Nov. 21, 1939. W. S. BAYLIS ET AL 2,180,576

ADSORBENT CLAY AND METHOD AND MEANS OF PRODUCING SAME

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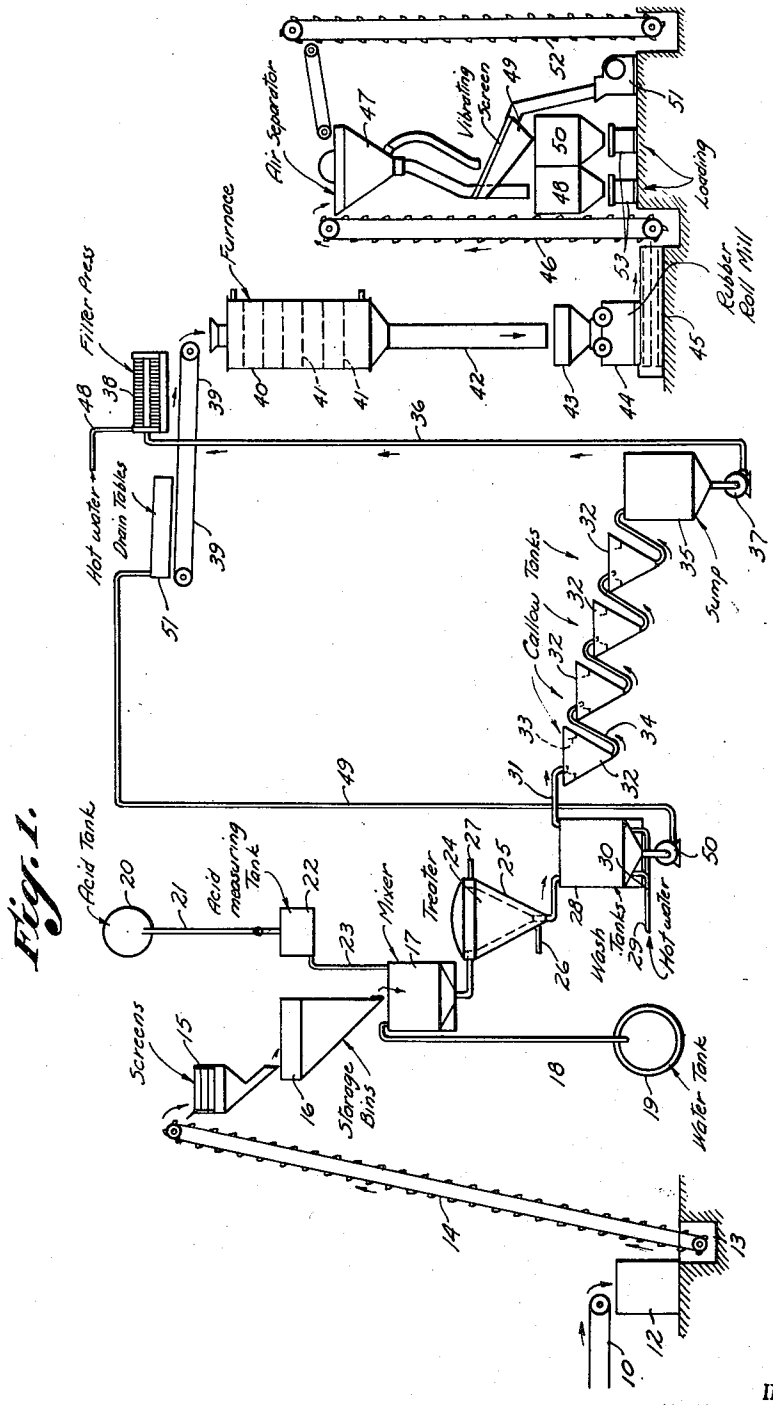


Fig. 1.

