GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGADISH BOSE ROAD, CALCUTTA-17.

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IMPROVEMENTS IN OR RELATING TO CHEMICAL BENEFICATION OF ILMENITE.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1 INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860)

The following specification particularly describes andascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by VEERARAGHAVA ARAVAMUTHAN, Scientist, YELLAMRAJU DURGA PRASADA RAO, Scientist and RAMASUBRAMANIAN RAGHAVAN, Senior Laboratory Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

This invention relates to Improvements in or relating to upgrading of titanium dioxide content of ilmenite from 55% to well above 75% by treatment with hydrochloric acid solutions at atmospheric pressures and in absence of catalyst.

Hitherto it has been proposed to eliminate the iron from ilmenite by reacting ilmenite with (a) concentrated sulphuric acid in the presence of catalysts like antimony oxide; (b) chlorine in the presence of carbon or carbon monoxide at high temperatures; (c) hydrochloric acid gas at 600-1000°C; (d) combined attack by hydrogen and chlorine in the temperature range 800-1000°C; (d) hydrochloric acid in 15-20% concentrations at temperatures upto 350°C and under pressures upto 40 atmospheres and digesting for 12-48 hours; (f) reducing the iron oxide present in the ilmenite to iron by carbon in an electric are furnace, sometimes in a blast furnace, followed by leaching out the iron in the mineral acids.

The object of this invention is to obviate these disadvantages by (a) utilising by product hydrochloric acid from any source such as from organic chlorination reactions for the elimination of iron from ilmenite utilising comparatively low temperatures and atmospheric pressures and conducting the experiment in simple equipment and (b) fixing up the chlorine content of waste chloride liquor (a mixture of iron chloride-hydrochloric acid) as manganese chloride by utilising the cheap and aboundantly available low grade high iron manganese ores.

The principles underlying this invention are (1) to get a porous mass of iron oxide in a simple way from the ilmenite containing 55% titanium dioxide which has very high reactivity for reaction with hydochloric acid of 15-25% concentration at atmospheric pressures and at temperatures of the order of 80-100°C; (2) full utilisation of iron chlorides and free hydrochloric acid which is necessarily obtained as a byproduct in the hydrochloric acid leaching process of ilmenite into a very valuable product viz., manganese chloride by preparing a very active manganous oxide-manganese dioxide mixtures from low as well as high grade ores of manganese by first reducing the ores to obtain manganous oxide along with magnetic oxide of iron followed by air oxidation of the same at high temperatures ranging upto 700°C.

The present invention provides process for the easy elimination of iron from ilmenite through the use of hydrochloric acid solution at atmospheric pressure at temperatures above 80°C in order to upgrade the titanium dioxide content of ilmenite from 55% to 80% and utilisation of the byproduct iron chloride solutions containing free hydochloric acid to obtain very pure manganese chloride from all grades of manganese oxide ores.

According to the present invention, the process for the elimination of iron from ilmenite through the use of hydrochloric acid is characterised in that the process steps are

(i) heating out of contact with air the ilmenite with carbonaceous material at about 600°C for about an hour,

(ii) leaching the cold mass from operation (i) with 15% hydrochloric acid at atmospheric pressure for about one hour at temperatures between 85° to 90°C,

(iii) repeating process (i) and (ii) a second time, and

(iv) the residue is then finally calcined at about 800°C for about an hour and leached with 15% hydrochloric acid, thus an ilmenite containing a titanium dioxide content of above 75% is obtained, with a mixture of ferrous chloride hydrochloric acid as byproduct,

(v) utilisation of byproduct ferrous chloride-hydrochloric acid mixtures (a) roast-reducing low grade or high grade manganese ore in about — 80 mesh size to get a mixture of Mn_3O_4 and Mn_2O_3 and Fe_3O_4; (b) this roast-reduced ore is treated with hot ferrous chloride-hydrochloric acid byproduct to get very pure manganese chloride solution which is filtered off from the only insolubles.

The heating out of contact with air the ilmenite with suitable carbonaceous material is done at temperatures not exceeding 600°C and time not exceeding one hour.

Mixed carbonaceous material such as coal, charcoal, fuel oil, saw dust mixtures is used.

Titanium dioxide concentrate containing above 75% titanium dioxide from ilmenite containing about 55% titanium dioxide and pure manganese chloride from low grade manganese ores and fines are obtained.

A flow sheet of the process is attached, Fig. 1 of the accompanying drawings.

