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ALIEN PROPERTY CUSTODIAN

IRON OXIDES AND METHOD OF PRODUCING SAME

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No Drawing. Application filed April 12, 1941

This invention relates to the production of iron oxides, and the object of the invention is the process whereby a comparatively pure iron oxide may be produced from raw materials such as ores, ore concentrates, iron oxide materials, and the like, as well as the produced oxide itself, possessing new and useful properties making it suitable for use as a pigment and for metallurgical purposes.

Another object of the invention is to provide valuable residue from iron-containing materials by extraction of iron, whereby concentrates of Mn, Cu, Al, Pb, a. o. may be obtained.

In our co-pending U. S. application Ser. No. -----, a process for extracting iron from ferrotitaniferous materials has been described. We have now discovered that a similar process can be applied on other raw materials containing iron. According to our process it is possible to produce valuable iron oxides from such materials, and also in certain cases to obtain residues containing valuable metal compounds in a concentrated state.

Our process for obtaining this new type of iron oxide comprises a conversion of the iron compounds in the raw material into metallic iron, preferably in a finely divided state, and a subsequent oxidation of such metallic iron to form an oxide of the desired type, and separation of said oxide from other materials being present.

The iron-bearing material may be ores such as iron ores used in the steel industry, or an ore concentrate obtained from an ore by any known mechanical, electrical or metallurgical process, or other known processes in ore dressing.

Also "purple ore" or other iron oxides or hydroxides available as by-products from different industries may be used as raw material. If the iron oxides in the raw material have already been converted into metallic iron in a suitable form, the material can be direct converted into iron oxides without previous reduction.

We prefer to use raw materials which before reduction have been crushed and disintegrated to sandlike fineness. If the raw material contains water, acids, undesirable organic matters, sulphur or other matter which can be removed by roasting or calcination, it will generally be advisable to subject the material to such roasting or calcination before it is used in our process.

In the reduction operation common reducing materials applied in reduction of iron ores are used; for instance coal, coke, charcoal, or reducing gases containing carbon monoxide, hydrogen, and the like. The required reduction tempera-

ture is dependant upon the reducing material applied. When using coal or coke or other solid carbon materials, the required reduction temperature for conversion of practically the whole iron content to metallic state has been found to be about 1000° C. When using gases for reduction, a somewhat lower temperature may be used with a similar effect, for instance, a temperature of 800°-900° C.

The reduction operation may be carried out by passing the charge through a rotary kiln heated by suitable means, but stationary retorts may also be used. Reduction in rotary kilns gives a continuous and uniform operation, and this type of apparatus is therefore preferred. It is important that the charge from the reduction kiln is cooled under such conditions that reoxidation is prevented, and the reduced material should not undergo any changes which render it less reactive in the subsequent oxidation process.

When using solid reducing material, like coke or charcoal, it is advisable to have so much of the reducing material in the charge that there is a surplus left in the finished reduced charge. It has been found that such a surplus of reducing material can be easily removed from the cooled charge by mechanical means, for instance, by washing with water or by magnetic separation. An effective cooling is obtained by quenching the reduced material in cold water.

To which extent the iron content should be reduced to metallic state, is dependant upon the quality of the raw material. In general it is desired to reduce as much iron to metallic state as can be easily attained in an economical way, and it is rarely advisable to reduce more than 95% of the iron to metallic state, as the last per cents of the iron require a comparatively long reduction time.

Having obtained a reduced material with the desired metallic iron content, the surplus of the reducing agent is removed by washing, or by other suitable means. Also gangue, ashes or other impurities may be removed before oxidation by washing or other means.

The reduced material or suitable metallic iron from other source is now subjected to a treatment for oxidation of the iron. This oxidation is carried out under such conditions that the iron oxides formed may be easily separated from the rest and are of a uniform, soft texture. The conditions which permit the attainment of the iron oxides in this form, constitute an important feature of our invention.