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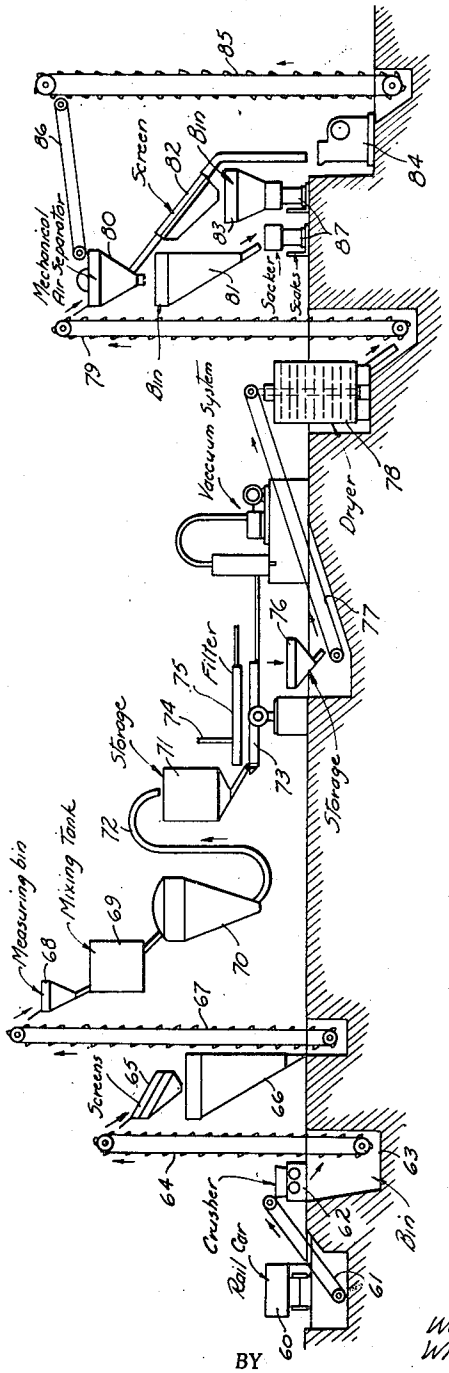
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Filed May 8, 1937 2 Sheets-Sheet 2

Fig. 2.



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UNITED STATES PATENT OFFICE

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ADSORBENT CLAY AND METHOD AND MEANS OF PRODUCING SAME

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Application May 8, 1937, Serial No. 141,575

5 Claims. (Cl. 252—2)

Our invention relates broadly to adsorbing agents and particularly to bleaching or decolorizing clays, it being the general purpose of our invention to provide a more efficient adsorptive agent in the form of a bleaching clay than has heretofore been known. In order to attain this major object, we have developed a novel method and means of treating adsorbent clays to increase their bleaching efficiency, which is much faster and more economical than present known processes, and which produces a more efficient adsorptive agent with new characteristics and specifications.

The adsorbent qualities of many raw earths have long been known and because they were first widely exploited and used in fulling cloth, they became known as fuller's earth. Many other fields of use for these raw bleaching earths were gradually opened up, among the most important of which were the bleaching and purifying of animal, vegetable, and petroleum oils, and with this extension of the utility of fuller's earth came an insistent demand for a more powerful and economical adsorbent. Other deposits of fuller's earth were discovered of about the same quality as the then known fuller's earths, and a group of clays generally designated as smectites, montmorillonites and bentonites were also discovered which, while of the same general nature as the clays then commonly known as fuller's earth, such as standard English fuller's earth, did not appear, by the tests which were applied, to have like adsorbent qualities. Because these particular tests which were applied to the smectites, montmorillonites, and bentonites did not show these clays to have any appreciable bleaching powers, it was erroneously concluded that they were not fuller's earths. Methods were then evolved for treating these latter clays which raised their bleaching power above that of the then known common fuller's earths, so that the early technicians further concluded that these clays were of some separate variety of rare earth having hitherto unknown qualities. However, it has now been firmly established that this classification was erroneous, and that all of the said clays are fundamentally hydrous aluminum silicates, properly classifiable as fuller's earths, and that the difference in their adsorptive powers is merely one of degree and not of kind.

The best explanation for this mixup in classifying the various clays is that the term "fuller's earth" is based upon commercial application and is purely descriptive of what the clay will do, while the other names given the various clays describe them from a petrographic standpoint. This explanation is well brought out by Dr. Paul F. Kerr in an article entitled Montmorillonite or Smectite as Constituents of Fuller's Earth and Bentonite, appearing in the American Mineralogist, vol. 17, No. 5, May, 1932. In this article, Dr. Kerr states:

"Three conclusions are supported by the investigation outlined in this paper: (1) The two hydrous aluminum silicates, montmorillonite and smectite, appear to be identical. (2) Both may be prominent as constituents of bentonite and fuller's earth. (3) Fuller's earth, from one or more long recognized European localities, has been formed by the alteration of volcanic ash to smectite (montmorillonite). This is a type of origin generally relied upon to determine bentonite."

