster, whereby water and free HCl in the wastes are driven off quickly, while FeCl_2 is hydrolyzed to produce iron oxide and hydrogen chloride. The regenerated iron oxides contain chloride ions, typically in the range of from about 800 parts per million to about 20,000 parts per million, particularly in the range of from about 800 to 5,000 parts per million, by weight of the regenerated iron oxides.

The sulfuric acid used in treating iron oxides in the instant invention can be any commercial or reagent grade sulfuric acid. Preferably, concentrated sulfuric acid is diluted with water, more preferably with deionized water or distilled water, before being used as the reagent for treating iron oxides. In a specific embodiment of the present invention, concentrated sulfuric acid with specific gravity of about 1.84 g/ml is diluted with about ten times to 100 times by volume of deionized water prior to being used for treating the iron oxide.

The molar amount of sulfuric acid in the sulfuric acid solution used for treating iron oxides is generally a molar amount of from 0.5 to 10, preferably from 1.0 to 5.0, more preferably from 1.8 to 2.5, still more preferably 2.0 times relative to the total molar amount of chloride present in the iron oxides to be treated.

The iron oxides may be treated with a sulfuric acid solution by any method known to one skilled in the art which would achieve thorough mixing of the iron oxides with the sulfuric acid solution. As a non-limiting example, the iron oxides may be slurried with the sulfuric solution followed by either decantation or filtering. As another non-limiting example, the iron oxides may also be wetted with the sulfuric acid solution and mulled to form a paste.

In the broadest aspect of the present invention, the iron oxides are treated with the sulfuric acid solution for at least a

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period of time sufficient to achieve thorough mixing of the sulfuric acid solution with the iron oxides. Typically, the treatment lasts from 1 minute to 48 hours. In a specific embodiment of the present invention, the treatment lasts from 3 minutes to 5 hours, more specifically from 10 minutes to 30 minutes.

The treatment of iron oxides with sulfuric acid solution can be conducted under a pressure from about 50 kPa to about 10000 kPa. In one specific embodiment of the present invention, it is conducted under ambient pressure. The treatment can be conducted in any suitable atmosphere. Non-limiting examples of the suitable atmosphere include air, other oxygen containing gaseous streams, and inert gaseous streams.

After the iron oxides are treated with sulfuric acid solution, they can be separated from the solution by any suitable separation method. Without intending to limit the scope of the invention, the treated iron oxides can be separated out by filtration, centrifugation, etc.

As a preferred embodiment of the present invention, the treated iron oxides, after being separated from the sulfuric acid solution, are subsequently heated at an elevated temperature. The heating and/or calcining is typically conducted at a temperature ranging from 1° above the ambient temperature to 1400 °C for a period of time sufficient to dry or calcine the treated iron oxides completely. Typically, the iron oxides are calcined and/or dried for from 1 minute to 100 hours. This heating step can be a simple drying process, a calcination process, or a staged drying and calcination process. The heating is conducted under a pressure typically from 10 kPa to 1100 kPa. As a non-limiting example, the heating step can be conducted under ambient pressure. The heating step can be conducted under any suitable atmospheres. Non-limiting examples of the suitable atmospheres for the heating step include air, oxygen containing gaseous streams, inert gaseous streams, and vacuum.

In one specific embodiment of the present invention, the iron oxides are treated with a sulfuric acid solution and the treated iron oxides are separated from the solution without subsequent

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heating. The treated iron oxides can optionally be dried in air at ambient temperature and ambient pressure. In another specific embodiment of the present invention, the iron oxides are dried in air at a temperature between 30 °C and 300 °C, preferably between 50 °C and 300 °C, more preferably between 100 °C and 300 °C, for a period of time ranging from 1 minute to 72 hours, preferably from 2 minutes to one hour, more preferably from 10 minutes to 30 minutes. In a preferred embodiment, the treated iron oxides are subsequently calcined for a period of time from 1 minute to 72 hours, preferably from 15 minutes to 10 hours, more preferably from 30 minutes to 2 hours. In another preferred embodiment, the iron oxides are first dried at a temperature between 30 °C and 300 °C, preferably between 120 °C and 200 °C for a period of time ranging from 1 minute to 72 hours, preferably from 2 minutes to one hour, more preferably from 10 minutes to 30 minutes, and then calcined for a period of time from 1 minute to 72 hours, preferably from 15 minutes to 10 hours, more preferably from 30 minutes to 2 hours.

