

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Production of Anosovite from Titaniferous Minerals

We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, a body corporate established under the Science and Industry Research Act 1949, of 314 Albert Street, East Melbourne, in the State of Victoria, Commonwealth of Australia, and WESTERN TITANIUM N.L. a body corporate, of 100 Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides a method of treating the titaniferous minerals ilmenite, iron-containing rutile, and their alteration products so as to convert them largely to a material which contains a high proportion of titanium in the trivalent state and has a much higher degree of solubility in dilute acids than the original mineral. The material so formed is suitable for the production of titanium oxide pigment by either the conventional acid process or the more recently developed chloride vapour phase process.

Ilmenite is a mineral composed largely of iron titanate (FeTiO_3) in which ferrous iron predominates over the ferric form. It may also contain minor amounts of various elements such as manganese, magnesium, chromium and vanadium. After heat treatment of the natural mineral or its synthetic equivalent, the ratio of ferric to ferrous iron present in the heat treated product may vary from 0.1 to 1.0. The titanium present in the natural mineral is essentially in the tetravalent state.

Rutile is a mineral containing 95% to sub-

stantially 100% TiO_2 , generally with minor amounts of various other elements; naturally-occurring rutile always contains iron.

The weathering of ilmenite or rutile in an oxidising atmosphere produces what are called "alteration products." Alteration products of ilmenite generally show a higher TiO_2 content, and a higher ferric to ferrous iron ratio than their precursor; they are sometimes referred to as leucoxene.

Ilmenite is the main raw material used for the preparation of titanium dioxide white pigments, but suffers from certain disadvantages in this type of application. It does not yield more than 60% of titanium dioxide on a weight basis, because of the high proportion of oxygen and iron associated with titanium. It is also difficult to dissolve in mineral acids. In the usual process of pigment manufacture, the initial digestion of ilmenite is accomplished by the use of strong sulphuric acid at high temperatures, a step well known to be rather unpredictable, dangerous and often inefficient. Also, since the iron in the mineral is necessarily taken into solution during this initial digestion, problems arise in the subsequent separation and disposal of the unwanted ferrous sulphate so produced. Rutile and leucoxene are generally insoluble in acid and cannot be used efficiently in pigment production by the acid process.

Although processes for the reduction of ilmenite to various mixtures of metallic and oxide or sulphide phases are known, the titanium-bearing phases produced by these known processes have always been materials which, to our knowledge, either resist digestion in strong mineral acids but contain more

[Price 5s. 0d.]

than 75% by weight of TiO_2 , or show a higher degree of acid-solubility at a TiO_2 content less than 75%. The rutile phases produced in previous processes designed to reduce ilmenite in solid granular form are examples of the first type of product in which a high content of TiO_2 is coupled with extreme resistance to acid digestion. Slags formed in processes whereby ilmenite is smelted with fluxes and reducing agents are examples of the second type of product, which can be digested by mineral acids under ordinary conditions of pigment manufacture but contain less than 75% of TiO_2 because of the quantity of flux necessarily remaining in the slag.

The present invention provides a process of pretreating titaniferous minerals of the aforementioned types to produce a particular phase called "anosovite," containing substantially all the titanium values originally present in the mineral. The other main phase produced in this treatment is metallic iron, which may be separated physically or chemically from the anosovite by any of the methods previously described in the literature.

The process of the present invention comprises pre-heating ilmenite, iron-containing rutile, or an alteration product, thereof in granular form in an oxidising atmosphere at between 950°C and 1320°C in the presence of a magnesium compound in an amount such that the mineral grains become coated with magnesian pseudobrookite, and thereafter heating the product of the pre-heating stage with a reducing agent at a temperature of at least 1130°C to produce a mixture of metallic iron and anosovite, the reducing step being carried out in the presence of sufficient divalent ions selected from magnesium, iron, titanium and manganese to ensure that the anosovite structure is maintained on cooling the product.

Anosovite is a stabilised variety of the high-temperature form of Ti_2O_3 , having the deformed orthorhombic structure of pseudobrookite. It has the composition:



where A is Mg, divalent Mn, Ti, Fe, or a mixture thereof; and B is Al, or trivalent Ti, Cr, or a mixture thereof; and where $x+y=1$.

The content of the oxide component AO in the defined composition must be sufficient to preserve the substance in the deformed orthorhombic structure as it cools from its formation temperature to room temperature, otherwise it will spontaneously convert below 177°C to a low-temperature monoclinic form of Ti_2O_3 , accompanied by small amounts of rutile. On an atomic basis the minimum proportion of the component "A" that must be present in the anosovite to prevent such con-

version is 0.04, i.e. at least 4% of the total number of cations in the anosovite. As already indicated the amount of magnesium introduced during the pre-heating step, and optionally also before or during the reduction must be correlated with the amounts of iron, manganese, aluminium and chromium present in the starting mineral and the temperature of the preheating and reduction to ensure that this condition is satisfied.

