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METHOD OF IMPROVING THE ADSORBENT AND DECOLORIZING PROPERTIES OF GEORGIA-FLORIDA FULLER'S EARTH

William S. W. McCarter, Ardmore, Pa., assignor to Attapulgus Clay Company, Philadelphia, Pa., a corporation of Delaware

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The present invention relates to a process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, and relates more particularly to increase the effective life of such earth upon repeated use and regeneration in the field of oil decolorization and refining.

It has been known heretofore that the decolorizing efficiency of Georgia-Florida type fuller's earth may be substantially increased upon both a weight and volume basis by mixing with raw fuller's earth a small amount of a water-soluble alkaline reagent and sufficient water to render the earth plastic, extruding the mixture at an elevated pressure, drying the extruded earth, reducing the dried earth to granular particles, and calcining the granular particles at 800° F. to 1200° F. Such process is disclosed and claimed in United States Patent 2,363,876 to W. A. LaLande, Jr.

In utilizing fuller's earth for the treatment of petroleum products, especially for the decolorization of lubricating oils, petrolatum, and waxes, it is the practice to percolate the petroleum fraction through thermally activated fuller's earth until the desired degree of refining or decolorization is no longer obtained. It is not feasible, economically, to discard the used earth at this point. Instead, the earth must be treated to restore its adsorptive properties for reuse. This regenerative treatment usually involves washing the spent earth with a solvent such as naphtha, purging the washed spent earth with steam, drying the steamed earth, and calcining or burning the dried earth in the presence of air to oxidize and remove strongly adsorbed tars, asphalts, and other carbonaceous matter.

I have found that under this regenerative treatment, the fuller's earth containing the added alkaline reagent produced according to the LaLande process aforementioned, rapidly deteriorates in decolorizing or adsorptive efficiency. I have also found, however, that this deterioration in efficiency can be decreased substantially, without any effect upon the beneficial action of the alkaline reagent, by neutralizing the alkaline reagent at any one of several stages during the preparation of the improved earth following the initial mixing or impregnation of the earth with the alkaline reagent. The neutralization is effected using a mineral acid, preferably diluted

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with water if the initial acid was concentrated. Acids such as sulfuric, hydrochloric, nitric, phosphoric, or hydrofluoric may be used, preference being had for sulfuric acid due to its availability, cheapness, and relative ease of handling. The amount of acid used is only that necessary to neutralize the alkaline reagent originally incorporated in the earth, since amounts greater than the stoichiometric equivalent are not beneficial and, in fact, may have an adverse effect upon the earth. As a matter of fact, it is well known that Georgia-Florida fuller's earth is not improved by conventional acid activation as practiced with montmorillonite sub-bentonites, and fuller's earth from the vicinity of Attapulgus, Georgia, is actually harmed by acid leaching (U. S. Dept. Interior, Geol. Survey #3 (1933) pages 45–49). It is, therefore, emphasized that the neutralization of the fuller's earth containing added alkaline reagent, in accordance with this invention, is not an acid activating treatment and is not to be confused therewith.

In carrying out this invention, the amount of alkaline reagent initially incorporated in the fuller's earth must be held within the range of 0.1% to 1.75% by weight, based upon the dry or volatile-free earth, otherwise the adsorbent or decolorizing efficiency is adversely affected, even though the alkalized earth is subsequently neutrailized with mineral acid. It is preferred to use from about 0.75% to 1.50% of alkaline reagent, about 1% of a reagent such as sodium hydroxide giving excellent results. Among the reagents reacting alkaline in aqueous solution which may be employed in accordance with this invention are the oxides, hydroxides, peroxides, carbonates, bicarbonates, secondary and tertiary phosphates, and silicates of Na, K, Li, and NH_4 which are soluble in water to substantial extent. Due to their availability, effectiveness, and non-corrosive properties, the alkali metal hydroxides, and particularly sodium hydroxide, are preferred. Other alkaline reacting substances which may be employed are the alkoxide and phenolates of strong bases; soluble magnesium, calcium, and barium salts of weak acids; alkali metal aluminates, zincates, plumbites, arsenites, aresenates, antimonoites, stannites, stannates, chromites, manganates, and phosphites; amides of metals forming soluble strong bases, quaternary bases

such as tetralkyl ammonium hydroxides, tetraryl ammonium hydroxides, and mixed alkaryl ammonium hydroxides; hydrazine, hydroxylamine, and other soluble organic bases.