Example I

The process broadly consists in treating—200 mesh size ilmenite containing about 55% titanium dioxide. One kg of the finely powdered ilmenite in—200 mesh size is mixed with 300 cc of fuel oil and heated in a closed vessel for about half an hour at 600°C. The product after colling is treated with 1200 cc of 15% hrdrochloric acid and digested for two hours at atmospheric pressure. It is then filtered. The residue from this operation is mixed with 150 cc of fuel oil and heated again at 600°C for about half an hour. The mass from this operation is leached with 800 cc of 15% hydrochloric acid for about one hour and filtered. The residue from the second operation is heated to 800°C and kept at 800°C for about half an hour and after cooling is leached with 1200 cc of 15% hydrochloric acid in the presence or absence of iron scrap for about one hour. The final residue on washing is more than 75% titanium dioxide concentrate. The filtrate from these three operations is mixed together and reacted with roast-reduced manganese ore containing a mixture of Mn_3O_4-Mn_2O_3-Fe_2O_4 besides alumina and silica. About 660 gm of low grade manganese ore (40% manganese) was used in the roast-reduced condition for reaction with the iron chloride-hydrochloric acid solutions. About 700 gm of manganese chloride is obtained.

Example II

One kg of—200 mesh size ilmenite, 120 cc of furnace oil and 200 gm of saw dust have been utilised

in the place of 300 cc of fuel oil for the first reduction and 60 cc of furnace oil and 100 gm of saw dust have been used in the place of 150 cc of fuel oil in the second stage reduction. Same results were obtained as in example I.

Example III

750 gm of ilmenite in—200 mesh size with 250 cc of furnace oil, 200 cc of water and a few ccs of very good commercially available wetting agent are thoroughly ground to form a slurry, dried and the vapours ignited after 10 minutes and the mass raked. The total time taken was 20 minutes. 735 gm of the calcine are obtained.

100 gm of the calcine were taken for leaching and the results given are based on values obtained with a dozen experiments conducted with 100 gm lots of the calcine.

100 gm of the calcine are ground well and reacted with 325 cc of 20% hydrochloric acid by the procedure already described. The residue from this operation weighed 70 gm and on roasting gave 65 gm of material having a titanium dioxide content of 81.6%. 180 gm of low grade manganese ore containing about 30% manganese was roast-reduced and then oxidised and the 150 gm of this roast-reduced ore containing a mixture of Mn_2O_3 and Mn_3O_4 was treated with the byproduct containing free hydrochloric acid and iron chlorides. 151 gm of manganese chloride was obtained.

Noteworking features

(1) A process for the elimination of iron from ilmenite through the use of hydrochloric acid solution has been invented. The byproduct from this operation consisting of a mixture of iron chloride-hydrochloric acid is reacted with roast-reduced low grade manganese ore to obtain pure manganese chloride solution. Thus, two useful products viz., about 75% titanium dioxide concentrate from ilmenites containing about 55% titanium dioxide is obtained and also very pure manganese chloride solutions from low grade, high iron manganese ores containing about 30% manganese.

(2) Low grade ilmenite containing about 55% titanium dioxide suitable for hydrochloric acid leaching is obtained by heating ilmenite out of contact with air at 600°C for about half an hour in the presence of carbonaceous fuel in the form of fuel, oil, saw dust and mixtures thereof and the like in suitable proportions and is then leached with 15% hydrochloric acid (such as the one obtained as a byproduct from alkali chlorine industry, in the manufacture of organic chlorine compounds etc.) at atmospheric pressure for about two hours. The residue from this operation is subjected to the same procedure at least once again and the residue from the second operation is heated at 800°C and finally leached with hydrochloric acid at atmospheric pressure for about one hour.

(3) As claimed in (1) and (2), the iron chloride-hydrochloric acid obtained in the said three leaching steps is mixed together and reacted with roast-reduced low grade, high iron manganese ore. The manganese ore containing about 30% manganese is mixed with 10-15% of its weight of charcoal and heated out of contact with air for about half an hour and then roasted for 15 minutes before reacting with iron chloride- hydrochloric acid solutions. The roast-reduced manganese ore and the iron chloride hydrochloric acid solutions are heated upto 80°C for about half an hour and filtered to recover pure manganese chloride solutions.

WE CLAIM :

1. A process for the elimination of iron from ilmenite through the use of hydrochloric acid which is characterised in that the process steps are

(i) heating out of contact with air the ilmenite with carbonaceous material at about 600°C for about an hour,

(ii) leaching the cold mass from operation (i) with 15% hydrochloric acid at atmospheric pressure for about one hour at temperatures between 85° to 90°C,

(iii) repeating process (i) and (ii) a second time, and

(iv) the residue is then finally calcined at about 800°C for about an hour and leached with 15% hydrochloric acid, thus an ilmenite containing a titanium dioxide content of above 75% is obtained, with a mixture of ferrous chloride hydrochloric acid as byproduct,

(v) utilisation of byproduct ferrous chloride-hydrochloric acid mixtures (a) roast-reducing low grade or high grade manganese ore in about — 80 mesh size to get a mixture of Mn_3O_4 and Mn_2O_3 and Fe_2O_3; (b) this roast-reduced ore is treated with hot ferrous chloride-hydrochloric acid byproduct to get very pure manganese chloride solution which is filtered off from the only insolubles.