"Examinations of thin sections of smectite demonstrate that in two of the localities studied the clay has been derived by the alteration of volcanic ash. Such an origin should lead to the conclusion that, by modern definition, the clay is bentonite. We are thus placed in the apparently peculiar position of renaming a clay bentonite, which has long been called fuller's earth. It should be pointed out, therefore, that bentonite is a rock definition, while the term fuller's earth is based upon commercial application. A naturally adsorptive clay of standard efficiency would be known as fuller's earth. This material might very well, at the same time, be derived from volcanic ash, and hence would be bentonite from the petrographic standpoint."

The foregoing views are shared by P. G. Nutting of the U. S. G. S., who has very ably expounded a theory regarding the adsorptivity of various clays which has had a wide acceptance. Briefly, this theory holds that clay particles are potential bleaching agents for oil when their surfaces hold H and OH radicals adsorbed in a thin layer, which when driven off by heating leave open bonds which select the darker and more basic constituents from oils at raised temperatures. The pursuit of this theory and many tests have shown that between what were formerly described as separate classes, to-wit fuller's earths and activable clays there are scores of clays having all intermediate degrees of bleaching behavior, so that the once considered clear-cut division between these two classes of bleaching clays has now been entirely obliterated and it is generally admitted that many so-called fuller's earths are derived from bentonites (hydrated volcanic ash, low in silica) by natural leaching in surface water.

It is likewise generally admitted that clays of apparently similar chemical composition may vary greatly in their bleaching power and their ability to be improved by acid treatment, while, on the other hand, many clays differing widely in composition, may be similar in bleaching power and readily susceptible to acid treatment. This finding is borne out by observation on the molecular structure of various clays as revealed by X-ray patterns, for it has been found that relatively inactive raw clay after treatment with acid generally shows little or no change in molecular structure even though its adsorptivity is increased. About the most that can be said positively at the present time, is that all bleaching clays are fundamentally hydrous aluminum silicates, properly classifiable as fuller's earths and that their relative bleaching qualities in their raw state probably depend upon the amount of natural leaching which they have undergone in nature.

As further evidence of the fact that these clays, variously termed bentonite, smectite, montmorillonite, and the like are really fuller's earths, we have found as the result of many years' experience in the art of acid treating clays that clays which are not initially adsorbent in their raw state will not produce commercially satisfactory bleaching clays, no matter how much acid treatment they are given. Our tests on many clays such as Otay, Chambers, Tehachipi, and the like which have been often described in the literature as not being fuller's earths show that all of these clays have some bleaching effect on cottonseed oil and must, therefore, be properly classified as fuller's earths.

In spite of the great amount of research work done in this field and the discovery that all known bleaching clays are hydrous aluminum silicates, all of the present known processes for treating adsorbent clays have been built up on the erroneous theory that the clays which were called variously bentonite, smectite, and montmorillonite were not fuller's earths but were each a separate and distinct type of rare earth, and consequently the various processes for treating these clays have been developed to handle a specific clay, usually from a specific deposit.

It is one of the principal objects of our invention to provide a process, and apparatus for practicing that process, which is universally applicable to all hydrous aluminum silicates or fuller's earths and which process will change the characteristics of and raise the natural bleaching power of many fuller's earths to a point far in excess of any known bleaching clays now on the market. As previously mentioned there is a wide variation in the natural adsorbent qualities of the various fuller's earths and the adsorptivity of the resulting product will also vary depending upon the particular clay treated, although so far as we know there is no fixed relationship between the original adsorptive power of the raw clay and that of the finished product. It is also well known that certain fuller's earths of natural adsorbent qualities cannot be improved by treatment. This is probably due to the fact that there is present in the fuller's earth a substance which is not altered or which is not removed by the treatment, and which is probably zeolite of the general formula—$2SiO_2 \cdot Al_2O_2 \cdot Na_2O \cdot 6H_2O$.

The clays which we prefer to use in the practice of our invention are as mentioned, hydrous aluminum silicates and may be classed petrographically as bentonites, from their appearance and many of their characteristics, and on the other hand as true fuller's earths as defined by the U. S. Bureau of Standards, for they will bleach cottonseed oil equal to English fuller's earth, and further will bleach by percolation and adsorb grease from wool, which are the other two generally accepted tests of fuller's earth.