In accordance with the present invention, raw fuller's earth of the type obtained from the Georgia-Florida fuller's earth deposits and containing natural moisture (40% to 50% by weight) is passed to a roll crusher wherein the lumpy earth is reduced to relatively flat fragments. The earth from the crusher is introduced into a conventional pug mill in which the earth is intimately mixed with the alkaline reagent in aqueous solution, the quantity of agent being of the order of 0.1% to 1.75% by weight, based upon volatile-free earth, and preferably about 1% by weight. Depending upon the initial moisture content of the raw earth, the concentration of the alkaline solution is adjusted to give a total volatile matter content (V. M.) in the earth of the order of 45% to 60% by weight, and preferably 52% to 56% by weight. The plastic, alkalized earth may then be subjected to any of the following procedures involving neutralizing and converting the earth into an improved adsorbent and decolorizing agent.

For example, the plastic earth containing 1% of sodium hydroxide and 54% volatile content (water) was mixed with sufficient dilute sulfuric acid (25% concentration) only to neutralize the added alkali, the neutralized earth was washed with water to remove the soluble salts formed, and the washed earth was dried to 54% volatile content. This earth was then extruded through an auger extrusion machine having a 2 inch diameter auger and a barrel 14 inches in length provided at the discharge end with a die plate 1 inch thick containing a plurality of ¼ inch diameter apertures. Extrusion was accomplished at a fairly high pressure, i. e., above 100 pounds per square inch, the usual pressure range being of the order of 400 to 1200 pounds per square inch. The moist, extruded earth discharged from the die plate apertures was dried at 250° F. to 300° F. to a volatile content of about 15% by weight. The dried earth was then reduced to granular particles by grinding, and the resulting particles of desired size, for example, 30–60 mesh were calcined at 900° F. for 30 minutes, and the calcined product was screened to remove particles finer than 60 mesh. The calcination step may be performed at any temperature within the range of 800° F. to 1200° F., and the particle size may be varied as desired.

The decolorizing efficiency of the improved fuller's earth was determined by solution filtration of Pennsylvania cylinder oil stock (60% by volume naphtha—40% by volume cylinder stock) through a given weight of earth at 135° F. to 6 N. P. A. color. The volume of filtrate of 6 N. P. A. color thus obtained, when compared with the volume of filtrate of the same color obtained by filtration through commercial fuller's earth, is indicative of the decolorizing efficiency of the improved earth. Commercial fuller's earth is obtained by drying raw Georgia-Florida earth, grinding, screening to 30–60 mesh, calcining at 900° F., and removing particles finer than 60 mesh by rescreening. The weight efficiency and volume efficiency upon the first use of commercial fuller's earth is arbitrarily designated 100%. To determine efficiency upon repeated use and regeneration of the improved earth, the used improved earth was drained of oil, washed with naphtha, steamed and air blown, and finally recalcined at 1100° F. for 30 minutes. Volatile matter content (V. M.) was determined by heating a sample of earth at 1800° F. for 20 minutes and noting the loss in weight.

The results obtained upon repeated use and regeneration of the earth prepared as above described are given in the following table.

