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3,666,513

TREATMENT OF MINERALS

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U.S. Cl. 106—288 B

9 Claims

ABSTRACT OF THE DISCLOSURE

A process for improving the brightness of phyllosilicate minerals containing ferric ions in solid solution within the crystal lattice of the minerals. The process comprises the steps of bleaching by a reducing bleaching agent an intercalation complex of a phyllosilicate mineral and thereafter decomposing the intercalation complex under non-oxidising conditions.

BACKGROUND OF THE INVENTION

This invention relates to a process for improving the brightness of phyllosilicate minerals, i.e. silicate minerals which have a layer lattice crystal structure, for example minerals of the kandite group such as kaolinite, dickite, nacrite and halloysite.

The three main causes of discolouration of phyllosilicate minerals which are white or light-coloured when pure are:

- discrete particles of mineral impurities which contain ferric ions or other highly coloured ions;
- discrete particles of organic impurities; and
- ferric ions which are in solid solution within the particles of the desired mineral and which occupy sites in the crystal lattice of the latter.

It is known to reduce the discolouration due to cause (a) by, for example, a high-intensity magnetic separation process or by a bleaching process using a reducing bleaching agent or by a combination of both processes. It is also known to reduce the discolouration due to cause (b) by destroying the organic impurities.

However, there has not been disclosed a satisfactory process for obviating the discolouration of a phyllosilicate mineral due to cause (c). The difficulty of attacking ferric ions contained within the particles of the desired mineral, for example a kaolinitic clay, resides in the fact that when the mineral is in its normal crystalline state the ferric ions are inaccessible to the bleaching agent. Thus, for example, in the case of kaolinitic clay minerals, ferric ions are substituted for aluminium ions in the crystal lattice in sites in the body of the mineral particles i.e. in sites other than those at the surface of the mineral particle. The presence of such ferric ions in the crystal lattice of kaolinite has been confirmed by Mossbauer effect measurements as described by P. J. Malden and R. E. Meads in "Nature," vol. 215, page 844, 1967.

It is an object of the present invention to provide a process for improving the brightness of silicate minerals having a layer lattice crystal structure and discoloured by the presence of ferric ions which are in solid solution within the particles of the mineral.

SUMMARY OF THE INVENTION

Accordingly the present invention provides a process for improving the brightness of silicate minerals having a layer-lattice crystal structure, e.g. minerals of the kandite group such as kaolinite, halloysite, nacrite, and dickite, which process comprises the steps of:

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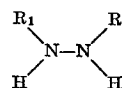
- contacting the silicate mineral in aqueous suspension with (i) an intercalating agent which is capable of forming with the mineral an intercalation complex and (ii) a reducing bleaching agent which is capable of converting ferric ions in the mineral to ferrous ions; and
- decomposing the intercalation complex under non-oxidising conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

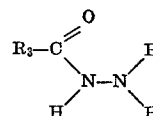
Preferably, the treatment of the silicate mineral with the intercalating agent and reducing bleaching agent is carried out for at least two hours.

The amount of intercalating agent used is preferably such that the mole ratio of silicate mineral having a layer-lattice crystal structure to intercalating agent does not exceed 3:2.

It has been found that hydrazine is capable of acting both as an intercalating agent and as a reducing bleaching agent capable of reducing ferric ions in solid solution within the crystal lattice to ferrous ions. Other compounds which are capable of acting both as an intercalating agent and as a reducing bleaching agent include substituted hydrazines of the general formula:



wherein R_1 is hydrogen or C_1-C_6 alkyl and R_2 is C_1-C_6 alkyl; and primary hydrazides of the general formula:



wherein R_3 is hydrogen or C_1-C_6 alkyl.

Other intercalating agents which can be used but which do not also act as reducing bleaching agents, include urea, formamide and acetamide.

When using hydrazine, the concentration of the hydrazine in the aqueous suspending liquid should be in the range from 0.1 to about 20 molar. As noted hereinabove, the mole ratio of silicate mineral to intercalating agent preferably does not exceed 3:2 so that in the case of a kaolinitic clay which consists substantially of kaolinite, the weight ratio of kaolinite (mol. wt. 258) to hydrazine (mol. wt. 32) preferably does not exceed 12:1. Thus, when the concentration of the hydrazine solution is 0.1 M the clay solids content of the suspension preferably does not exceed 3.7% by weight, whereas at high hydrazine concentrations (up to about 20 M) the solids content of the aqueous suspension is limited only by the need for the suspension to be of a workable consistency (i.e. a maximum solids content of about 75% by weight).

The temperature at which the treatment is carried out depends, inter alia, on the concentration of the intercalating agent in the aqueous suspension. It is found with hydrazine or urea, for example, that at high concentrations the rate of intercalation increases with temperature whereas at low concentrations the rate of intercalation decreases with temperature.

The silicate mineral can be separated from the suspending medium by, for example, filtration, centrifuging, decantation or sedimentation.

