

PATENT SPECIFICATION

(11) 1 464 482

1 464 482

- (21) Application No. 33638/75 (22) Filed 12 Aug. 1975
 (31) Convention Application No. 500 807
 (32) Filed 28 Aug. 1974 in
 (33) United States of America (US)
 (44) Complete Specification published 16 Feb. 1977
 (51) INT CL² C01B 33/20
 (52) Index at acceptance C1A M9



(54) PRODUCTION OF MONTMORILLONITE OF UNIFORM PARTICLE SIZE

(71) We, DRESSER INDUSTRIES, INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, of The Dresser Building, Elm and Akard Streets, Dallas, Texas 75221, United States of America, 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:—

The present invention relates to a method of processing raw montmorillonite whereby a product having a particular relatively uniform particle size is obtained.

The treatment of montmorillonites commonly consists of crushing the raw material to a size varying from approximately $1\frac{1}{2}$ inch to $\frac{1}{2}$ inch in thickness, drying the crushed material in a concurrent rotary dryer to approximately 15% moisture, or 6%, depending upon whether or not flash drying is used, and then grinding the product in a roller mill to the desired fineness.

This procedure is fraught with problems. It is difficult to obtain a good particle size distribution for drying from the primary crushing of the wet montmorillonite, since handling of the wet mass leads to plugging of the crusher and screen equipment. Montmorillonite dried in conventional dryers, such as a conventional rotary dryer, tends to become under-dried, in the case of large particles, and over-dried, in the case of small particles. Grinding in a Raymond mill of the roller type presents problems of over-grinding, partly due to the internal design of the roller mill. The massive rolls and the huge support equipment creates so much congestion within the mill, that the static pressure becomes too great for the air system to overcome and cleanly remove particles already ground to the desired fineness. Part of the over-grinding is also caused by the more friable nature of a dried montmorillonite as compared with a tough wet material.

The bulk loading and bag packing of an

overground montmorillonite is very difficult because the rate of deaeration is much slower than that of a product having a uniform particle size distribution. 50

Montmorillonite is a magnesium clay mineral approximating in composition to $5 \text{ Al}_2\text{O}_3 \cdot 2 \text{ MgO} \cdot 24 \text{ SiO}_2 \cdot 6 \text{ H}_2\text{O}$; some of the H^+ ions are usually replaced by Na^+ or by Ca^{2+} . 55

Montmorillonite minerals generally have a chemical analysis within the following ranges:

Chemical Components	Range (%)
SiO_2	50 to 55
Al_2O_3	15 to 20
Fe_2O_3	0.05 to 7
FeO	0 to 1
MgO	2 to 7
CaO	0.5 to 4
TiO_2	0 to .4
Alkalies	0 to 3

Structurally, montmorillonite is composed of units made up of 2 silica tetrahedral sheets with a central alumina octahedral sheet. All of the tips of the tetrahedrons point in the same direction and toward the centre of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become O instead of OH. Microscopically, the large masses within the mineral appear to be stackings of flake-shaped units without regular outlines. Some of the individual particles appear to be about 0.002 micron thick, from which it can be concluded that at least some montmorillonites break down relatively easily to flakes approaching unit cell thickness. Pulverized montmorillonite is a mass of mineral fragments which adhere together strongly when dry, but are separable when dispersed in water. 80

We have now developed a method of

processing raw montmorillonite to provide a product which has montmorillonite having a relatively uniform particle size, and which has good deaeration properties and density.

In accordance with the present invention, there is provided a method of processing raw montmorillonite, which comprises (a) simultaneously drying and comminuting raw montmorillonite having a moisture content of at least 20% to produce discrete particles of montmorillonite, at least 50% by weight of which have a particle size of -200 mesh and (b) air classifying the particles to obtain a product with a Fisher Average Diameter of between 6 and 30 microns.

The mesh sizes referred to herein are U.S. standard mesh sizes. Fisher Average Diameters are determined with a Fisher sub-sieve sizer following the manufacturers instructions.