After the iron oxides are dried and optionally calcined, a sample of the treated iron oxides can be analyzed with a suitable analytical method(s) to determine the chloride content. The post-treatment chloride content is then compared with the chloride content measured prior to the treatment.

The invention will be exemplified by the following illustrative embodiments.

Illustrative Embodiments

The following illustrative embodiments describe typical techniques of the present invention for reducing chloride content in the regenerated iron oxides and the typical techniques for measuring the chloride contents of the iron oxides. The chloride contents were determined using Kevex Model 770 Energy Dispersive X-Ray Fluorescence Instrument.

Part A: Regenerated Iron Oxide

The ferric oxide used in the present embodiment was a commercial product of regenerated iron oxide produced from hydrochloric acid waste liquid generated from steel pickling. The

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chloride content of this regenerated iron oxide was about 1400 parts per million by weight of the regenerated iron oxide.

600 grams of the regenerated iron oxide were used for each Illustrative Embodiment below. The total amount of the chloride present in the 600 grams of regenerated iron oxide with 1400 parts per million (ppm) of chloride was estimated to be about 0.84 grams or 0.0237 moles based on mathematical calculation.

Part B: Preparation of H_2SO_4 solution

B-1: H_2SO_4 Solution of 1:1 Ratio Relative to Cl

1.3 millilitres of concentrated sulfuric acid with specific gravity of 1.84 g/ml were added to 61.7 millilitres of deionized water to make a solution of about 63 millilitres containing approximately 0.0237 moles of H_2SO_4 , which was equal to the molar amount of the chloride contained in the 600 grams of regenerated iron oxide from Part A above.

B-2: H_2SO_4 Solution of 2:1 Ratio Relative to Chloride

2.6 millilitres of concentrated sulfuric acid with specific gravity of 1.84 g/ml were added to 60.4 millilitres of water to make a solution of about 63 millilitres by volume containing approximately 2 X 0.0237 moles of H_2SO_4 which was twice the molar amount of the chloride present in the 600 grams of the regenerated ferric oxide from Part A.

Part C: Reduction of Chloride in Ferric Oxide

I. H_2SO_4 TREATMENT FOLLOWED BY DRYING

Method I-1: Treatment with H_2SO_4 , 2:1/Dried at 50 °C

600 grams of the regenerated iron oxide from Part A above were mulled for 15 minutes. During mulling, 63 millilitres of the H_2SO_4 solution, prepared from B-2 above, containing a molar amount of H_2SO_4 in the H_2SO_4 solution of about twice the amount of chloride contained in 600 grams of the regenerated iron oxide, were added gradually to the regenerated iron oxide. The wet iron oxide powder was filtered through a 2.83 mm (#7 mesh) screen and then dried for 15 minutes at 50 °C under ambient pressure. The chloride content of the dried sample was 1200 parts per million by weight of the total iron oxides.

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Method I-2: Treatment with H_2SO_4 , 2:1/Dried at 120 °C

600 grams of the regenerated iron oxide from Part A above were treated with the same H_2SO_4 solution in the same way as Method I-1 above, except that subsequent to the filtration step the treated iron oxide powder was dried at 120 °C at ambient pressure for 15 minutes. The chloride content of the dried sample was 720 ppm.

Method I-3: Treatment with H_2SO_4 , 1:1/Dried at 170 °C

600 grams of the regenerated iron oxide from Part A were mullied for 15 minutes. During mulling, 63 millilitres of the H_2SO_4 solution, prepared from B-1 above, containing a molar amount of H_2SO_4 in the H_2SO_4 solution about equal to the molar amount of chloride contained in 600 grams of the regenerated iron oxide, were added gradually to the regenerated iron oxide. The wet iron oxide powder was filtered through a 2.83 mm (#7 mesh) screen and then dried for 15 minutes at 170 °C under ambient pressure. The chloride content of the dried sample was 550 parts per million by weight of the total iron oxides.

