

Specification No. 59713. Application No. 59713, dated 22nd February 1957. Complete Specification left on 20th December 1957. (Accepted 20th August 1958.)

## PROVISIONAL SPECIFICATION.

### PRODUCTION OF PURE MANGANESE SULPHATE AND HIGH GRADE IRON OXIDE FROM LOW GRADE MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

*The following specification describes the nature of this invention.*

THIS IS AN INVENTION BY THIRUMANGALAM RENGASWAMI VENKATASUBRAMANIAN (SENIOR LABORATORY ASSISTANT, AND VEERARAGAVA ARAVAMUTHAN SENIOR SCIENTIFIC OFFICER, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, ALAGAPPA COLLEGE, P.O. KARAIKUDI, S. RLY. INDIA, BOTH INDIAN CITIZENS.

This invention relates to utilization of waste sulphate pickle liquor from iron and steel industries for the production of manganese sulphate and ferric oxide.

The invention has particular reference to improvements in or relating to the utilization of waste sulphate pickle liquor from iron and steel industries for the production of manganese sulphate and ferric oxide from manganese ores with special reference to the treatment of low grade ores of high iron and silica contents.

Although the use of waste pickle liquor for the production of manganese sulphate from manganese dioxide (or pyrolusite ore) or manganese carbonate (natural or synthetic) is covered by an Indian Patent No. 42281, no mention is made there regarding the use of low-grade manganese ores for the said purpose. The process described here is different from the one described in the Indian Patent 42281. In the present process ferric sulphate and manganese sulphate are produced initially and ferric oxide is obtained by preferential thermal decomposition of the mixed sulphates. Manganese sulphate remains undecomposed. The earlier patent referred to above relates only to the reaction between waste pickle liquor and manganese dioxide or pyrolusite ore for the production of manganese sulphate and ferric oxide in one stage. If this method is applied to low-grade ores, iron oxide suitable for use as a pigment cannot be directly obtained as a residue because it will be contaminated with varying proportions of different forms of iron oxides present initially and unacted upon in the ore, silica, etc., besides ferric oxide formed as a result of reaction. Hence it has to be further purified if the pigment grade of ferric oxide is to be obtained.

In the present process which is applicable not only to pyrolusite ore but also to low-grade, high iron silica ores containing only about 30 per cent. manganese, manganese sulphate and ferric sulphate produced by interaction between waste pickle liquor and ore is leached out first. This initial leaching step is not included in the patent 42281 but is considered essential in the present process to get high purity ferric oxide and manganese sulphate in subsequent steps.

The method evolved by us consists in reacting -100 mesh size low-grade manganese ores with pickle liquor in proper proportions at 85-95°C., filtering off the ferric sulphate-manganese sulphate solution evaporating it to dryness and decomposing the solid at 650-700°C. The sulphurous gases expelled can be collected and utilised. Pure manganese sulphate is leached out from the residue leaving behind pure ferric oxide, if necessary with the addition of small amounts of manganese carbonate.

In a typical experiment the following results were obtained:

50 gms. of manganese ore containing 33.51 per cent. manganese and 22.3 per cent. iron was treated with pickle liquor containing 167 gms. of ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 36 gms. of sulphuric acid in 411 ccs. of water, 225 ccs. of manganese sulphate solution containing 6 per cent. manganese and less than 0.1 per cent. iron was got. This represents more than 80 per cent. extraction of the manganese originally present in 50 gms. of the ore. 33 gms. of ferric oxide containing 66.04 per

cent. iron was obtained as a valuable byproduct suitable for use as a pigment. The quality of iron oxide thus obtained satisfies the requirements prescribed for iron oxide pigment by the Indian Standards Institution. The manganese sulphate solution has been found to be suitable for the production of battery grade manganese dioxide.

An additional advantage (the important advantage being the utilisation of low-grade high iron-silica manganese ores) of our process is that besides waste pickle liquor mixtures of waste pickle liquor and the cell effluent (a mixture of manganese sulphate and sulphuric acid) from electrolytic manganese dioxide plants can also be utilized for the production of pure manganese sulphate from low-grade manganese ore.

*Modified procedure for utilising pickle liquor in combination with cell effluent from electrolytic manganese plants:*

The production of pure manganese sulphate and pure iron hydroxide from low-grade manganese ores and waste pickle liquor can also be carried out using pickle liquor in conjunction with the cell effluent from electrolytic manganese plants. The following modification of the procedure is necessary because of the presence of ammonium sulphate in cell effluent from electrolytic manganese plants. After obtaining a mixture of manganese and ferric sulphates in solution by treating low-grade ore with pickle liquor as described earlier iron is eliminated as hydroxide by adding manganese carbonate. The manganese carbonate necessary for the process is obtained from the cell effluent from the electrolytic manganese plants (containing a mixture of manganese sulphate, ammonium sulphate and sulphuric acid) by neutralising it with ammonia and then reacting in the presence of carbon dioxide and ammonia. Manganese carbonate is precipitated and ammonium sulphate is obtained in solution as a valuable byproduct. Conclusions on the said lines were arrived at as a result of numerous experiments with artificially made cell effluent from electrolytic manganese producing plants.