2. A process as claimed in claim 1 wherein the heating out of contact with air the ilmenite with suitable carbonaceous material is done at temperatures not exceeding 600°C and time not exceeding one hour.

3. A process as claimed in claim 1 or 2 wherein mixed carbonaceous material such as coal, charcoal, fuel oil, saw dust mixtures is used.

4. A process for the elimination of iron from ilmenite to obtain beneficiated ilmenite containing well above 75% TiO_2 and pure manganese chloride substantially as hereinbefore described.

Dated this 9th day of January, 1968.

(Sd./-)
PATENTS OFFICER,
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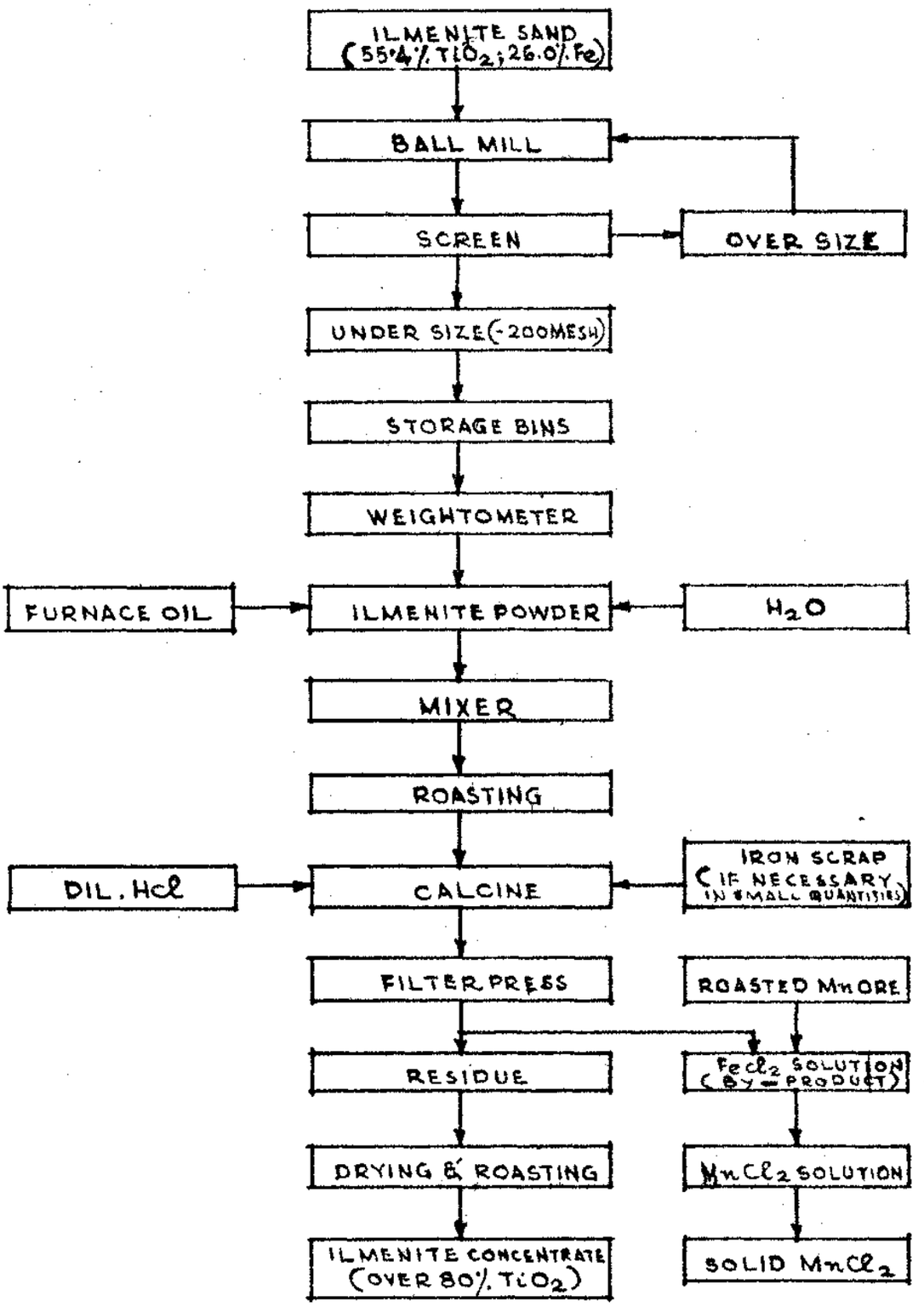
No. OF SHEETS :- 1.

No. 110153

SHEET No. :- 1.

FLOW SHEET – CHEMICAL BENEFICIATION OF ILMENITE IN HYDROCHLORIC ACID MEDIUM.



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