Method I-4: Treatment with H_2SO_4 , 2:1/Dried at 170 °C

600 grams of the regenerated iron oxide from Part A above were treated with the same H_2SO_4 solution in the same way as Method I-2 above, except that subsequent to the filtration step the treated iron oxide powder was dried at 170 °C at ambient pressure. The chloride content of the dried sample was 510 ppm.

The results of study I are shown in Table I below.

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TABLE I

REGENERATED IRON OXIDE CHLORIDE REDUCTION STUDY I

Sample	Chloride Reduction Method	Treating Solution	Heating Condition	Chloride Content ppm	Chloride Reduction %
Untreated Commercial RIO	None	None	None	1400	---
I-1	H ₂ SO ₄ 2:1 Dried	H ₂ SO ₄ 2:1	50 °C	1200	14%
I-2	H ₂ SO ₄ 2:1 Dried	H ₂ SO ₄ 2:1	120 °C	720	49%
I-3	H ₂ SO ₄ 1:1 Dried	H ₂ SO ₄ 1:1	170 °C	550	61%
I-4	H ₂ SO ₄ 2:1 Dried	H ₂ SO ₄ 2:1	170 °C	510	64%

II. H₂SO₄ TREATMENT FOLLOWED BY DRYING AND CALCININGMethod C-1: Comparative Embodiment - Calcination without H₂SO₄

600 grams of the regenerated iron oxide from Part A above were mulled for 15 minutes without the addition of any H₂SO₄ solution. The mulled iron oxide were then dried for 15 minutes at 170 °C. Thirty grams of the dried oxide were calcined in a static kiln under air having one atmosphere pressure for one hour at 825 °C. The resulted chloride content was 810 ppm.

Method C-2: Comparative Embodiment - Treatment with H₂O/ Calcined

600 grams of the regenerated iron oxide from Part A above were mulled for 15 minutes. During mulling, 63 millilitres of deionized water were gradually added to the regenerated iron oxide. The wet iron oxide powder was filtered through a 2.83 mm (#7 mesh) screen and then dried for 15 minutes at 170 °C. Thirty grams of the dried oxide were calcined in a static kiln under air having one atmosphere

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pressure for one hour at 825 °C. The resulting chloride content was 880 ppm.

Method II-1: Treatment with H₂SO₄, 1:1/Dried/Calcined

5 Thirty grams of the dried oxide from Method I-3 above were calcined in a static kiln under air having one atmosphere pressure for one hour at 825 °C. The chloride content of the resulting sample was 510 ppm.

Method II-2: Treatment with H₂SO₄, 2:1/Dried/Calcined

10 Thirty grams of the dried oxide from Method I-4 above were calcined in a static kiln in air with one atmosphere pressure for one hour at 825 °C. The chloride content of the resulting sample was 390 ppm.

The results of study II are shown in Table II below.

TABLE II
REGENERATED IRON OXIDE CHLORIDE REDUCTION STUDY II

Sample	Chloride Reduction Method	Treating Solution	Heating Condition	Chloride Content ppm	Chloride Reduction %
Untreated Commercial RIO	None	None	None	1400	---
C-1	Dried & Calcined	None	170 °C & 825 °C	810	42%
C-2	H ₂ O Dried & Calcined	H ₂ O	170 °C & 825 °C	880	37%
II-1	H ₂ SO ₄ 1:1 Dried & Calcined	H ₂ SO ₄ 1:1	170 °C & 825 °C	510	64%
II-2	H ₂ SO ₄ 2:1 Dried & Calcined	H ₂ SO ₄ 2:1	170 °C & 825 °C	390	72%

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III. H₂SO₄ TREATMENT WITHOUT SUBSEQUENT DRYING/CALCINING**Method C-3: Comparative Embodiment - Treatment with H₂O**

600 grams of the regenerated iron oxide from Part A above were mulled for 15 minutes. During mulling, 63 millilitres of the deionized water were gradually added to the regenerated iron oxide. The wet iron oxide powder was filtered through a #7 mesh screen. The chloride content was 10,200 ppm.