The process described here is also different from the method of Hoak and Coul (Chemical Engineering Progress (1950) Vol. 46, No. 3., pp. 158-162) for utilizing low grade manganese ores by reacting them with waste pickle liquors. Hoak and Coul concentrated their attention on preventing the formation of ferric sulphate along with manganese sulphate during the leaching operations. Contrary to this we find it advantageous to leach out manganese as manganese sulphate along with ferric sulphate which is subsequently used for recovering pure manganese sulphate and iron oxide. Hoak and Coul eliminated iron by the addition of precipitated chalk and concentrated their attention only on the production of manganese oxide concentrates from low-grade ores through the intermediate formation of manganese sulphate and chloride. Thus the valuable sulphate content of pickler liquor eliminated as a product of low value, viz., calcium sulphate and in a country like India which is deficient in sulphur resources such a method cannot be economical.

From the above it will be clear that the process described here is superior to other methods patented for the

production of pure manganese sulphate and pigment grade ferric oxide from manganese ores and waste pickle liquor and has wider application because,

- (1) it utilises low-grade manganese ores;
- (2) it utilises waste pickle liquor as such;
- (3) it utilises waste pickle liquor in conjunction with the cell effluent from electrolytic manganese dioxide plant; and

- (4) it utilises waste pickle liquor in conjunction with the cell effluent from electrolytic manganese plants.

R. BHASKAR PAI

Patents Officer,

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 7th day of February, 1957.

## COMPLETE SPECIFICATION.

### PRODUCTION OF PURE MANGANESE SULPHATE AND HIGH GRADE IRON OXIDE FROM LOW GRADE MANGANESE ORES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-I, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (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 THIRUMANGALAM RENGASWAMI VENKATASUBRAMANIAN SENIOR LABORATORY ASSISTANT, AND VEERARAGAVA ARAVAMUTHAN SENIOR SCIENTIFIC OFFICER, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, ALAGAPPA COLLEGE, P.O., KARAIKUDI, S. RLY. INDIA, BOTH INDIAN CITIZENS.

This invention relates to utilization of waste sulphate pickle liquor from iron and steel industries for the production of manganese sulphate and ferric oxide.

The invention has particular reference to improvements in or relating to the utilization of waste sulphate pickle liquor from iron and steel industries for the production of manganese sulphate and ferric oxide from manganese ores with special reference to the treatment of low grade ores of high iron and silica contents.

Although the use of waste pickle liquor for the production of manganese sulphate from manganese dioxide (or pyrolusite ore) or manganese carbonate (natural or synthetic) is covered by an Indian Patent (No. 42281), no mention is made there regarding the use of low-grade manganese ores for the said purpose. The process described here is different from the one described in the Indian Patent 42281. According to the present invention, ferric sulphate and manganese sulphate are produced initially and ferric oxide is obtained by preferential thermal decomposition of the mixed sulphates. Manganese sulphate remains undecomposed. The earlier patent referred to above relates only to the reaction between waste pickle liquor and manganese dioxide or pyrolusite ore for the production of manganese sulphate and ferric oxide in one stage. If this method is applied to low grade ores, iron oxide suitable for use as a pigment cannot be directly obtained as a residue because it will be contaminated with varying proportions of different forms of iron oxides present initially and unacted upon in the ore, silica, besides ferric oxide formed as a result of reaction. Hence it has to be further purified if the pigment grade of ferric oxide is to be obtained.

In the present process which is applicable not only to pyrolusite ore but also to low-grade, high iron silica ores containing low percentages of manganese, manganese sulphate and ferric sulphate produced by interaction between waste pickle liquor and ore is leached out first. This initial leaching step is not included in the patent 42281 but is considered essential in the present process to get high purity ferric oxide and manganese sulphate in subsequent steps.

The method evolved by us consists in reacting -100 mesh size low-grade manganese ores with pickle liquor at 85-95°C. in the stoichiometric proportion required by the equation  $\text{MnO}_2 + 2 \text{FeSO}_4 + 2\text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$ . After filtration of the slurry ferric sulphate-manganese sulphate solution is evaporated to dryness and the solids decomposed at 650-700°C. The sulphurous gases expelled can be collected and utilised. Practically pure manganese sulphate is leached out from the residue, leaving behind pure ferric oxide. Traces of iron present in the manganese sulphate solution is eliminated by boiling with small amounts of manganese carbonate.