The particle size of the material produced according to the invention is preferably substantially uniform and from 5 to 40 microns. The -200 mesh material preferably constitutes between 70 and 80% by weight of the product obtained in step (a).

Attapulgite minerals, when processed in a similar manner (see U.S. Patent No. 3,079,333) produced an unpredictable product. Attapulgite, when colloiddally dispersed in water or salt solution, thickens in the same way as a result of the orientation in the vehicle of the colloidal attapulgite needles. However, montmorillonite minerals differ from attapulgite in their chemical and physical make-up.

It is somewhat surprising that it is possible to obtain a uniform product from raw montmorillonite material, in the upper sub-sieve size ranges — a so-called dustless granular material — by grinding the material such that most of the material is comminuted to -200 mesh. It would generally be expected that a heterogeneous size gradation would result from such a process.

Airborne dust has a particle size of approximately 1 to 3 microns. Montmorillonite material processed according to the invention is substantially free of dust of such a particle size, so that montmorillonite treated according to the invention does not constitute a hazard in this respect to the environment or to workers who handle the material.

Thus montmorillonite processed according to the invention to achieve uniform size gradation without the production of dust has advantages from the environmental and ecological point of view, and may be employed in many fields, such as petroleum discovery and recovery, refining and preparation of organic materials; pelletizing of ores; controlling of soil properties; water clarification; and production of various grades of cement. The montmorillonite produced according to the invention may also be used, for example, as

fillers or in fillers; foundry sand binders; desiccants, absorbents and molecular sieves; pharmaceuticals, cosmetics; and active diluents in the formulation of insecticides.

The montmorillonite used as starting material in the process of the invention is as taken from the mine, that is without pre-processing, although a primary grinding to about -1½ inch or so, may sometimes be desirable depending on the drying and grinding apparatus to be employed.

A preferred embodiment of the process of the invention will now be described by way of example. The moist raw feed material is subjected to rapid drying by direct contact with high velocity, hot dry moisture-absorptive gases, and, simultaneously, the particles are comminuted so that drying takes place while fine particles are suspended in the gas (preferably air) which is circulating at high velocity in the dryer. The moist feed is preferably dropped into a stream of hot dry gas and the gas stream carries the feed to a suitable mill, and carries the dried fine particles formed in the mill to an air classifier. Good results have been obtained using an Imp mill (a product of Raymond Division, Combustion Engineering, Inc.; "Imp" is a Trade Mark) or a hammer mill with means to circulate hot air at high velocity through the feed material. In the hammer mill, hammers are mounted on arms which are provided on a shaft adapted to rotate at high speed. The principal action of the mill is one of impact rather than the compression which takes place in roller type mills. Fracture of the feed is also effected in the hammer mill by the rubbing of montmorillonite particles against each other in the rapidly moving gaseous suspension of the particles. These mills contain an internal classification mechanism which may be used to effect the air classifying step of the process of the invention. However, the material can also be removed after a single pass through the drying and comminution stage and fed to a separate air classifier to obtain higher Fisher Average Diameters. Another apparatus which can be utilized is a cage mill which has rotors concentric with each other and successive rotors are adapted to operated in opposite directions. In such a mill, the feed is beaten by the action of bars on rings of the rotors. Other types of grinding mills, provided with means for rapid positive circulation of drying gases, may also be used.

As stated previously, the size reduction in the mill is preferably controlled so that the product is between 70 and 80% by weight -200 mesh, and we have unexpectedly found that most of the -200 mesh material has a particle size between 5 and 40 microns which is considered to be uniform. The Fisher Average Diameter of the product after air classification is between 6 and 30 microns

depending upon the feed material, and usually between 6 and 25 microns, since it is difficult to obtain material of uniform particle size with a Fisher Average Diameter of more than 25 microns with the equipment presently available.

As mentioned above, an important feature of the preferred process of the invention is that rapid drying is effected by the action of hot, high velocity moisture-absorptive gases so that drying takes place while the particles are suspended in the gas. The gases may have velocities of 50 to 70 feet per second or higher and inlet temperatures from 200°F. to 1000°F. The residence period of the feed within the dryer will depend on numerous factors including the mill capacity, gas velocity and temperature and drying efficiency but is of very short duration, generally under a minute. Since drying is extremely rapid, the montmorillonite particles do not attain the temperature of the drying gas, and the product temperature in the dryer is well below that at which water of hydration is removed from the mineral lattice, i.e., below about 350°F. and usually from about 100 to 200°F. The gases may be direct or indirect combustion products, the only requirement being that they have the capacity to absorb moisture from the feed and are inert towards the montmorillonite. Dry air is the preferred gas.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only, Example 1 being by way of comparison.

Example 1.

This Example illustrates the treatment of montmorillonite by a conventional procedure, viz. drying the raw material in a rotary dryer followed by milling in a Raymond mill of the roller type to provide a product of which 70 to 80% by weight was -200 mesh particle size.

The raw material was partially dried in a rotary externally fired dryer having a vent temperature of 180 to 250°F. The material retention time in the dryer was 30—40

minutes. The partially dried (15—18% moisture) material was fed to a Raymond roller mill provided with a classifier (which, however, was not employed in the present experiment) and was milled and dried simultaneously with hot gases to a fineness such that 70 to 80% by weight was -200 mesh, the moisture content of the product being 6 to 10%. The average particle diameter was determined on the dried sample which included the +200 mesh material. On various samples, the Fisher Average Diameter was 3.7, 3.8, 4.0, 4.2 and 4.3 microns. Reducing the moisture content completely in the rotary dryer with no drying during milling gives similar results.

Examples 2 to 7.

Montmorillonite samples were employed which had a density of 58 pounds per cubic foot, a moisture content of 23%, and the following size distribution:

Fineness	Weight Percent
- 1 inch + $\frac{3}{4}$ inch	0.2%
- $\frac{3}{4}$ inch + $\frac{1}{2}$ inch	2.4
- $\frac{1}{2}$ inch + $\frac{1}{4}$ inch	14.4
- $\frac{1}{4}$ inch + 6 mesh	38.8
- 6 mesh + 10 mesh	24.1
- 10 mesh + 20 mesh	4.8
- 20 mesh + 40 mesh	10.0
- 40 mesh + 60 mesh	3.3
- 60 mesh + 100 mesh	1.1
- 100 mesh + 200 mesh	0.5
- 200 mesh	0.2

The samples were crushed and dried in a No. 2 Imp dryer mill with four rows of hammers. The venturi was a 12 inch by 14 inch chamber. The mill inlet temperature was about 1200°F. The fans were run at 3480 RPM and the spinner at 200 RPM with 16 blades. The dried and comminuted product having a particle size predominantly -200 mesh was air classified within the mill. Relevant process conditions and properties of the products obtained are given in Table I below.

TABLE I

Example	2	3	4	5	6	7
Mill (rpm)	4320	4320	4320	4320		4320
Amps (load)	21	21	22	20		20
H.P. (load)	6	6	6.5	5.6		5.6
Venturi Temp. (°F.)	165°	230°	185°	205°		170°
Fan Inlet Temp. (°F.)	110°	130°	120°	112°		112°
Fan Inlet Velocity Pressure (in. H ₂ O)	1.1"	1.1"	1.3"	1.9"		1.5"
Static Pressure Mill (in. H ₂ O)	0.5"	.75"	.75"	.75"		1.0"
Control Temp. (°F.)	110°	150°	125°	120°		110°
lbs./Hr. of Product	192	228	324	156		258
Fisher Average Diameter (microns)	7.3	8.5	6.8	12.0	12.5	11.5
Product Moisture (%)	3.8	1.2	3.9	2.2	3.3	5.0

The product obtained in Example 7 was further processed by feeding it to a 16" Aero Separator (air classifier) at a rate of 64.8 lbs/hr. The fan inlet temperature was 70°F. and its speed was 3480 RPM. The spinner speed was 250 RPM. The Fisher Average Diameter of the material obtained was 15 microns.

The rate of deaeration of the products of Examples 2 to 7, as compared with a montmorillonite product obtained by a known process, may be seen from Table II below which presents the density of the montmorillonite product (in lbs/ft³) as a function of time after introduction of the montmorillonite into

a graduated cylinder and shaking the cylinder. Each sample was introduced into a graduated cylinder, shaken the same number of times to effect aeration, and placed on a level surface. The density of the montmorillonite material was then calculated at the times indicated in Table II from the observed volume of material in the graduated cylinder.

The more rapid rate of deaeration of products obtained according to the invention as compared with that of montmorillonite products obtained by standard processing enables the products of the invention to be packed and packaged more rapidly than many known montmorillonite products.

TABLE II

Rate of Deaeration

Time (Sec.)	Example No. I						Standard Processing
	2	3	4	5	6	7	
0	37.1	38.0	35.4	44.5	44.5	45.1	33.7
5	39.4	39.9	37.1	45.1	45.1	45.8	36.6
10		40.5	38.0				37.9
15							38.9
20							39.9
30							40.5

WHAT WE CLAIM IS:—

1. A method of processing raw montmorillonite, which comprises (a) simultaneously drying and comminuting raw montmorillonite having a moisture content of at least 20% to produce discrete particles of montmorillonite, at least 50% by weight of which have a particle size of -200 mesh and (b) air classifying the particles to obtain a product with a Fisher Average Diameter of between 6 and 30 microns.
2. A process according to claim 1, in which the Fisher Average Diameter of the product is between 6 and 25 microns.
3. A process according to claim 1 or 2, in which between 70 and 80% by weight of the product obtained in step (a) consists of -200 mesh particles.
4. A process according to any of claims 1 to 3, in which substantially all the particles in the product obtained in step (b) have a particle size of between 5 and 40 microns.
5. A process according to any of claims 1

to 4, in which, in step (a), the montmorillonite is suspended in high velocity moisture absorptive gas at a temperature of from 200°F to 1000°F for a time of up to 1 minute whereby drying of the montmorillonite is effected.

6. A process according to any of claims 1 to 5, in which the product from step (b) is subjected to further air classifying in order to increase its Fisher Average Diameter.

7. A process according to claim 1, substantially as herein described in Examples 2 to 7.

8. Montmorillonite which has been treated by a process as claimed in any of claims 1 to 7.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Hoborn,
London, W.C.1.

TABLE II

Rate of Deaeration

Time (Sec.)	Example No. I						Standard Processing
	2	3	4	5	6	7	
0	37.1	38.0	35.4	44.5	44.5	45.1	33.7
5	39.4	39.9	37.1	45.1	45.1	45.8	36.6
10		40.5	38.0				37.9
15							38.9
20							39.9
30							40.5

WHAT WE CLAIM IS:—

1. A method of processing raw montmorillonite, which comprises (a) simultaneously drying and comminuting raw montmorillonite having a moisture content of at least 20% to produce discrete particles of montmorillonite, at least 50% by weight of which have a particle size of -200 mesh and (b) air classifying the particles to obtain a product with a Fisher Average Diameter of between 6 and 30 microns.
2. A process according to claim 1, in which the Fisher Average Diameter of the product is between 6 and 25 microns.
3. A process according to claim 1 or 2, in which between 70 and 80% by weight of the product obtained in step (a) consists of -200 mesh particles.
4. A process according to any of claims 1 to 3, in which substantially all the particles in the product obtained in step (b) have a particle size of between 5 and 40 microns.
5. A process according to any of claims 1

to 4, in which, in step (a), the montmorillonite is suspended in high velocity moisture absorptive gas at a temperature of from 200°F to 1000°F for a time of up to 1 minute whereby drying of the montmorillonite is effected.

6. A process according to any of claims 1 to 5, in which the product from step (b) is subjected to further air classifying in order to increase its Fisher Average Diameter.

7. A process according to claim 1, substantially as herein described in Examples 2 to 7.

8. Montmorillonite which has been treated by a process as claimed in any of claims 1 to 7.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Hoborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