The oxidation of the iron is carried out at low

temperature, preferably below 100° C, air and water being admitted and in some cases also steam. Temperatures of about 120° C have also been used with success. The admission of air, water or possibly steam is carried out under strictly controlled conditions in order to keep the temperature of the charge at the desired point, for instance, between 40° and 90° C.

The oxidation of the metallic iron to iron oxides is a strongly exothermic reaction. On account of the heat of oxidation the temperature of the material will generally rise, but steam or hot gases are often being admitted to speed up the process. Water will usually have to be introduced in order to keep the desired temperatures, the water evaporated balancing the heat developed by the oxidation.

It has been found that a certain amount of water in the charge promotes the oxidation velocity, and effects the formation of such iron oxides which can be subsequently easily separated from the residue by mechanical means.

The condition of the charge during oxidation may be characterized as semi-dry or slightly wet. The amount of water necessary to obtain this state is different for each kind of ore, depending upon the wetability of the material. For most of the materials an amount up to 20% of the weight of the reduced material has proved sufficient at the beginning of the oxidation process. In some cases 6-10% of water has given the best results. Factors as particle size, degree of reduction, quality of ore, a. o. play an important part in the adjustment of the most favourable water addition, and it is therefore difficult to give more exact figures.

In order to keep the mass in the desired wet condition during the oxidation, water is added to replace the water evaporated besides the water absorbed by the iron oxides formed.

It will be understood that application of steam during oxidation will particularly come into question when more heat is lost by evaporation, radiation, and conduction than generated by the exothermic reaction. It will, however, in many cases be an advantage to start the oxidation by admission of steam.

If the oxidation is carried out at temperatures above 200° C, the iron oxides formed will usually be hard and not easily removable from the residue. The iron oxides formed at such high temperatures have another appearance than the oxides formed at lower temperature.

The oxidation operation may be carried out in stationary or rotary apparatus. It has been found that rotary drums are well suited for the oxidation process, as in such apparatus a continuous operation is possible, and the admission of water, air and steam is easily effected and controlled. It will be understood that in such apparatus the oxidizing gases get well in contact with the material to be treated.

The oxidation may be carried out in one or more steps dependent upon the material and the apparatus used. When using rotary drums, or apparatus like a Wedge furnace for oxidation, the operation is generally carried out in a single step.

Experiments have proved that the oxidation of the iron may be accelerated by using additions of electrolytes, as NaCl, NH₄Cl, MgCl₂, CuCl₂ HCl, FeCl₃. Also the presence of CO₂ or CO₂-containing gases accelerates the oxidation of the metallic iron to a considerable extent.

When the oxidation has been completed, the

charge is subjected to a treatment for separating the iron oxides from the rest. As the soft iron oxides at this stage exist in mechanical mixture with the coarser residue and are not chemically combined with same, the separation may be effected by subjecting the charge to strong agitation in water or by some sort of motion which causes the particles to rub or grind against each other. This operation may be carried out in rotary drums, ore classifiers, or other suitable apparatus. By such operation the iron oxides are suspended in water and may be separated from the residue by washing and decantation.

The iron oxides suspended in water will easily settle when left in settling tanks, and may also be filtered in filter presses or other filtration apparatus, preferably after having been thickened in settling tanks.

The further treatment of the filtered or dewatered iron oxide product will depend on the particular commercial application of same.

The separation of the iron oxides from the residue may also be effected by other means than described, for instance, by electro-magnetic treatment, wet flotation, electro-flotation, air-separation or other means in which advantage is taken of the different physical properties of the iron oxides and the residue. The black iron oxides are strongly magnetic.

The iron oxide product may be used in the preparation of iron oxide pigments. When dried at low temperatures and subsequently disintegrated, it forms an excellent black oxide of iron pigment. The chemical composition appears to be close to Fe₃O₄ with some combined water, or it may be practically anhydrous if the drying temperature has been sufficiently high. The products are of even, uniform structure and of soft texture, the colour being deep black and the tinting strength and hiding power very good, compared with other black inorganic pigments. They also show a low content of water-soluble matter and a practically neutral reaction when tested for pH. The products may be used with advantage in paints, lacquers, enamels, printing ink and for similar purposes. It has been found that paint films, pigmented with our products, show excellent drying properties, and the dry film may be obtained with high gloss, if desired.

The oxidation process may also be carried out in such a way that the iron oxide products get a more or less distinct brownish tone, probably due to a further oxidation of some of the material to Fe₂O₃. In this case the tinting strength is considerably increased. Oxides with more or less distinct brown, yellow or red shades are obtained, mainly when the oxidation takes place in a charge in which the quantity of metallic iron is comparatively low, and the oxidation is allowed to proceed to products of the type Fe₂O₃. In the event the charge is not stirred sufficiently, the yellow or red shades also appear on the surface of the mass. The colour and tone of the iron oxides are influenced by many factors during preparation, as pH, content of water, addition of catalysts.

The iron oxides may also be calcined at higher temperatures, for instance, at 400°-1000° C, preferably under oxidizing conditions in order to obtain iron oxides of different shades and properties.

The iron oxide pigments obtained may be disintegrated or pulverized according to the fineness desired. Air-separation, wet-milling with or without dispersion and classification, elutriation

or other means for obtaining even and uniform products may be applied.

Also in synthetic products of different kinds like linoleum, rubber products and the like our iron oxides are useful as fillers or pigments or both. Magnetite electrodes may also be made of our product.

The product from our process is further very useful as raw material in the iron and steel industry due to its high purity and particularly to the absence of phosphorus and sulphur. When dried or calcined, the iron oxides are obtained in lumps, which can be transported in bulk without further treatment. In some cases it is preferred to briquet or sinter the oxides.

It will be understood that our process may find application in the utilization of iron ores of different origin in the iron and steel industry, making it possible to extract iron from the ores in the form of high grade iron oxides free from undesirable impurities. Ores with a low iron content and other iron ores which are inferior on account of their content of impurities may thus be utilized.

In general our process may be applied to iron-containing ores which by the reduction yield metallic iron and a rest which upon the subsequent oxidation is separable from the iron oxide formed. When using finely divided metallic iron or iron oxides as raw material containing no undesired impurities, there will be no rest to be separated from the oxide formed.

When the raw material contains valuable metals besides iron, concentrates of these are contained in the residue. Such residues may easily be free from gangue and other impurities by mechanical means. Concentrates of metals such as manganese, copper, chromium, aluminium, anadium, columbium, have been obtained.

By our reduction treatment of manganese-iron oxide materials the iron is converted into metallic state, whereas the manganese remains in the product as an oxide. The reduced material may be freed from undesired impurities by washing whereafter it is subjected to an oxidation process in a similar manner as described for other iron containing ores. The metallic iron is converted into an iron oxide and is separated from the coarser manganese concentrate which is left practically unattacked.

In general the oxidation of the metallic iron should be carried so far that only a few per cents, say 1-3% of metallic iron, will remain in the oxidized and washed residue, but in some cases, for instance, when the manganese concentrate is to be used for preparation of ferromanganese, it may be an advantage to leave a considerable amount of metallic iron in the concentrate.

The residue containing the manganese oxides may be free from undesired impurities by mechanical means as, for instance, shaking tables, by magnetic treatment, or flotation, in order to obtain a manganese concentrate in a comparatively pure state.

Copper often occurs together with iron in chalcopryrite, bornite, and in copper containing pyrites and similar minerals.

In such minerals the copper as well as iron are usually present as sulphides. Before subjecting the copper-iron ore to the combined reducing and oxidizing operation as described, the ore is usually roasted in order to remove sulphur. During this roasting the iron is converted into oxides. In some cases it is an advantage to roast the ore

at such a temperature that a sintering of the copper occurs. The reduction may be carried out as described above.