The anosovite produced by the new process contains from 75% to 100%, preferably from 90% to 100%, of its weight in a form "equivalent" to TiO_2 , and having a high rate of digestion in sulphuric acid in the conventional "acid" process for pigment manufacture. By "equivalent" we mean that the material does not necessarily contain TiO_2 , as such in its structure, but that on digestion in sulphuric acid, followed by steps of oxidation and hydrolysis of the solution, a certain dry weight of TiO_2 can be obtained and expressed as a percentage of the original weight of the material used in the digestion step. This percentage we term the " TiO_2 -equivalent" of our product: it is a means of expressing its potential content of titanium values.

The reducing step of the process is preferably carried out in a rotary kiln, and the production of magnesium pseudobrookite on the surfaces of the mineral grains is very important because its refractory nature prevents agglomeration of the material in the rotary kiln.

The addition of a sodium salt to the charge during the reduction step has a beneficial effect on the distribution of metallic iron in the product, but is not essential to the process. The salt may be sodium chloride or sodium sulphate.

The magnesium compound is normally a salt, the preferred compound being magnesium carbonate. If more than the equivalent of 3.0% MgO by weight is added, difficulties may arise in obtaining anosovite having the desired equivalent TiO_2 content of at least 90% by weight. The presence of at least the equivalent of 0.6% of MgO by weight in the pre-heating stage ensures that sufficient divalent ions are present in the reducing stage for the production of anosovite.

Preferably, the reduction stage is carried out at a temperature between 1200°C and 1300°C . Carbon is the preferred and usual reducing agent.

The lower limit of the temperature range of the pre-heating stage is related to the minimum temperature of formation of magnesium pseudobrookite, whilst the upper limit is determined by the onset of sintering effects which make the heating difficult in practice. This pre-heating may conveniently be performed in air for at least one hour.

The convenient upper limit of the temperature range in the reduction step is 1320°C because above this temperature production difficulties, particularly agglomeration, prevent the use of a rotary kiln. Also increasing amounts of the carbides and nitrides of titanium and iron are generated at temperatures above this limit and such compounds are undesirable in the product.

The lower limit of the temperature range in the reduction step, 1130°C, is determined by the maximum temperature at which an acid-insoluble phase, tagirovite, can exist in equilibrium with carbon. Tagirovite is Ti_2O_3 having the structure of corundum, and below 1130°C, persists as a most undesirable component of the products of reduction of most titaniferous ores. In the present invention the titaniferous material is coated with a refractory layer of magnesium pseudobrookite so that it can be handled in a rotary kiln, without agglomeration, at temperatures which prevent the appearance of tagirovite.

In typical procedures for carrying out the process according to this invention, grains of ilmenite, iron-containing rutile, or alteration products thereof, or any mixture of these minerals having a diameter of between 50 and 500 microns are heated in air with between 0.6 and 3.0% by weight of magnesium carbonate calculated as MgO . At 950°C, the pre-heat period is generally from 1 to 2 hours, whilst at 1300°C a period of from 10 to 30 minutes normally suffices.

On completion of the pre-heat, the product is fed to a rotary kiln containing sufficient carbon to give a reduction mixture, by weight, of one to two parts of the pre-heated product to one part of carbon. The temperature of the reduction kiln is maintained between 1200°C and 1300°C and the residence time of the charge at this temperature is from 1½ to 2 hours, the material being fed out of the heating zone into an integral cooler in which the atmosphere is maintained substantially free of oxygen until the product temperature falls below 100°C. The product is substantially a mixture of anosovite and metallic iron. On separating the metallic iron from the mixture by any suitable means and dissolving the anosovite fraction in sulphuric acid, the "equivalent" composition range of the anosovite produced from various titaniferous ores was determined to be as follows:—

(Equivalent)	by weight
TiO_2	90—103%
FeO	0.2—6.3%
MgO	0.2—3.7%
MnO	1.3—1.7%
SiO_2	0.6—1.8%

These anosovite samples were produced from titaniferous ores containing various impuri-

ties, as is evident from the analysis above. The total amount of divalent oxides present and capable of stabilising the anosovite structure ($FeO+MgO+MnO+TiO$) is considerably in excess of the minimum proportion of 0.04 of the total number of cations in a unit of the above formula, but this is largely an indication that in the reduction step, segregation of iron into a discrete metallic phase was not perfectly achieved. This is probably because lignitic coal char was used as the form of carbon in the example described and also the rotary kiln was not perfectly sealed against ingress of some free oxygen.

WHAT WE CLAIM IS:—

1. A process for producing anosovite and metallic iron from a titaniferous mineral chosen from ilmenite, iron-containing rutile, and their alteration products, which comprises pre-heating the said mineral in granular form in an oxidising atmosphere at between 950°C and 1320°C in the presence of a magnesium compound in an amount such that the mineral grains become coated with magnesium pseudobrookite, and thereafter heating the product of the pre-heating stage with a reducing agent at a temperature of at least 1130°C to produce a mixture of metallic iron and anosovite, the reducing step being carried out in the presence of sufficient divalent ions selected from magnesium iron, titanium and manganese to ensure that the anosovite structure is maintained on cooling the product.

2. A process as claimed in claim 1, in which the magnesium compound is present in an amount of at least 0.6% by weight calculated as MgO .

3. A process as claimed in claim 2, in which the magnesium compound is present in an amount of between 0.6% and 3.0% by weight calculated as MgO .

4. A process as claimed in claim 2 or claim 3, in which the magnesium compound is added in the form of magnesium carbonate.

5. A process as claimed in any one of the preceding claims in which the metallic iron is subsequently separated from the anosovite.

6. A process as claimed in any one of the preceding claims, in which the reducing treatment is carried out at a temperature of less than 1320°C.

7. A process as claimed in claim 6, in which the product of the pre-heating stage is mixed with carbon to give a reduction mixture comprising between one and two parts of the pre-heated product to one part of carbon by weight.

8. A process as claimed in claim 7, in which the reducing treatment is carried out at a temperature between 1200°C and 1300°C.

9. A process as claimed in any one of the preceding claims in which the reducing treatment is carried out in a rotary kiln.



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The convenient upper limit of the temperature range in the reduction step is 1320°C because above this temperature production difficulties, particularly agglomeration, prevent the use of a rotary kiln. Also increasing amounts of the carbides and nitrides of titanium and iron are generated at temperatures above this limit and such compounds are undesirable in the product.

The lower limit of the temperature range in the reduction step, 1130°C, is determined by the maximum temperature at which an acid-insoluble phase, tagirovite, can exist in equilibrium with carbon. Tagirovite is Ti_2O_3 , having the structure of corundum, and below 1130°C, persists as a most undesirable component of the products of reduction of most titaniferous ores. In the present invention the titaniferous material is coated with a refractory layer of magnesium pseudobrookite so that it can be handled in a rotary kiln, without agglomeration, at temperatures which prevent the appearance of tagirovite.

In typical procedures for carrying out the process according to this invention, grains of ilmenite, iron-containing rutile, or alteration products thereof, or any mixture of these minerals having a diameter of between 50 and 500 microns are heated in air with between 0.6 and 3.0% by weight of magnesium carbonate calculated as MgO . At 950°C, the pre-heat period is generally from 1 to 2 hours, whilst at 1300°C a period of from 10 to 30 minutes normally suffices.

On completion of the pre-heat, the product is fed to a rotary kiln containing sufficient carbon to give a reduction mixture, by weight, of one to two parts of the pre-heated product to one part of carbon. The temperature of the reduction kiln is maintained between 1200°C and 1300°C and the residence time of the charge at this temperature is from 1½ to 2 hours, the material being fed out of the heating zone into an integral cooler in which the atmosphere is maintained substantially free of oxygen until the product temperature falls below 100°C. The product is substantially a mixture of anosovite and metallic iron. On separating the metallic iron from the mixture by any suitable means and dissolving the anosovite fraction in sulphuric acid, the "equivalent" composition range of the anosovite produced from various titaniferous ores was determined to be as follows:—

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WHAT WE CLAIM IS:—

1. A process for producing anosovite and metallic iron from a titaniferous mineral chosen from ilmenite, iron-containing rutile, and their alteration products, which comprises pre-heating the said mineral in granular form in an oxidising atmosphere at between 950°C and 1320°C in the presence of a magnesium compound in an amount such that the mineral grains become coated with magnesium pseudobrookite, and thereafter heating the product of the pre-heating stage with a reducing agent at a temperature of at least 1130°C to produce a mixture of metallic iron and anosovite, the reducing step being carried out in the presence of sufficient divalent ions selected from magnesium iron, titanium and manganese to ensure that the anosovite structure is maintained on cooling the product.

2. A process as claimed in claim 1, in which the magnesium compound is present in an amount of at least 0.6% by weight calculated as MgO .

3. A process as claimed in claim 2, in which the magnesium compound is present in an amount of between 0.6% and 3.0% by weight calculated as MgO .

4. A process as claimed in claim 2 or claim 3, in which the magnesium compound is added in the form of magnesium carbonate.

5. A process as claimed in any one of the preceding claims in which the metallic iron is subsequently separated from the anosovite.

6. A process as claimed in any one of the preceding claims, in which the reducing treatment is carried out at a temperature of less than 1320°C.

7. A process as claimed in claim 6, in which the product of the pre-heating stage is mixed with carbon to give a reduction mixture comprising between one and two parts of the pre-heated product to one part of carbon by weight.

8. A process as claimed in claim 7, in which the reducing treatment is carried out at a temperature between 1200°C and 1300°C.

9. A process as claimed in any one of the preceding claims in which the reducing treatment is carried out in a rotary kiln.

10. A process as claimed in claim 9, in which the product of the reducing treatment is fed from the rotary kiln to a cooler in which the atmosphere is kept substantially free of oxygen until the product temperature has fallen below 100°C.

11. A process as claimed in any one of the preceding claims in which a sodium salt is added to the charge during the reduction step.

12. A process according to claim 1 substantially as hereinbefore described. 10

13. Anosovite when produced by a process according to any one of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
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Gray's Inn, London, W.C.1.

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