Advantageously, the intercalation complex is decomposed by separating the intercalated and bleached silicate mineral from the aqueous suspending liquid in which it was contacted with the intercalating agent and bleaching agent, washing the intercalated and bleached silicate mineral with an aqueous washing medium under non-oxidising conditions, separating the washed silicate mineral from the

aqueous washing medium, and drying the washed silicate mineral. The washing of the intercalated and bleached silicate mineral with an aqueous washing medium under non-oxidising conditions is preferably carried out by resuspending the intercalated and bleached silicate mineral in an aqueous solution of an oxygen scavenger to remove the intercalating agent, and thereafter separating the silicate mineral from the aqueous washing medium and re-washing it with water. Alternatively, the intercalated and bleached silicate mineral is washed with de-oxygenated water and in a non-oxidising atmosphere.

When the separated, intercalated and bleached silicate mineral is treated with an aqueous solution of an oxygen scavenger to remove the intercalating agent, the oxygen scavenger is preferably sodium or zinc dithionite, but other reducing agents which react with oxygen in solution can also be used, for example a solution of sulphur dioxide containing a trace amount of a copper salt catalyst, the solution being kept just acid to prevent precipitation of the copper salt catalyst. When using sodium or zinc dithionite the concentration of the dithionite should be in the range 0.02 to 5.0 gm. of dithionite per 100 ml. solution and the quantity of solution used should be such as to remove all of the intercalating agent from the silicate mineral, thus causing the mineral lattice to revert to its normal, unexpanded spacing. In this way the presence of free oxygen in solution, which would reoxidise ferrous ions to ferric ions, is avoided until the silicate mineral is no longer expanded.

After the intercalation complex has been decomposed, the silicate mineral is generally dried. In the case of kaolinitic clays, the drying is carried out under conditions such that the maximum temperature of the silicate mineral does not exceed 120° C. and preferably does not exceed 80° C. In some cases it may be desirable to dry the silicate mineral with or in the presence of an oxygen-free gas, e.g. nitrogen.

The process of the invention can be used in conjunction with other oxidising or reducing bleaching processes, i.e. other oxidising or reducing processes can be carried out before or after the process of the invention. Thus, in one embodiment of the invention, the silicate mineral is treated with an oxidising bleaching agent, for example ozone, hydrogen peroxide, chlorine, chlorine water, an organic peroxy compound, e.g. peracetic acid or perbenzoic acid, or permonosulphuric or perdisulphuric acid, before the treatment with the intercalating agent and reducing bleaching agent.

The invention is illustrated by the following example.

EXAMPLE

10 gm. of each of the following kaolinitic clays were stirred at room temperature into 150 ml. of an 11 molar aqueous hydrazine solution.

Clay A: This was a sample of an English china clay, having a particle size distribution such that 80% by weight consisted of particles smaller than 2 microns equivalent spherical diameter, which had been bleached in a conventional manner by treatment with sodium dithionite in an amount equivalent to about 0.2% by weight based on the weight of dry clay to give percentage reflectances to light of 458 and 574 millimicrons wavelength, as measured on an ELREPHO brightness meter, of 90.2% and 92.9% respectively.

Clay B: This was a sample prepared by subjecting Clay A to treatment, at pH 4.5, with an oxidising bleaching agent in the form of a 100 vol. (30%) hydrogen peroxide solution, followed by boiling for 4 hours to decompose excess peroxide.

Clay C: This sample was prepared by subjecting an English china clay, which had been refined in the laboratory so that substantially all of it consisted of particles between 1 micron and 2.5 microns equivalent spherical diameter, to treatment in a high intensity magnetic separator in the manner disclosed in U. K. patent specification No. 1,077,242, and thereafter bleaching it firstly with

about 0.2% by weight of sodium dithionite, based on the weight of the dry clay, and secondly with an oxidising bleaching agent in the form of chlorine water containing 0.3 gm. of chlorine in 100 ml. of solution.

Clay D: This was a sample of a kaolinitic clay from Georgia, U.S.A., having a particle size distribution such that 93% by weight consisted of particles smaller than 2 microns equivalent spherical diameter, which had been bleached by treatment with sodium dithionite in an amount equivalent to about 0.2% by weight of dithionite based on the weight of dry clay.

Each stirred mixture of kaolinitic clay and aqueous hydrazine solution was left to stand at room temperature for 4 hours. At the end of this period the intercalated and bleached clay was separated from the aqueous suspending medium by filtration and washed with an aqueous solution of an oxygen scavenger viz an aqueous solution containing 2 gm. of sodium dithionite per 100 ml. of solution.

When all the hydrazine had been removed, each clay was separated by filtration from the aqueous washing medium and the filter cake was reslurried with water to remove the sodium dithionite. The clay was then refiltered, washed in acetone and dried in a current of air at room temperature.

When dry, the percentage reflectances to light of 458 and 574 millimicrons wavelengths were measured using an ELREPHO brightness meter fitted with the appropriate filters. The results are given in Table I below.