Furthermore, the bleaching clays resulting from our process, besides having a definitely higher bleaching efficiency lend themselves to a universal utility which none of the now known bleaching clays are susceptible, i. e. they can be used for contact filtration as exclusively employed by the animal and vegetable oil industry and as employed in the petroleum industry to a limited extent and also in percolation filtration as employed more generally in the petroleum industry, which latter quality is not found in the treated clays now on the market.

Another characteristic of our bleaching clay is its increased ability to bleach and purify a great variety of vegetable oils and fats, and its great stability because of the substantially complete elimination of lime. In this regard we have found that the product of our process can be used very satisfactorily in treating linseed and other oils, now only treatable with the German clays made by a hydrochloric acid process.

We have also found that by practicing the process of our invention, we are enabled to produce a substantially neutral bleaching clay with a very high efficiency, whereas with prior known processes it has been impossible to achieve this result without employing neutralizing chemicals or clays, or other special treatment, to reduce the natural acidity of the treated clay. This is of course a distinct advantage in all bleaching activities and particularly valuable in clays designed to bleach animal and vegetable oils refined for edible purposes.

These and other objects and advantages of our invention will become apparent from the following description of preferred forms of our invention, and from the accompanying drawings therein referred to, in which:

Fig. 1 is a diagrammatic side elevation of one form of apparatus for carrying out our process.

Fig. 2 is a diagrammatic illustration of a modified form of apparatus for carrying out our invention.

When bleaching oils by percolation it is, of course, desirable to employ rather coarse granular clays, and when bleaching by contact filtration, it is most desirable to have relatively fine clays, although in each instance it is necessary for the most efficient treatment that the natural graininess of the clay be preserved. We have found that our process functions equally well on hard and soft clays and further that hard clays lend themselves naturally to the production of a coarse product suitable for percolation, and that soft clays by our treatment can be easily made to produce a small particle sized product of excellent quality for contact filtration. Our process of treating the clays is fundamentally the same in each case, but there are minor variations due to practical considerations raised by the physical characteristics of the clays. Consequently, in the interest of brevity we will describe the process as a whole, pointing out as we proceed, the variations therein that are deemed advisable when treating hard or soft clays.

Referring now to Fig. 1 wherein is illustrated one suitable apparatus for practicing our novel process, the numeral 10 indicates a conveyor of any suitable type upon which the mined clay is

deposited from cars or trucks not shown. The clay as mined often is in the form of large lumps which should be broken up, by any convenient means, preferably prior to its being deposited upon the conveyor 10, so that it can be readily handled. If a relatively soft clay is being treated such as that mined from a deposit near Shoshone, California, it may be deposited in a storage bin 12, and later dropped into a pit 13 to be raised by an elevator 14 to storage bins 16, or if desired, it can be conveyed directly to the elevated storage bins 16 by any other convenient means.

If a relatively hard clay or very granular clay, such as mined from a deposit near Lovelock, Nevada, is to be treated in order to produce a percolating clay, it is preferably screened to size, and if necessary is put through a sizing mill (not shown) before being screened. As one convenient way of accomplishing the screening we provide a series of screens 15 immediately above the storage bin 16, through which this coarse clay can be passed from the elevator 14 after being picked up out of a pit 13. It will be understood, of course, that Fig. 1 of the drawings is merely diagrammatic and that a number of bins or elevators may be provided to accommodate the various types of clays, and further that a suitable by-pass may be used to feed the soft clays directly from the elevator 14 to bins 16 without passing through screens 15 if desired.

It should be noted at this point, however, that in neither of the above-mentioned cases, is the clay ground or crushed in such a manner as to destroy its natural grain size, which, as will be hereinafter discussed in detail, is both novel and extremely advantageous.

The numeral 17 indicates a mixing tank which may be of conventional type and may be of wood, metal lined with lead, or other suitable material. Connected to the mixing tank 17 by a pipe 18 is a hot water storage tank 19 which is provided with suitable valve means (not shown) for controlling the flow into mixer 17. An acid storage tank 20 may be disposed above the mixer 17 and is connected by a pipe 21 to an acid measuring tank 22 placed above the mixer 17 and connected thereto by a feed pipe 23. The mixing tank 17 is preferably underneath the storage bins 16 which are adapted to feed clay separately or concurrently into the mixer as desired.