#### EXAMPLE 1.

In a typical experiment the following results were obtained:

50 grams of manganese ore containing 33.5 per cent. manganese and 22.3 per cent. iron was leached with 500 ml. pickle liquor containing 167 gms. of hydrated ferrous sulphate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) and 36 gms. of sulphuric acid at 85-95°C. The reaction was carried out in a pyrex glass beaker of 600 ml. capacity. Heating was done by immersing a glass coil into which steam was passed. The slurry was mechanically stirred during the reaction and water was periodically added to maintain the volume constant. After the reaction was over (30-40 minutes) the slurry was filtered by employing a water suction filter. 400 ml. of filtrate containing 3.4 per cent. manganese and 5.5 per cent. of iron (as manganese and ferric sulphates) was obtained. This was evaporated first in a silica dish to dryness and then sintered at 650°-700°C. for an hour by a nichrome wire wound electric resistance furnace. The residue which was in the form of a cake was powdered and leached with boiling water for 15 to 20 minutes. The slurry was filtered. 225 ccs. of manganese sulphate solution containing 6 per cent. manganese (w/v) and less than 0.1 per cent. iron (w/v) was thus obtained. This represents more than 80 per cent. extraction of the manganese originally present in 50 gms. of the ore. 33 gms. of ferric oxide containing 66.04 per cent. iron was obtained as a byproduct. The quality of iron oxide thus obtained satisfied the requirements prescribed for iron oxide pigment by the Indian Standards Institution. The manganese sulphate solution was found to be suitable for the production of battery grade manganese dioxide.

The same experiment was repeated on a larger scale using the following modifications. Instead of a pyrex glass beaker, a lead lined vessel (of internal dimensions 60 cm. x 30 cm. x 30 cm.) was used as leaching tank and 4 Kgms. of ore was leached using 36 litres of pickle liquor containing 15 per cent.  $\text{FeSO}_4$  and 5 per cent.  $\text{H}_2\text{SO}_4$  (w/v). A silica sheathed electric immersion heater was used for heating the solution and the slurry was stirred by means of a 1/12 HP electrically operated stirrer. "Denever" filter was used in conjunction with laboratory water suction pump for filtering the slurry. Vessels made of naturally occurring stone available in adjoining areas of Salem in South India were used for evaporating the extract and sintering the solid. Same results were obtained as in the laboratory scale experiment—that is, from 4 Kgms of ore 16 litres of manganese sulphate solution (containing 6 per cent. Mn (w/v) or 3 Kgms of solid  $\text{MnSO}_4$ ) and 2.6 Kgms of red ferric oxide were obtained.

An additional advantage (the important advantage being the utilisation of low-grade high iron-silica manganese ores) of our process is that besides waste pickle

liquor mixtures of waste pickle liquor and the cell effluent (a mixture of manganese sulphate and sulphuric acid) from electrolytic manganese dioxide plants can also be utilised for the production of pure manganese sulphate from low-grade manganese ore.

*Modified procedure for utilising pickle liquor in combination with cell effluent from electrolytic manganese plants:*

The production of pure manganese sulphate and pure iron hydroxide from low-grade manganese ores and waste pickle liquor can also be carried out using pickle liquor in conjunction with the cell effluent from electrolytic manganese plants. The following modification of the procedure is necessary because of the presence of ammonium sulphate in cell effluent from electrolytic manganese plants. After obtaining a mixture of manganese and ferric sulphates in solution by treating low-grade ore with pickle liquor as described earlier, iron is eliminated as hydroxide by adding manganese carbonate. The manganese carbonate necessary for the process is obtained from the cell effluent from the electrolytic manganese plants (containing a mixture of manganese sulphate, ammonium sulphate and sulphuric acid) by neutralising it with ammonia and then reacting in the presence of carbon dioxide and ammonia. Manganese carbonate is precipitated and ammonium sulphate is obtained in solution as a valuable byproduct. Conclusions on the said lines were arrived as a result of numerous experiments with artificially made cell effluent from electrolytic manganese producing plants.

#### EXAMPLE 2.

(i) An artificial mixture of manganese sulphate, ammonium sulphate and dilute sulphuric acid corresponding to the composition of cell effluent of a typical electrolytic manganese plant, was prepared. The mixture had the following composition.

Manganese (as sulphate)	10 gms./litre.
$(\text{NH}_4)_2\text{SO}_4$	135 gms./litre.
$\text{H}_2\text{SO}_4$	50 gms./litre.

1 litre of this mixture was taken, and neutralised by adding liquor ammonia until the free acid was completely neutralised. To this neutralised solution 22 gms. of ammonium bicarbonate (solid) was added to completely precipitate manganese as manganese carbonate. The precipitated manganese carbonate was filtered, washed with water containing dissolved carbon dioxide dried and weighed 20 gms. of manganese carbonate was obtained corresponding to 95 per cent. recovery of the manganese originally present.

(ii) 700 ccs. of a mixture of manganese sulphate and ferric sulphate containing 55 gms of manganese per litre and 112 gms. of iron (both Molar with respect to manganese and ferric sulphates) was taken and heated to  $80^\circ$  to  $90^\circ\text{C}$ . 241 grams of finely powdered freshly precipitated manganese carbonate was added to precipitate iron as hydroxide, the slurry was filtered and the extract was evaporated, heated to dryness and weighed as anhydrous manganese sulphate. 350 grams of  $\text{MnSO}_4$  were obtained. The washed slurry of basic ferric sulphate and ferric hydroxide was sintered to  $700^\circ\text{C}$ . and washed with water and dried. 106 grams of ferric oxide was obtained.

The process described here is also different from the method of Hoak and Coul (Chemical Engineering Progress (1950) VI. 46, No. 3, pp. 158-162) for utilizing low-grade manganese ores by reacting them with waste pickle liquors. Hoak and Coul concentrated their attention on preventing the formation of ferric sulphate along with manganese sulphate during the leaching operations. Contrary to this we find it advantageous to leach out manganese as manganese sulphate along with ferric sulphate which is subsequently used for recovering pure manganese sulphate and iron oxide. Hoak and Coul eliminated iron by the addition of precipitated chalk and concentrated their attention only on the production of manganese oxide concentrates from low-grade ores through the intermediate formation of man-

ganese sulphate and chloride. Thus the valuable sulphate content of pickle liquor was eliminated as a product of low value, viz., calcium sulphate and in a country like India which is deficient in sulphur resources such a method cannot be economical.

From the above it will be clear that the process described here is superior to other methods patented for the production of pure manganese sulphate and pigment grade ferric oxide from manganese ores and waste pickle liquor and has wider application because,

- (1) it utilises low-grade manganese ores;
- (2) it utilises waste pickle liquor as such;
- (3) it utilises waste pickle liquor in conjunction with the cell effluent from electrolytic manganese dioxide plants; and
- (4) it utilises waste pickle liquor in conjunction with the cell effluent from electrolytic manganese plants.

We claim:

1. A process for the production of manganese sulphate from manganese ores which consist in reacting the ore with waste pickle liquor to produce ferric sulphate and manganese sulphate and subjecting the mixed sulphates to thermal decomposition to obtain ferric oxide, manganese sulphate remaining undecomposed.
2. A process as claimed in Claim 1 wherein the manganese ore consists of pyrolusite ore or highly ferruginous silicious low-grade manganese ore.
3. A process as claimed in Claim 1 or 2 wherein a mixture of manganese sulphate and ferric sulphate is first produced in solution by interaction between waste pickle liquor and ore and separated out from the unreacted residue by filtration.
4. A process as claimed in any of the preceding claims wherein -100 mesh or any lower particle size low grade manganese ore is reacted with pickle liquor containing 5-15 per cent.  $\text{FeSO}_4$  and 0.5 per cent.  $\text{H}_2\text{SO}_4$ , filtering off the ferric sulphate-manganese sulphate solution, evaporating it to dryness and decomposing the solid at  $650-700^\circ\text{C}$ ., resulting in expulsion of sulphurous gases which can be collected and utilized, and a residue.
5. A process as claimed in Claim 5 wherein pure manganese sulphate is leached out from the residue leaving behind pure ferric oxide.
6. A process as claimed in Claim 1 wherein a mixture of waste pickle liquor and the cell effluent (a mixture of manganese sulphate and sulphuric acid) from electrolytic manganese dioxide plants is used.
7. A process as claimed in Claim 6, wherein after obtaining a mixture of manganese and ferric sulphate in solution, iron is eliminated as hydroxide by adding manganese carbonate.
8. A process as claimed in Claim 7, wherein the manganese carbonate is obtained from the cell effluent from the electrolytic manganese plant (containing a mixture of manganese sulphate, ammonium sulphate and sulphuric acid) by neutralising it with ammonia and then reacting in the presence of carbon dioxide and ammonia, whereby manganese carbonate is precipitated and ammonium sulphate is obtained in solution as a valuable by-product.
9. A process for the production of manganese sulphate from manganese ores substantially as described in the examples.
10. Pure manganese sulphate and high grade iron oxide obtained from manganese ores, particularly low-grade manganese ores, according to a process substantially as hereinbefore described.

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Dated this 27th day of November 1957.