The reduced material is freed from any surplus of reducing agent, and the reduced ore may now be subjected to a mechanical treatment by which silicates, gangue and other compounds are separated from the copper-iron concentrate.

The oxidation of the copper-iron material and the separation therefrom of the iron oxides formed are carried out in practically the same manner as described for other iron ores.

We have described our product as iron oxide. By this term is understood iron oxides which may contain hydroxides or hydrates or mixtures thereof. We are not quite sure of the exact composition of our product, but no undue limitation should be derived from our expression which agrees as closely as possible with present terminology.

Below are given some practical examples of the invention:

Example 1

A low grade iron ore was mixed with coal and heated under reducing conditions at 950°-1000° C in a rotary kiln. After reduction the product contained 57% metallic iron. The discharge was quenched in water.

The reduced material was transferred to a tank and washed in a continuous flow of water, whereby surplus of coke, ashes and a part of the gangue were removed.

The reduced ore was then dewatered by filtration and taken to a rotary drum for oxidation of the metallic iron.

The drum was rotated and air introduced, whereby the temperature of the charge rose to about 60° C. At this temperature a rapid oxidation was taking place. During the operation the charge was kept in a semi-dry or slightly wet condition at about 70° C by addition of water, and the rotation continued until practically all the metallic iron had been oxidized.

The charge was then transferred to another rotary drum, where the iron oxide was brought into suspension by washing with water. The overflow from the drum was pumped to a settling tank. After settling the iron oxide pulp was filtered, washed and discharged as a thick cake.

The filter cake was dried at 60° C, and a magnetic product in the form of a soft, uniform powder with deep black colour was obtained.

Example 2

Purple ore obtained by roasting pyrites was reduced at 950°-1000°C by coke in a rotary kiln. The reduced material contained 75% of metallic iron. The reduced product was oxidized as described in example 1. In this case a small amount of magnesium chloride (MgCl₂) was added in order to activate the surface of the metallic iron and accelerate the oxidation. The temperature during oxidation was 60°-90°C. A sample of the mass taken after an oxidation period of 4 hours showed that about 65% of the iron had been converted into iron oxides. By further oxidation practically all the metallic iron was converted into iron oxide, which was treated as in example 1.

Example 3

A manganese ore containing 9.1% Mn and 28.1% Fe was mixed with coal and reduced at 950°-1000°C in a rotary kiln. By reduction 82% of the iron in the ore had been converted to the

metallic state. The discharge was quenched in water.

The reduced material was stirred with water, and after removal of the surplus of carbon, de-watered and taken to a rotary drum for oxidation. A small amount of hydrochloric acid was added to accelerate the oxidation.

The charge was kept in motion and air and steam admitted until the charge had a temperature of about 50°C. The charge was then treated as described in example 1, and after 6 hours' oxidation more than 90% of the iron had been converted into iron oxides.

An analysis of the concentrate showed that 80% of the iron content of the original ore had been removed, and the content of manganese had increased correspondingly. The iron oxide removed contained less than 0.5% Mn.

Example 4

A copper-iron sulphide ore which contained 18% Cu, was roasted until the sulphur was nearly completely removed, and reduced until about 90% of the iron in the ore had been converted to the

metallic state. The reduced product contained 42.5% metallic iron. The discharge was quenched in water.

The oxidation was carried out as described in example 1. On account of the heat of oxidation the temperature rose to 90°C without any admission of steam. The charge was kept between 60° and 90°C during oxidation by small addition of water, which at the same time kept the mass at a rather constant moisture content. The charge was treated as described in example 1.

Example 5

Finely divided iron filings freed from oil, grease, etc. were oxidized in stationary wooden troughs, and the mass was occasionally stirred.

By regulated introduction of air, water, and steam the temperature of the mass rose to about 70° C and was kept at this temperature during the oxidation process. After practically all the metallic iron had been oxidized, the mass was filtered, dried, pulverized, and air-separated.

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