TABLE I

Clay.....	A	B	C	D
Before treatment:				
Percentage reflectance to light of 458 mμ.....	89.2	92.4	95.7	89.8
Percentage reflectance to light of 574 mμ.....	92.8	95.0	97.1	93.7
After treatment:				
Percentage reflectance to light of 458 mμ.....	91.4	95.1	98.0	91.7
Percentage reflectance to light of 574 mμ.....	93.3	95.7	97.9	93.8
Increase in percentage reflectance to light of 458 mμ.....	2.2	2.7	2.3	1.9
Increase in percentage reflectance to light of 574 mμ.....	0.5	0.7	0.8	0.1

It will be noted that in the case of Clay A the percentage reflectances to light of 458 and 574 millimicrons wavelength are 1.2 and 0.4 percent, respectively, greater than was obtained by the conventional bleach with sodium dithionite alone (90.2% and 92.9%). It will also be noted that with Clays B and C, which had been pretreated with an oxidising bleaching agent, there was a greater proportionate decrease in the residual colour (the difference between the percentage reflectance to yellow light of 574 millimicrons and violet light of 458 millimicrons) than with Clays A and D which had not been so pretreated.

I claim:

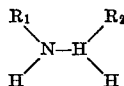
1. A process for improving the brightness of silicate minerals having a layer-lattice crystal structure and containing ferric ions in solid solution within the mineral, which comprises the steps of:

(a) contacting the silicate mineral in aqueous suspension with (i) an intercalating agent which is capable of forming with the silicate mineral an intercalation complex and (ii) a reducing bleaching agent which is capable of converting ferric ions in the mineral to ferrous ions; and

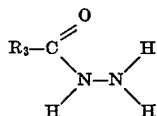
(b) decomposing the intercalation complex by separating the intercalated and bleached silicate mineral from the aqueous suspending liquid in which it was contacted with the intercalating and bleaching agent, washing the intercalated and bleached silicate mineral with an aqueous washing medium under non-oxidizing conditions, separating the washed silicate mineral from the aqueous washing medium, and drying the washed silicate mineral.

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2. A process according to claim 1, wherein the intercalating agent and reducing bleaching agent are the same compound and are selected from the group consisting of hydrazine; substituted hydrazines of the general formula:



wherein R_1 is selected from hydrogen and C_1-C_6 alkyl groups and R_2 is selected from C_1-C_6 alkyl groups; and primary hydrazides of the general formula:

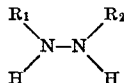


wherein R_3 is selected from hydrogen and C_1-C_6 alkyl groups.

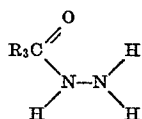
3. A process according to claim 1, wherein the amount of intercalating agent used is such that the mole ratio of silicate mineral having a layer-lattice crystal structure to intercalating agent does not exceed 3:2.

4. A process for improving the brightness of a silicate mineral which is of the kandite group and which contains discolouring ferric ions in solid solution within said silicate mineral, which process comprises the steps of:

(a) contacting the silicate mineral for at least two hours with a compound which is an intercalating agent and a reducing bleaching agent and which is selected from the groups consisting of hydrazine; substituted hydrazines of the general formula:



wherein R_1 is selected from hydrogen and C_1-C_6 alkyl groups and R_2 is selected from C_1-C_6 alkyl groups; and primary hydrazides of the general formula:



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wherein R_3 is selected from hydrogen and C_1-C_6 alkyl groups; and

(b) decomposing the intercalation complex by separating the intercalated and bleached silicate mineral from the aqueous suspending liquid in which it was contacted with the intercalating and bleaching agent, washing the intercalated and bleached silicate mineral with an aqueous washing medium under non-oxidising conditions, separating the washed silicate mineral from the aqueous washing medium, and drying the washed silicate mineral.

5. A process according to claim 4, wherein the silicate mineral having a layer-lattice crystal structure is a kaolinitic clay and wherein the amount of intercalating agent used is such that the mole ratio of silicate mineral having a layer-lattice crystal structure to intercalating agent does not exceed 3:2.

6. A process according to claim 4, wherein the washing of the intercalated and bleached silicate mineral with an aqueous washing medium under non-oxidising conditions is carried out by resuspending the intercalated and bleached silicate mineral in an aqueous solution of an oxygen scavenger to remove the intercalating agent, and thereafter separating the silicate mineral from the aqueous washing medium and rewashing it with water.

7. A process according to claim 6, wherein the oxygen scavenger is sodium or zinc dithionite.

8. A process according to claim 5, wherein the washed silicate mineral is dried under conditions such that the temperature of the silicate mineral does not exceed 80°C .

9. A process according to claim 4, wherein the washed silicate mineral is dried with or in the presence of an oxygen-free gas.

References Cited

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40 JAMES E. POER, Primary Examiner

U.S. Cl. X.R.

106-72; 23-110 P

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,666,513 Dated May 30, 1972

Inventor(s) PETER JAMES MALDEN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading

---Claims priority, application British, March 26, 1969,
15,925---

Signed and sealed this 8th day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents