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IMPROVED FULLER'S EARTH AND PREPARATION THEREOF

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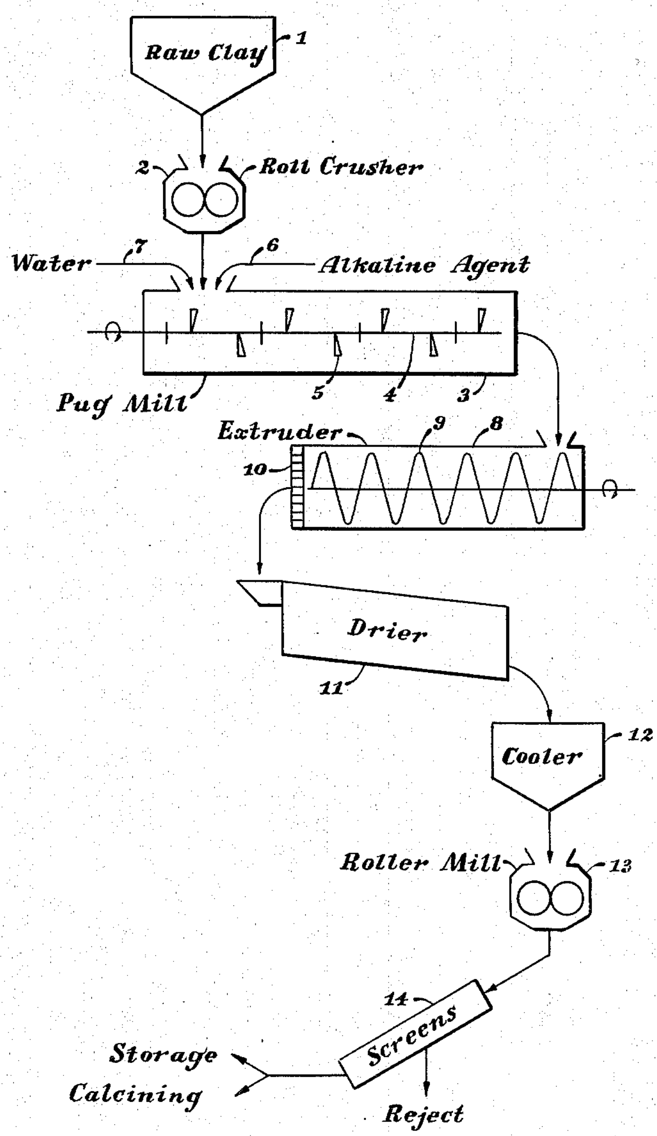

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IMPROVED FULLER'S EARTH AND PREPARATION THEREOF

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9 Claims. (Cl. 252—270)

The present invention relates to a process for increasing the adsorptive capacity, and particularly the decolorizing or bleaching efficiency of argillaceous substances such as fuller's earth of the Georgia-Florida type.

This application is a continuation-in-part of my application Serial No. 298,563, filed October 9, 1939, and entitled "Substance Preparation."

In the production of granular fuller's earth for use in the treatment of petroleum products, and especially for decolorization of lubricating oils and waxes, it has been conventional practice to dry the raw fuller's earth, crush the dried earth, screen the crushed material to obtain granular particles of the desired size, for example, 30—60 mesh, and thereafter heat or calcine the granular particles at temperatures of the order of from 900° F. to 1200° F., prior to utilizing the earth as a decolorizer. Fuller's earth produced in this manner, and employed in large quantities for decolorizing hydrocarbon oils and waxes, has an average volatile content (mostly water) of the order of from 3.5% to 4% by weight, a volume weight of the order of from 30 to 33 lbs. per cu. ft., and a decolorizing efficiency arbitrarily designated at 100% on both the weight and volume basis.

The decolorizing efficiency of some types of fuller's earths may be improved by a process wherein the fuller's earth containing sufficient water to render it plastic is subjected to a grinding, kneading and mixing action under substantial pressure, for example, of the order of from 400 to 1200 pounds per square inch, and then extruded through a die-plate provided with a plurality of orifices. The earth is then dried, ground, screened and calcined to produce, for example, a granular earth of 30—60 mesh, which has improved decolorizing properties for mineral oils. Tests upon numerous samples of fuller's earths which respond to increase in decolorizing efficiency when processed in the manner last above referred to, indicates that the decolorizing efficiency upon a weight basis is markedly improved, that the decolorizing efficiency upon a volume basis is also improved, but to a lesser degree than upon the weight basis, and that the volume weight of the processed earth (e. g. pounds per cubic foot) is substantially lower than that of samples of the respective fuller's earths not so processed. Typical of the properties of a fuller's earth before and after so processing, are the following:

	Before	After
Decolorizing efficiency (weight basis) per cent	100	124
Decolorizing efficiency (volume basis) do	100	118
Volume weight (calcined) lbs. per cu. ft.	31-32	27-30.5

In accordance with the present invention, I have found that the adsorptive capacity, and particularly the decolorizing efficiency of fuller's earths for hydrocarbon oils may be markedly increased in a relatively simple and inexpensive manner. More specifically, in accordance with my invention, I have been able to increase the decolorizing efficiency of fuller's earth upon the volume basis to a very substantial extent, and usually at the same time increase the decolorizing efficiency upon the weight basis. Furthermore, I have been able to effect an advantageous increase in volume weight (lbs./cu. ft.) of the fuller's earth treated in accordance with my process. By thus increasing the volume weight, the decolorizing capacity of a filter of given volume may be increased, for example, by 20 to 40%.

My invention is particularly applicable to the treatment of those fuller's earths, which, upon being subjected to grinding, kneading, mixing and extrusion under substantial pressure in water-moist or plastic condition, and thereafter being dried, screened and calcined, will exhibit a decrease in volume weight and an increase in decolorizing efficiency. Such behavior is characteristic of the majority of the fuller's earths of the Georgia-Florida type, for example, those obtained from Decatur County, Georgia, and Gadsden County, Florida. However, materials such as clays from Nagodoches, Texas, and clays from Creede, Colorado, do not behave in this manner, and are unsuitable for my purpose.

In accordance with my invention, Georgia-Florida type fuller's earth, in moist condition, is intimately admixed with a chemical agent which reacts alkaline in aqueous solution, the mixture is extruded at elevated pressure in a suitable extrusion machine. The extruded material is dried and then reduced to granular particles of desired size by crushing and screening, and the granular particles are finally heated or calcined at temperatures of the order of from 200° F. to 1400° F., and preferably at temperatures of from 800° F. to 1200° F., prior to use as a decolorizing medium for hydrocarbon oils. The quantity of alkaline agent employed may range from 0.1% to about 1.75% by weight, based upon volatile-free fuller's earth, and is preferably of the order of from 1.00 to 1.50% by weight. Since the volatile content of fuller's earth varies considerably with the source of the material, the quantity of water to be used in making up the alkaline solution to be admixed with the earth likewise must be varied, in order that the total volatile content of the earth be kept within the desired limits, i. e., 45% to 60% by weight, during the mixing and extrusion operation. In general, the concentration of alkaline agent in the aqueous solution to be mixed with the fuller's earth is of the order of from 1% to 6% by weight. By "volatile content" or "volatile matter" is meant those constituents of fuller's earth which are volatilized or driven off by heating the earth for a period of 20 minutes at a temperature of substantially 1800° F. The mixing operation may be accomplished in any suitable device capable of effecting intimate contact between the fuller's earth and the solution of alkaline agent, for example, a pug mill. The extrustion operation is preferably carried out in a continuous screw extrusion machine in which a mixing, grinding, and shearing action under elevated pressure may be obtained. The time required for mixing and extrusion is generally a function of the type of device utilized, and in all cases must be sufficient to permit a thorough incorporation of the alkaline solution in the fuller's earth. Periods of the order of from 10 to 15 minutes or longer may be employed. The temperature at which mixing and extrusion is carried out may range from atmospheric to about 200° F., and is preferably of the order of from 70° F. to 100° F. While it is preferred to employ raw fuller's earth containing natural moisture as the starting material, earths which have been dried and rewetted may also be utilized. When employing a continuous extrusion press to obtain a mixing, grinding and shearing action under elevated pressure, one may prepare the charge for the press in the following manner. The raw fuller's earth, in the form of lumps, may be subjected to a preliminary crushing to reduce the lumps, and the reduced earth may be mixed directly with the solution of alkaline agent, for example, in a pug mill, care being taken to adjust the concentration of the solution so that the water content thereof plus the natural water content of the earth will give a plastic material having a volatile content between 45% and 60% by weight.