Number of Uses	1	2	3	4	5	6
V. M., per cent	3.0	2.0	1.9	1.9	1.9	2.0
Vol. Wt., lbs./cu. ft.	31.1	31.6	32.6	33.1	33.4	33.8
Wt. efficiency, per cent	131	136	141	141	136	130
Vol. efficiency, per cent	127	133	134	144	142	137

In the above example, neutralization of the earth was effected immediately after the thorough incorporation of the alkaline reagent in the earth. However, the same beneficial results may be obtained by neutralization after extrusion, as is illustrated below.

For example, 1% of sodium hydroxide and sufficient water to give 54% volatile matter content was added to raw fuller's earth in a pug mill and the mixture was thoroughly milled. The resulting plastic, alkalized earth was then extruded as in the first example, and the extruded earth was then treated with dilute sulfuric acid in an amount chemically equivalent to the alkali initially added. Following the neutralization, the earth was water washed to remove soluble salts, dried to 54% volatile content, again extruded, dried, ground, screened to 30–60 mesh, and calcined at 900° F., the material finer than 60 mesh thereafter being screened out. The decolorization tests upon this improved earth are set forth below, and were carried out as in Example 1.

Number of Uses	1	2	3	4	5	6
V. M., per cent	3.1	2.1	1.9	1.7	1.8	1.8
Vol. Wt., lbs./cu. ft.	31.1	32.2	33.3	33.4	33.8	34.3
Wt. efficiency, per cent	139	145	145	141	138	134
Vol. efficiency, per cent	134	145	149	145	146	144

In Example 2, neutralization was effected after extrusion, and a second extrusion was required, since the initial extrudate disintegrated into fines during the neutralization. In another modification of this invention, 1% of sodium hydroxide and sufficient water to give 54% volatile content was added to raw fuller's earth in a pug mill and the mixture was thoroughly milled. The resulting plastic, alkalized earth was then extruded as in the first example, and the extruded earth was dried and thereafter treated with sufficient sulfuric acid to neutralize the added alkali. During neutralization, the extrudate disintegrated into fines, and this material was water washed to remove soluble salts. The washed earth was redried to 54% volatile content, again extruded, dried, ground, screened to 30–60 mesh, and calcined at 900° F., the material finer than 60 mesh being thereafter screened out. The decolorization tests upon this improved earth are set forth below, and were carried out as in Example 1.

Number of Uses	1	2	3	4	5	6
V. M., percent	3.0	2.4	1.9	1.6	1.6	1.7
Vol. Wt., lbs./cu. ft.	31.6	32.7	33.6	33.8	34.4	35.1
Wt. efficiency, percent	134	134	138	136	133	128
Vol. efficiency, percent	132	135	145	147	143	140

In Example 3, neutralization was carried out after the initial extrusion and drying. However, as shown in the following Example 4, neutraliza-

tion may be effected after calcination at elevated temperature, i. e., 800° F. to 1200° F., and preferably 900° F. In this modification, 1% of sodium hydroxide and sufficient water to give 54% volatile content was added to raw fuller's earth in a pug mill and the mixture was thoroughly milled. The resulting plastic, alkalized earth was then extruded as in the first example, and the extruded material was dried, then ground and screened to 30–60 mesh. This earth was then calcined at 900° F. for 30 minutes, and the calcined earth, after cooling, and removal of particles finer than 60 mesh, was treated with sulfuric acid in an amount sufficient only to neutralize the alkali initially added. The neutralized earth was water washed to remove soluble salts and dried at elevated temperature. The tests upon this material are shown in the following table, and were carried out as in Example 1.

Number of Uses	1	2	3	4	5	6
V. M., Percent	2.9	2.2	2.0	1.9	1.9	2.0
Vol. Wt. lbs./cu. ft.	34.4	34.4	35.4	35.5	35.5	35.6
Wt. efficiency, percent	135	136	131	125	121	120
Vol. efficiency, percent	143	144	145	138	134	133

In order to compare the efficiency of the fuller's earth produced in accordance with this invention, with alkalized fuller's earth of the prior art which has not been neutralized, the following example is presented. To raw fuller's earth was added 1% of sodium hydroxide and sufficient water to give a volatile content of 54%, and the mixture was thoroughly milled in a pug mill. The resulting plastic earth was then extruded as in Example 1 and the extruded earth was dried, ground, and screened to 30–60 mesh, calcined at 900° F. for 30 minutes, and again screened to remove particles finer than 60 mesh. In this instance, no neutralization was carried out at any stage of the process. The calcined 30–60 mesh earth was then tested for decolorizing efficiency as in Example 1, and the results are given in the following table.

Number of Uses	1	2	3	4	5	6
V. M., percent	3.2	2.5	2.0	1.8	1.7	1.7
Vol. Wt., lbs./cu. ft.	31.9	32.9	33.8	34.4	34.6	34.6
Wt. efficiency, percent	136	137	133	126	107	97
Vol. efficiency, percent	134	143	136	135	114	102

It will be noted from the above that the unneutralized earth, after the 4th use and regeneration, rapidly declined in both weight and volume efficiency, whereas the earths prepared in accordance with this invention retain a relatively high decolorizing efficiency even after the 6th use and regeneration. Although not shown here, these earths still retain a high efficiency even through 10 to 15 cycles of use, and the rate of decrease in efficiency is very slow in comparison with unneutralized, alkalized earths.

In carrying out the neutralization step, it is important that only sufficient mineral acid be used to react with the alkaline reagent initially incorporated in the earth. In other words, chemically equivalent or stoichiometric amounts of acid are employed, there being no excess acid which might react with the earth and cause degradation thereof. The concentration of the acid may vary over a considerable range, i. e., 5% to 85%, however, it is preferred to use relatively dilute acid, for example, sulfuric acid of 10% to 25% concentration.

To illustrate the effect of an excess amount of acid in treating the alkalized earth, the following example is given. To raw fuller's earth was added 1% of sodium hydroxide and sufficient water to give 54% volatile content, and the plastic earth was milled and then extruded as described in Example 1. The extruded earth was dried at 750° F. to prevent disintegration in the dilute acid subsequently employed to neutralize the earth. The dried earth was ground and screened to 30–60 mesh, and then divided into two equal parts. One part was neutralized with a stoichiometric proportion of dilute sulfuric acid, while the second part was treated with 3 times the stoichiometric proportion of acid. The treated earths were then water washed to remove soluble salts, dried, and calcined at 900° F. for 30 minutes, any material finer than 60 mesh then being separated by screening. The earth samples were then tested as described in Example 1, and the sample neutralized with a stoichiometric amount of acid had a volume weight of 32.6 pounds per cubic foot and a volume efficiency of 127%, whereas the sample treated with 3 times the stoichiometric amount of acid had a volume weight of 31.8 and a volume efficiency of 119.8%. It is, therefore, apparent that the use of acid in excess of that required to effect neutralization is detrimental to the efficiency of the earth.

While, in general, it is customary to employ fuller's earth of 30–60 mesh for the percolation decolorization of oils, it is of course within the scope of this invention to produce earths of any desired mesh, for example, 4–8, 10–60, 20–80, or even finely divided earth of 100, 200, 300 or finer mesh. In the processing of the earth, it is the usual practice to simply dry the final product, for example, at 250° F. to 400° F. to a volatile matter content of about 15% by weight, and market same at that volatile content. Prior to use in decolorizing oils or other materials, the user generally calcines the product at 800° F. to 1200° F. to a volatile content of 1.5% to 3% by weight. The improved earths of this invention may be employed in the decolorization or refining of hydrocarbon oils, waxes, animal and vegetable oils and fats, and the like.

I claim:

1. In a process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth involving mixing the earth with from 0.1% to 1.75% by weight of a water-soluble alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, extruding the plastic earth at elevated pressure, and drying the extruded earth, the step which consists in treating the earth with mineral acid in an amount sufficient only to neutralize the added alkaline reagent after said reagent has been thoroughly incorporated in the earth.

2. In a process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth involving mixing the earth with from 0.1% to 1.75% by weight of a water-soluble alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, extruding the plastic earth at elevated pressure, and drying the extruded earth, the step which consists in treating the earth with sulfuric acid in an amount stoichiometrically equivalent to the alkaline reagent added, after said reagent has been thoroughly incorporated in the earth.

3. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth from 0.1% to 1.75% by weight of a water-soluble

alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, treating the earth with mineral acid in an amount sufficient only to neutralize the added alkaline reagent, water washing the treated earth to remove soluble salts, adjusting the water content of the washed earth to a value between 45% and 60%, extruding the washed earth at elevated pressure, and drying the extruded earth.

4. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth 1% by weight of sodium hydroxide and sufficient water to give a plastic earth containing from 52% to 56% of water, treating the earth with sulfuric acid in an amount sufficient only to neutralize the added sodium hydroxide, water washing the treated earth to remove soluble salts, adjusting the water content of the washed earth to a value between 52% to 56%, extruding the washed earth at elevated pressure, and drying the extruded earth.

5. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth from 0.1% to 1.75% by weight, of a water-soluble alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, extruding the plastic earth at elevated pressure, treating the extruded earth with mineral acid in an amount sufficient only to neutralize the added alkaline reagent, water washing the treated earth to remove soluble salts, adjusting the water content of the washed earth to a value between 45% and 60%, extruding the washed earth at elevated pressure, and drying the extruded earth.

6. A proces for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth 1% by weight of sodium hydroxide and sufficient water to give a plastic earth containing from 52% to 56% of water, extruding the plastic earth at elevated pressure, treating the extruded earth with sulfuric acid in an amount sufficient only to neutralize the added sodium hydroxide, water washing the treated earth to remove soluble salts, adjusting the water content of the washed earth to a value between 52% to 56%, extruding the washed earth at elevated pressure, and drying the extruded earth.

7. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth from 0.1% to 1.75% by weight of a water-soluble alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, extruding the plastic earth at elevated pressure, drying the extruded earth, treating the dried earth with mineral acid in an amount sufficient only to neutralize the added alkaline reagent, water washing the neutralized earth to remove soluble salts, adjusting the water content of the washed earth to a value between 45% and 60%, extruding the washed earth at elevated pressure, and drying the extruded earth.

8. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth 1% by weight of sodium hydroxide and sufficient water to give a plastic earth containing from 52% to 56% of water, extruding the plastic earth at elevated pressure, drying the extruded earth, treating the dried earth with sulfuric acid in an amount sufficient only to neutralize the added sodium hydroxide, water washing the neutralized earth to remove soluble salts, adjusting the water content of the washed earth to a value between 52% to 56%, extruding the washed earth at elevated pressure, and drying the extruded earth.

9. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth from 0.1% to 1.75% by weight of a water-soluble alkaline reagent and sufficient water to give a plastic earth containing from 45% to 60% of water, extruding the plastic earth at elevated pressure, drying the extruded earth, calcining the dried earth at 800° F. to 1200° F., treating the calcined earth with mineral acid in an amount sufficient only to neutralize the added alkaline reagent, water washing the neutralized earth to remove soluble salts, and drying the washed earth.

10. A process for improving the decolorizing efficiency of Georgia-Florida type fuller's earth, which comprises intimately mixing with the earth 1% by weight of sodium hydroxide and sufficient water to give a plastic earth containing from 52% to 56% of water, extruding the plastic earth at elevated pressure, drying the extruded earth, calcining the dried earth at 800° F. to 1200° F., treating the calcined earth with sulfuric acid in an amount sufficient only to neutralize the added sodium hydroxide, water washing the neutralized earth to remove soluble salts, and drying the washed earth.

WILLIAM S. W. McCARTER.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,363,876	La Lande	Nov. 28, 1944