In the preferred method of practicing our invention, we first introduce a suitable amount of hot water into the mixer 17 from the tank 19 and then add a predetermined amount of acid thereto from the measuring tank 22. The temperature of both the water and acid should be as high as compatible with ready mixing so that the resulting temperature of the mixture will be as high as possible. We prefer to use sulphuric acid, because of its ready availability and low cost, although we can use hydrochloric or other suitable acid if desired for particular reasons. The concentration of the acid may be varied between fairly wide limits depending upon the type of clay being treated, the size of the clay particles and the subsequent steps of the process, but we find that the best results are generally obtained by employing between 15% and 50% by weight with respect to the weight of clay of 66° Baumé acid or its equivalent. After the acid and water have been thoroughly mixed and the temperature has risen because thereof, a suitable amount of clay is admitted to the mixer 17 from the bins 16, or from elevator 14, and the mixture is agitated by any convenient means for a short while to make a flowable pulp. As one example of suitable proportions for use with a clay mined near Shoshone, California, we may use the following:

	Pounds
Clay	500
Water	500
Acid	125

If this mixture is gently agitated for a few minutes, a good flowable pulp is obtained. The pulp is kept in tank 17 just long enough to thoroughly mix it and make a flowable pulp, for excessive agitation or prolonged mixing has a tendency to break down the particles.

From the mixing tank 17, the pulp is run into a closed treating tank 24, where the pulp is treated under pressure. While the shape of treating tank 24 may, of course, be varied considerably, we have found by repeated experiments that a conical tank such as illustrated gives by far the best results, the slope of the walls being such that a minimum of dilution and agitation are had. The treating tank 24 is adapted to be heated by any convenient means such as a jacket 25 through which hot oil or other fluid can be circulated, by means of inlet and outlet pipes 26 and 27 respectively. In treating relatively large quantities of pulp, it may be found advisable to supplement the heating jacket 25 with means for injecting steam into the mixture, which, besides cutting down the time factor, gives improved control, or if desired, the heating can be provided merely by injecting steam into the mixture. The temperature of the pulp is raised (as by any of the means mentioned) to a point where a predetermined pressure above atmospheric, is caused to exist in the treating tank 24 due to its constant volume. A suitable treating tank pressure for most clays is from 40 to 60 pounds per square inch, although we have found by extensive experiments upon a great number of clays that the workable limits may vary from approximately 30 to 80 pounds per square inch, depending upon conditions and the particular clay involved. Considerable latitude is also allowable in the time of treating, some clays requiring as little as one hour of the pressure treatment, while, in other cases, the most beneficial results are obtained by treating for 4 or 5 hours. The time factor also varies considerably according to the method employed for applying the temperature and pressure. Generally speaking, the shorter the treating period, the more rapidly can the pressure and temperature be brought up to the proper point, without any damage to the clay particles.

We have found that treating the pulp under pressure has a distinct advantage over hitherto known methods, and that the resulting product has an efficiency far above that of any of the bleaching clays now on the market, either in this country or abroad. When raw clay is treated by conventional methods in an open tank and violently agitated with steam or other means, the ebullition of the liquid destroys the structure of the clay and breaks the grain down to a powdered or semipowdered form where the greater percentage of the resulting product will pass through a 300 mesh screen. Likewise to get complete treatment by the open tank method, it is usually necessary to treat the clay from 8 to 9 hours, and, of course, the longer the open air treatment, the greater the breakdown in the grain. By our method, however, as mentioned, violent agitation

is dispensed with and the average time of treatment is normally from 1 to 1½ hours and only occasionally as great as 4 or 5 hours, so that the natural graininess of the clay is preserved, giving a much improved product.

While we are not in a position to state positively what the chemical and physical reactions are in the treating tank, we do know that, as the acid penetrates the clay particles, certain salts are formed from the reaction of the acid with the various oxides in the clays, and that most of the salts go into solution. By treating under pressure without agitation, it appears that better and quicker penetration of the acid is secured without any breaking down of the grain structures, and a maximum of oxides are converted into soluble salts in a minimum of time. Also it is found that there is no disintegration of the grain particles, and that the acid is caused to have an increased opening up or cleansing action to greatly increase the adsorptive power of the clay particles. Because the resulting granular product shows a definite superiority in bleaching efficiency over the flaky or powdery types of treated clay now currently produced by others, it would seem that the pressure treatment either increases the adsorptive surfaces of the clay by a more thorough cleansing action or perhaps by compressing or expelling occluded air particles, or causes the treated particles to have a greater number of open bonds according to the Nutting theory, or possibly both effects are obtained. It is generally concluded that the treatment of clays is facilitated by increased temperatures, and by providing a closed treating tank where the pressure can be built up, it is possible to raise the temperature of the mixture above the maximum obtainable in open tanks. For example, the maximum working temperature for the acid mixture in open tanks is approximately 212°–216° Fahrenheit, whereas with our closed tank and a pressure of say 50# we can treat at a temperature close to 300° F. which is a distinct advantage, hitherto unobtainable by open tank treating.

In producing a bleaching clay of general utility and high stability, it is, of course, desirable to eliminate or at least minimize lime salts, particularly if certain vegetable oils are to be bleached. If hydrochloric acid is used, little trouble in this regard is experienced, for the calcium chlorides formed are soluble and are readily removed by washing. However, calcium sulphate is but slightly soluble and, if formed in any great quantity, greatly retards the bleaching efficiency and is one of the principal causes of instability and loss of bleaching efficiency in the clay itself. We prefer to use, therfore, a raw clay containing practically no lime, but we have found that, if lime is present in the raw clay that, by our process of pressure treatment, the formation of calcium sulphate is retarded or substantially suppressed, or if formed is in such form as to be more readily washed out, so that our resulting product has a selective action on certain vegetable oils similar to the action of clays produced by the use of HCl, whereas when H_2SO_4 is employed with the open tank method, most of the lime salts are precipitated in the clay pores or on the clay particles, and cannot be satisfactorily eliminated.

The preservation of the natural graininess of the clay is also instrumental in the elimination of acid and the consequent production of a substantially neutral clay, which as mentioned before is a distinct advantage. Likewise, the results of many tests have shown that the grainy product of our process is outstandingly superior to known clays in the matter of filtration rates.

After the clay mixture has been sufficiently treated in the tank 24, it is, when using the apparatus of Fig. 1, immediately flowed into a wash tank or tanks 28 into which hot water is continuously fed from the bottom by the pipe 29. The lower part of the wash tank is provided with a conical perforated baffle plate 30 adapted to receive and hold the heavier or coarser particles of clay as they settle out of the solution and allow the wash water to flow up therethrough. By this immediate washing with fresh hot water flowing up through the pulp, the major part of the unconsumed acid and acid salts is removed from the clay particles very rapidly and the precipitation of calcium salts is further suppressed or prevented. A continuous flow of wash water is maintained and the overflowing liquor carries in addition to the acid and acid salts most of the clay fines via pipe 31 into a callow tank 32 which may be of substantially conventional design, having a generally conical shape and a launder 33 around its upper edges. By keeping the liquid level properly adjusted, some of the salts and acid will overflow into the launder and the fines will be carried on down, partially by settling action and partly due to the current of the liquid which flows out of the callow tank through an opening at the bottom. An outlet pipe 34 is connected to the opening in the lower end of the callow tank and preferably leads into a second callow tank of similar construction which is disposed somewhat below the first callow tank to insure sufficient hydrostatic pressure to permit a steady flow through the pipe 34. It will be understood, of course, that the number of callow tanks may be varied depending upon conditions, but we have found that a series of four such tanks as illustrated gives very satisfactory results. The action in each of the tanks is similar, the salts and acid flowing off into the launder and the fines being carried on through the tank with the remaining liquid. If desired, all of the launders may be connected to a common drain or sewer not shown. By this method of washing the treated clay, all of the undesirable salts (sulphates if H_2SO_4 has been used) and the excess acid are washed out of the clay pores efficiently and quickly without in any way damaging the clay or reducing its effectiveness, and a minimum quantity of wash water is used. The elimination of the acid liquor containing the acid salts and the washing of the clay may be hastened by flowing hot water into the callow tanks by pipes (not shown).

From the last callow tank 32 the thickened pulp composed principally of the fines of the clay, partially washed, is discharged into a sump tank 35 and pumped up through a pipe 36 by a pump 37 to a filter press 38 which may be of any convenient design, into which water at or near boiling and/or steam may be introduced by means of a pipe 48 to complete the removal of any remaining acid and acid salts in the clay. After the clay in the filter press has been completely washed, steamed and partially dried, it may be dumped on a conveyor belt 39 and carried to a drier 40. There are numerous types of driers now on the market which will satisfactorily perform this step of our process, one such being the well-known Herreshoff furnace where the clay is progressively dried on successively lower

hearths 41, and finally discharged from the bottom of the furnace by suitable means such as chute 42 to fall into a bin 43. We prefer to dry the clay at low temperatures with a corresponding time factor rather than submit it to a hot blast. If the clay is dried too quickly at high temperatures, we have found that the moisture content in the clay is converted into steam and, being forced out of the clay, results in breaking down the clay particles, thus destroying the natural graininess of the clay and producing an excessive amount of fine clay; in other words, the clay particles explode.

The dried clay may then be passed through a set of rubber rollers 44 to break up any soft lumps or agglomerated fine particles that may be present, and is then fed by any convenient means such as the screw conveyor 45 to an elevator 46 which carries it to the separating apparatus. While various means may be used for this step of our process, we prefer to employ an air separator 47.

It should be here noted that because of the nature and characteristics of bleaching clays made by known methods for contact filtration, it has been generally considered necessary to avoid segregation of particle sizes during the process, so that each lot will contain its aliquot part of coarse and fine grains of colloidal materials. The product of our process, however, is of such a nature and so uniformly efficient that separation or segregation of particle sizes may be made, consequently we are able to produce and market several different products each of which has certain individual characteristics. It is thus seen that our process has great flexibility and allows us to produce with the same apparatus and procedure varying quantities of the different products according to the demand therefor.

In our preferred method the minus 300 mesh clay is separated in the air separator 47 from the plus 300 mesh and is discharged into a bin 48. The plus 300 mesh material may be discharged from separator 47 on to a 100 mesh vibrating screen 49 and the minus 100 mesh (100–300 mesh) material allowed to fall into a bin 50. The plus 100 mesh clay may then be fed through a grinder such as a Buhr mill 51, from whence it may be conveyed by any convenient means such as elevator 52 back up to the air separator 47 to be again separated in plus and minus 300 mesh as before. The bins 48 and 50 may be erected over suitable packers indicated by the numerals 53 where the clay is finally packaged for marketing. It is obvious that with this arrangement the finished material may be separated into other grades of varying mesh, as, for instance, the mechanical air separator 47 may be adjusted to produce a minus 100 mesh material and the plus 100 mesh material may be ground in the Buhr mill 51 and mixed back with the minus 100 mesh material, or the separator 47 may be adjusted to produce a minus 300 mesh material and the plus 300 mesh material may be ground through the Buhr mill 51 and mixed back with the minus 300 mesh material.

As previously mentioned, the coarser grains settle out of the pulp solution in the washing tank or tanks 28, and after the washing operation previously described has been completed, hot water is then introduced into the top of tank 28 and caused to flow downwardly through the accumulated coarse clay particles to finally wash them. The contents of the tank 28 are pumped through a pipe 49, by a pump 50 to a drain table 55, it being noted that when two wash tanks 28 are used, as illustrated in the drawings that two pumps, pipes and drain tables are preferably used, although one drain table may be employed for both. From the drain table, the partially dried clay may be discharged on the conveyor 39 and passed into the furnace 40 where it is thoroughly dried. The dried coarse clay may then be conveyed as by the elevator 46 to mechanical air separator 47 and from there handled in the manner previously described for the fine clay.

If a hard or granular clay of the Lovelock type is being treated by the foregoing method to produce a coarse mesh percolating clay, the apparatus may be simplified somewhat, by substituting a series of screens of suitable mesh in place of the air separator 47 and Buhr mill 51. The number of screens used and their respective mesh can be varied as desired and a separate bin is preferably provided for each screen, from which the various clays may be suitable packaged.

In Fig. 2 we have shown a modified form of apparatus for practicing our invention which is very similar to the form shown in Fig. 1 and which likewise by slight modifications can be efficiently used for treating both hard and soft clays, such as the Lovelock and Shoshone, respectively.

The numeral 60 indicates a car from which the raw clay is dumped on to a conveyor 61 and carried to a crusher or breaker 62, from which it is discharged into a bin 63 at the foot of an elevator 64. If a hard clay is being treated to produce a percolating clay, it may be discharged from the elevator 64 on to a series of screens 65 and thence into a bin 66. If a soft clay is being treated which is to be used for contact filtration it may be discharged directly into the storage bins 66 without being screened. The clay can then be picked up as needed from bins 66 by an elevator 67 and discharged into a measuring bin 68 from whence it passes to a mixing tank 69 where acid and water are added and the pulp is made up as previously explained in connection with the form of our apparatus shown in Fig. 1. When the pulp has been properly mixed it is introduced into a treating tank 70 which can be heated by any suitable means as previously described.