Among the chemical agents reacting alkaline in aqueous solution which may be employed in accordance with my invention are the hydroxides, oxides, peroxides, carbonates, bicarbonates, secondary and tertiary phosphates, silicates, sulfites and sulfides of Na, K, Li, and NH_4 which are soluble in water to substantial extent. Because of their avaliability, 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 alkoxides and phenolates of strong bases; alkali metal hydrosulfides and polysulfides; calcium and barium hydrosulfides and polysulfides; soluble magnesium, calcium, and barium salts of the weak acids; alkali metal aluminates, zincates, plumbites, arsenites, arsenates, antimonites, stannites, stannates, chromites, manganates, phosphites, hypophosphites, hydrosulfites, thiosulfates, hypochlorites, hydrogen sulfites; amides of metals forming soluble strong bases; quaternary bases such as tetraalkyl ammonium hydroxides, tetra-aryl ammonium hydroxides, and mixed alkylaryl ammonium hydroxides; hydrazine, hydroxylamine, urea; and other organic bases. While, in general, it is desirable to employ aqueous solutions of alkaline agents, advantageous results may be obtained by utilizing aqueous alcoholic solutions, or solutions containing small amounts of wetting agents such as fatty acid soaps, water-soluble sulfonic acid soaps, sulfonated alcohols, and the like, in addition to the alkaline agent.

My invention may be further illustrated with reference to the accompanying drawing, which shows diagrammatically a system suitable for carrying out my process.

Raw fuller's earth or "clay" of the type obtained from the Georgia-Florida fuller's earth deposits and containing natural moisture (45% to 55%) is passed from storage vessel 1 to the roll crusher 2 wherein the lumpy earth is reduced to relatively flat fragments which may be readily handled in the pug mill 3. The pug mill 3 consists of a housing and a longitudinal shaft 4 having a plurality of spirally disposed paddles 5 adapted to intimately mix the earth while advancing it toward the discharge end of the housing. The shaft may be rotated at a suitable speed by a motor or other source of power not shown. In the pug mill the earth is intimately admixed with the alkaline agent introduced in solution through line 6, the quantity of agent being of the order of 0.1% to 1.75% by weight, based on the volatile-free earth, and preferably about 1% by weight. Depending upon the initial moisture of the raw earth, the concentration of the alkaline solution introduced through line 6 is adjusted to give a total volatile content in the earth of the order of from 45% to 60% by weight, and preferably of the order of from 50% to 55% by weight. If necessary, water may be added to the earth in the pug mill by means of line 7.

Upon discharge from the pug mill 3, the plastic earth of proper moisture content and containing, for example, 1% of alkaline agent thoroughly dispersed therein, is introduced into an apparatus capable of exerting a mixing, grinding, and shearing action thereupon, preferably under elevated pressure. The apparatus, in the present instance, is shown as an auger-type, continuous extrusion press comprising a housing or barrel 8 provided with a rotatable screw 9 and a die plate 10 at the discharge end of the housing. The die plate 10 is provided with a plurality of orifices of suitable size and shape, such orifices generally having a diameter of from about one-eighth to about seven-eighths of an inch. The plastic earth containing the alkaline agent introduced into the housing 8 is subjected therein to an intensive mixing, grinding, and shearing action by means of the screw 9, and is finally extruded through the orifices of the die plate 10 at elevated pressures of the order of from 400 to 1200 lbs./sq. in., or higher. The moist, extruded earth discharged through the orifices of the die plate 10 is then passed through a drier 11 wherein it is dried, preferably at temperatures of from 250° F. to 300° F., to the desired volatile content, for example, 15% by weight. The heated earth from the drier 11 is cooled in tank 12 and passed to the roller mill 13, wherein the dried earth is reduced to granular particles. The granular material from mill 13 is thereafter screened in screen 14, and that portion having the desired particle size, for example, 30 to 60 mesh, is either passed to storage or calcined at elevated temperatures of the order of from 200° F. to 1400° F., and preferably at temperatures of from 800° F. to 1200° F. Dust or fines, resulting from the milling and screening operations (designated as "reject"), may be returned to the pug mill 3 or to the extrusion press for further processing. Or, such fines, being of themselves of improved adsorptive efficiency, may be employed in various processes, such as contact decolorization of hydrocarbon oils, or as catalysts or catalyst carriers, and the like. Oversize particles from screen 14 may be returned to the roller mill 13 and reduced to particles predominantly of the desired size, and thereafter screened as above described.

In order to further illustrate my invention and to show the advantages of my process over those employed heretofore, the following examples are presented. It is to be understood that such examples are merely illustrative and are not to be considered as limiting the scope of my invention. In the table are shown the results obtained by treating raw fuller's earth from the Attapulgus, Georgia, fuller's earth deposits, in the presence and in the absence of added chemical agents. For purposes of comparison there are included examples of commercial Georgia-Florida fuller's earth, and Georgia-Florida fuller's earth pugged in the presence and in the absence of chemical agents and then extruded.

Commercial fuller's earth (Example 1) was produced by drying raw fuller's earth (V. M. —48%), grinding the dried material, screening same to 30 to 60 mesh, and calcining or burning the 30 to 60 mesh earth at 900° F. for 20 minutes.

In the examples involving intimate grinding, kneading, mixing and extrusion in addition to pugging (Examples 2 to 19), the pugged earth was passed through a twin screw extrusion press having 2" diameter screws or augers approximately 14" in length, and a die plate 1" thick provided with a plurality of ¼" orifices. The extrusion press was operated at substantially constant load, i. e., about 3.5 amperes, the thruput of earth varying with volatile content thereof and with the effect of the chemical agent upon the earth. In all cases, the earth resulting from the pugging and extrusion operations was dried, ground and screened to 30 to 60 mesh, calcined or burned at 900° F., for 20 minutes, and then tested for volatile matter (V. M.), volume weight (lbs./cu. ft.), and decolorizing efficiency on both weight and volume basis. The decolorizing efficiency was determined by solution filtration of Pennsylvania "A" 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 treated earth.

Example	Pugging		Extrusion			Product			
	V. M., (wt. per cent)	Time, min.	V. M., (wt. per cent)	Ampere load	Thruput, (oz./min.)	V. M., (burned)	Vol. wt. (burned)	Efficiency: Wt. per cent	Efficiency: Vol. per cent
(1) Commercial fuller's earth						3.5	31.7	100.0	100.0
(2) Raw fuller's earth	53.5	15	53.5	3.5	34.6	3.4	29.6	121.2	114.3
(3) Raw fuller's earch+0.25% NaOH	53.6	15	53.6	3.5	33.5	3.8	32.1	125.0	125.7
(4) Raw fuller's earth+0.50% NaOH	53.8	15	53.8	3.5	32.8	3.6	32.8	123.4	126.4
(5) Raw fuller's earth+0.75% NaOH	54.0	15	54.0	3.5	33.3	3.7	32.8	124.7	128.2
(6) Raw fuller's earth+1.0% NaOH	53.4	15	53.4	3.5	32.3	3.7	33.8	124.2	131.7
(7) Raw fuller's earth+1.25% NaOH	54.2	15	54.2	3.5	38.8	3.4	34.3	127.3	137.0
(8) Raw fuller's earth+1.50% NaOH	54.3	15	54.3	3.5	38.6	3.5	35.4	124.2	137.9
(9) Raw fuller's earth+1.75% NaOH	53.4	15	53.4	3.5	32.7	3.7	36.3	120.5	137.0
(10) Raw fuller's earth+2.0% NaOH	53.5	15	53.5	3.5	31.5	4.0	36.2	116.2	132.2
(11) Raw fuller's earth+1.0% Na_2CO_3	53.7	15	53.7	3.5	36.6	3.8	32.5	122.5	125.2
(12) Raw fuller's earth+1.0% LiOH	53.5	15	53.5	3.5	34.8	3.0	33.1	123.2	128.4
(13) Raw fuller's earth+1.0% NH_4OH	53.7	15	53.7	3.5	14.3	4.0	30.2	127.0	120.7
(14) Raw fuller's earth+1.0% $NaHCO_3$	53.8	15	53.8	3.0	18.9	3.9	30.7	128.2	123.8
(15) Raw fuller's earth+1.0% Na_2HPO_4	53.8	15	53.8	2.5	33.5	3.2	31.3	123.0	120.7
(16) Raw fuller's earth+1.0% Na_3PO_4	53.8	15	53.8	3.5	36.4	4.0	31.2	128.4	125.4
(17) Raw fuller's earth+1.0% Na_2SiO_3	53.7	15	53.7	3.5	31.6	3.5	31.0	128.8	125.2
(18) Raw fuller's earth+1.0% Na_2S	53.4	15	53.4	2.6	10.9	3.9	32.7	125.1	127.4
(19) Raw fuller's earth+1.0% Na_2SO_3	53.2	15	53.2	2.5	7.4	4.3	31.4	124.2	122.0

It will be seen from Examples 3 to 9 and 10 to 19 that treatment of fuller's earth with chemical agents reacting alkaline in aqueous solution results in a marked increase in decolorizing efficiency, both on a weight and volume basis, as well as an increase in volume weight in the majority of the samples treated. Pugging raw fuller's earth with less than about 2% by weight of an alkaline agent, followed by extrusion (Examples 3 to 9 and 10 to 19), produces a substantial increase in volume weight, as well as a great improvement in decolorizing efficiency (particularly on a volume basis), as compared with commercial fuller's earth (Example 1), or raw fuller's earth which has simply been pugged with water and then extruded (Example 2). It will be noted that the weight efficiency of the treated earth in Example 10, using 2% NaOH, has fallen below that of the water-extruded earth (Example 2). Such decrease is substantial and undesirable, and it is therefore evident that the quantity of alkaline agent should be maintained below 2%, and preferably not higher than about 1.75%, in order to maintain the weight efficiency at least equal to and the volume efficiency greater than the corresponding efficiencies of water-extruded fuller's earth.

To further compare the efficiencies, on both the weight and volume basis, of water-extruded fuller's earth and earth containing different quantities of an alkaline reagent, i. e., NaOH, the following examples are presented. The processing and testing methods were identical with those described with reference to the examples given hereinbefore, with the exception that the raw Georgia-Florida type fuller's earth was taken from a different batch than that employed in the previous examples.

Earth samples	Commercial	Water extruded	1% NaOH extruded	2% NaOH extruded	3% NaOH extruded	10% NaOH extruded	45% NaOH extruded
Extrusion: Volatile matter ---- wt. percent	----------	54.2	53.8	53.4	54.0	53.5	54.0
Product (calcined 900° F.):							
Volatile matter ---- wt. percent	2.4	2.1	1.7	2.3	2.4	1.9	----------
Volume weight ---- lbs./cu. ft.	31.7	29.3	32.0	33.1	35.1	47.3	72.5
Decolorizing efficiency:							
Weight, percent efficiency	100	126	126	120	104	28	None
Volume, percent efficiency	100	117	128	125	114	42	None

From the above examples, it is apparent that extrusion of the earth containing 1% NaOH produced a substantial increase in volume efficiency over that of the water-extruded earth, but that with earths containing 2% or more of NaOH, the efficiencies decreased.

The argillaceous substances of the fuller's earth type produced in accordance with my invention and having substantially improved adsorptive properties may be employed in the decolorization of hydrocarbon oils, petrolatum, and hydrocarbon wax. Such improved argillaceous substances may also be utilized in the treatment of petroleum distillates for the removal of sulfur compounds, gum, and color-forming constituents, as well as catalysts or catalyst carriers in the cracking, reforming, polymerization, oxidation, hydrogenation, and dehydrogenation of hydrocarbon oils, waxes and gases.

While, herein, reference has been made to the production of granular particles particularly of 30–60 mesh size, it is to be understood that the production of particles of any desired size is within the scope of this invention. Depending upon the use to which my improved argillaceous substances are to be put, the particle size may vary to a considerable extent. For example, the particles may be of the following mesh sizes—180–300, 100–200, 60–90, 50–180, 30–60, 15–60, 15–30, 12–30, 10–30, 8–20, 4–8, and larger. The finer particle sizes, i. e., 100–200 or 180–300, are particularly adapted, for example, to contact decolorization, neutralization or adsorption, whereas the larger particle sizes, i. e., 15–30 or 30–60 are especially useful in percolation decolorization or other treatments.

I claim:

1. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises extruding at elevated pressure a plastic fuller's earth of the Georgia-Florida type intimately admixed with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent.

2. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises extruding at elevated pressure a plastic fuller's earth of the Georgia-Florida type intimately admixed with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent, and drying the extruded earth.

3. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises extruding at elevated pressure a plastic fuller's earth of the Georgia-Florida type intimately admixed with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent, drying the extruded earth, and reducing the dried earth to granular particles.

4. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises extruding at elevated pressure a plastic fuller's earth of the Georgia-Florida type intimately admixed with from 0.1% to 1.75% by weight, based upon volatile-free earth, of sodium hydroxide.

5. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises forming a plastic mixture of said earth with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent, and extruding said plastic mixture at elevated pressure.

6. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises forming a plastic mixture of said earth with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent, extruding said plastic mixture at elevated pressure, and drying the extruded earth.

7. A process for improving the adsorptive and bleaching efficiency of Georgia-Florida type fuller's earth, which comprises forming a plastic mixture of said earth with from 0.1% to 1.75% by weight, based upon volatile-free earth, of a substantially water-soluble alkaline agent, extruding said plastic mixture at elevated pressure, drying the extruded earth, and reducing the dried earth to granular particles.

8. Fuller's earth of the Georgia-Florida type impregnated with from 0.1% to 1.75% by weight of a substantially water-soluble alkaline agent.

9. Fuller's earth of the Georgia-Florida type impregnated with from 0.1% to 1.75% by weight of sodium hydroxide.

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