Method III-1: Treatment with H₂SO₄, 2:1 Undried/Uncalcined

600 grams of the regenerated iron oxide from Part A were mulled for 15 minutes. During mulling, 63 millilitres of the H₂SO₄ solution, prepared from B-2 above, containing a molar amount of H₂SO₄ in the H₂SO₄ solution of about twice the molar amount of chloride contained in 600 grams of the regenerated iron oxide, were added gradually to the regenerated iron oxide. The wet iron oxide powder was filtered through a 2.83 mm (#7 mesh) screen. The chloride content of the dried sample was 3,200 parts per million by weight of the total iron oxides.

The results of study III are shown in Table III below.

TABLE III
REGENERATED IRON OXIDE CHLORIDE REDUCTION STUDY III

Sample	Chloride Reduction Method	Treating Solution	Heating Condition	Chloride Content ppm	Chloride Reduction %
C-3 Damp Control	H ₂ O Undried & Uncalcined	H ₂ O	Undried Uncalcined	10,200	---
III-1	H ₂ SO ₄ 2:1	H ₂ SO ₄ 2:1	Undried Uncalcined	3200	70%

C L A I M S

1. A process for removing chloride from a chloride-containing iron oxide, which process comprises the steps of:
 - (a) mixing the chloride-containing iron oxide with a solution comprising H_2SO_4 to form a mixture; and
 - 5 (b) separating the iron oxide from the mixture formed in step (a).
2. The process as described in claim 1, wherein the solution comprising H_2SO_4 used in step (a) comprises a molar amount of H_2SO_4 to form 1.0-5.0 times the molar amount of chloride in the chloride-containing iron oxide.
- 10 3. The process as described in claim 1, wherein the solution comprising H_2SO_4 used in step (a) comprises a molar amount of H_2SO_4 of from 1.8-2.5 times the molar amount of chloride in the chloride-containing iron oxide.
4. The process as described in claim 2, wherein in step (a) the
15 iron oxide is mixed with said solution comprising H_2SO_4 for a period of time ranging from 1 minute to 48 hours.
5. The process as described in claim 1, wherein the iron oxide separated from step (b) is further heated at a temperature ranging from 1 °C above the ambient temperature to 1400 °C for a period of
20 time from 1 minute to 100 hours.
6. The process as described in claim 1, wherein the iron oxide separated from step (b) is further heated at a temperature ranging from 50 °C to 300 °C for a period of time ranging from 2 minutes to one hour.
- 25 7. The process as described in claim 1, wherein the iron oxide separated from step (b) is first heated at a temperature from 50 °C to 300 °C for a period of time ranging from 1 minute to 72 hours, and the iron oxide is thereafter heated at a temperature from 400 °C to 1400 °C and at a pressure of from 10 to 1100 kPa for a period of
30 time ranging from 1 minute to 72 hours.
8. The process as described in any one of claims 1-7, wherein the

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mixing in step (a) is conducted in an oxygen-containing gaseous stream.

9. The process as described in any one of claims 5-8, wherein the heating after step (b) is conducted in an oxygen-containing gaseous stream.

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10. A process according to any one of claims 1-9, wherein the regenerated iron oxide is produced from a hydrochloric acid waste liquid generated from steel pickling, and comprises from 800 to 5000 ppm by weight of chloride.



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ :
C01G 49/02

A1

(11) International Publication Number: **WO 95/25069**

(43) International Publication Date: 21 September 1995 (21.09.95)

(21) International Application Number: **PCT/EP95/00982**

(22) International Filing Date: **14 March 1995 (14.03.95)**

(30) Priority Data:
08/213,344 **15 March 1994 (15.03.94)** **US**

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(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, ~~SG~~, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, 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), ARIPO patent (KE, MW, SD, SZ, UG).

Published

*With international search report.
Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.*

RTmp

(54) Title: **REDUCTION OF RESIDUAL CHLORIDE IN IRON OXIDES**

(57) Abstract

A process for reducing the residual chloride present in iron oxides, particularly in regenerated iron oxides produced from hydrochloric acid waste liquid generated from steel pickling, by post-synthesis treatment of the iron oxides with sulfuric acid optionally followed by drying and calcining. The purified regenerated iron oxides are particular suitable for making iron oxide based catalysts such as ethylbenzene dehydrogenation catalysts and high-grade ferrites.

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