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


Index at acceptance—39L[III] 40F[IV(4)-14ID][XXXIII(8)].

IMPROVEMENTS IN OR RELATING TO CHEMICAL BENEFICENTATION OF ILMENITE—
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI, INDIA, AN INDIAN
REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (XXI of 1860).

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

This is an invention by VEERARAGHAV ARA- VAMUTHAN, Scientist, YELLAMRAJU DURGA PRA- SADA RAO, Scientist and RAMASUBRAMANIAM 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 aqua regia; (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 600-1000°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 by iron by carbon in an electric arc 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) firing up the chlorine content of waste chlorine liquor (a mixture of iron chloride-hydrochloric acid) as mangaenese chloride by utilising the cheap and abundantly 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 manner from the ilmenite containing 55% titanium dioxide which has very high reactivity for reaction with hydrochloric acid of 15-25% concentration at atmospheric pressures and at temperatures of the order of 80-100°C; (2) the 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, mangaenese chloride by preparing a very active manganese oxide-manganese dioxide mixtures from low as well as high grade ores of mangaenese by first reducing the ores to obtain manganese 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 hydrochloric acid to obtain very pure mangaenese 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 carbonateous 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 about 75% is obtained, it is a mixture of ferrous chloride hydrochloric acid as byproduct,
(v) utilisation of byproduct ferrous chloride-hydrochloric acid mixtures (a) roasting-reducing low grade or high grade mangaenese ore in about 60 mesh size to get a mixture of MnO, and MnO₂ and Fe₂O₃; (b) this roasting-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 carbonateous material is done at temperatures not exceeding 600°C and time not exceeding one hour.

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

Titanium dioxide concentrate containing above 75% titanium dioxide from ilmenite containing above 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% titania 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 cooling is treated with 1200 cc of 15% hydrochloric 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 rost-reduced manganese ore containing a mixture of MnO₂-MnO, etc., besides alumina and silica. About 600 gm of low grade manganese ore (40% manganese) was used in the rost-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

Price: TWO RUPEES.
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 1.

Example III

750 gm of ilmenite in—200 mesh size with 250 cc of furnace oil, 200 cc of water and a few cc of very good commercially available wetting agent are thoroughly ground to form a slurry, dried and the vapours ignited after 10 minutes and then milled. 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 roasted-reduced and then oxidised and the 150 gm of this roasted-reduced ore containing a mixture of MnO₂ and Mn₂O₃ was treated with the byproduct containing free hydrochloric acid and iron chlorides. 151 gm of manganese chloride was obtained.

Note working features

(1) A process for the elimination of iron from ilmenite through the use of hydrochloric acid which has been invented. The byproduct from this operation consisting of a mixture of iron chloride-hydrochloric acid is reacted with a mixture of iron chloride-hydrochloric acid until the mixture of iron chloride-hydrochloric acid becomes a mixture of iron chloride-hydrochloric acid and iron chlorides. 151 gm of manganese chloride was obtained.

(2) As claimed in (2) and (3), the iron chloride-hydrochloric acid obtained in the said three leaching steps is mixed together and reacted with roasting-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 roasting-reduced manganese ore and the iron chloride hydrochloric acid solutions are heated up to 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°C to 90°C,

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

(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 MnO₂ and Mn₂O₃ and Fe₂O₃; (b) this roast-reduced ore is treated with hot ferrous chloride-hydrochloric acid to get 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% TiO₂ and pure manganese chloride substantially as hereinbefore described.

Dated this 9th day of January, 1968.

(Sd./)

PATENTS OFFICER,
Council of Scientific & Industrial Research.
FLOW SHEET - CHEMICAL BENEFICIATION OF
ILMENITE IN HYDROCHLORIC ACID MEDIUM

ILMENITE SAND
(65% TiO₂, 12% Fe)

BALL MILL

SCREEN

OVER SIZE

UNDER SIZE (200MESH)

STORAGE BINS

WEIGHTOMETER

FURNACE OIL

ILMENITE POWDER

H₂O

MIXER

ROASTING

DIL. HCl

CALCINE

IRON SCRAP
(If necessary, in small quantities)

FILTER PRESSES

ROASTED MnO₂

RESIDUE

Fe₂Cl₆ SOLUTION
(By-product)

DRYING & ROASTING

MnCl₂ SOLUTION

ILMENITE CONCENTRATE
(Over 80% TiO₂)

SOLID MnCl₂