In this modified form of apparatus for practicing the process of our invention, the pulp after treatment is discharged into a storage tank or tanks 71 by any suitable means such as the siphon 72. From the storage tank 71 the slurry is passed to a vacuum type filter 73 such for instance as a Bee-Tee Gallagher type, where the acid liquor containing acid salts is filtered off leaving a cake of treated clay. As soon as the liquor has been extracted, water at or near its boiling point is introduced on to the filter as by a pipe 74 and the clay is thoroughly washed to eliminate the more readily removable acids and salts from the clay. When this has been done, a steam-tight cover 75 is clamped over the filter and steam is forced through the cake to complete the removal of acids and salts from the clay.

The residue in the filter may then be automatically discharged into a hopper 76 erected over one end of a conveyer 77, preferably of the Jeff-

rey-Traylor electric-vibrating type. If a vibrating conveyer is used, the clay is carried in a thin layer to a drier 78 which is also preferably of the Jeffrey-Traylor vibrating type. A drier of this kind permits accurate and absolute control of the moisture content of the clay issuing therefrom. After it leaves the drier 78 the clay may be conveyed as by an elevator 79 to a mechanical air separator 80 whose function and operation are the same as the air separator 47 of Fig. 1.

As before, if a soft clay is being treated, the separator 80 divides it into portions of suitable mesh, as for example plus and minus 300, the fines going to a bin 81 and the coarse to a vibrating screen 82 of say 100 mesh. The minus 100 mesh passes into a bin 83 and the plus 100 may be discharged into a Buhr mill 84 where it is ground and recharged into the air separator 80 by suitable means such as elevator 85 and conveyer belt 86. The variously sized clay of the different bins may then be packaged as by the packers 87.

If a hard percolating clay is being handled, the air separator 80 and mill 84 may be eliminated and a set of suitable screens substituted therefor, each screen preferably having its own bin to receive the clay and store it until packaging.

As previously mentioned, the clays which we prefer to use, while generally of what is termed bentonitic structure are nevertheless, fuller's earth, one such clay which we are using having a Lovibond scale reading of 5 Yellow—3.6 Red as against standard English fuller's earth having a reading of 5 Yellow—4.04 Red.

Clays of the hydrous aluminum silicate type have a natural grain size or graininess in their raw state, that is, the lumps or particles are an agglomeration of many individual grains, each of which plays its part in the bleaching of oils.

When treated clays are used for contact filtration, it is, of course, advisable to have the particle size relatively small so that the clay can be readily mixed throughout the oil and a maximum of clay surfaces will be presented to the oil. With previously known processes, where the clay is treated in open tanks, there is considerable natural diminution in the particle size because of the treatment, and this has been supplemented by grinding to produce a very fine material. However, in getting small particle sizes these processes have broken down the individual grains so that the greater portion of their resulting product has been flaky or powdery in form.

One of the advantages of preserving the natural grain structure of the clay, is that it is possible by proper washing methods, such for example as hereinbefore disclosed, to eliminate substantially all free acid, and we are able to produce clays on a commercial basis with an acidity due to free acid as low as .1 of 1%, or describing them another way, with a pH of approximately 7.0.

We have discovered that this breaking down or disintegration of the individual grains very materially reduces the bleaching efficiency of the treated clay, and that our treated clay which is distinctly granular in form, no matter how fine it is screened, has a much higher bleaching efficiency than any of the domestic or foreign clays now on the market. This same comparison holds true no matter what particle size is being tested, and in fact the difference in efficiencies is more marked with the larger particle sizes.

This distinction between the quality and efficiency of our treated clays and common domestic and foreign clays treated by known processes is well illustrated in the following tabulations which are the result of many comparative tests made by us:

Table No. 1

Mesh	A well-known foreign clay	A well-known domestic clay	Our clay
−100	25	25	25−2
−200	25−¼	25−2	25−7
−300	25−1	25−2.5	25−9
100−200	25+12	25+30	25+0.5
200−300	25+11	25+6	25−3
−300	25−1	25−2.5	25−10

The above figures all refer to Lovibond scale readings with a well-known German clay taken as a standard with an arbitrary scale reading of 25.

A reading of 25−2 for instance, indicates that the product is 2 full points lighter red on the scale than the standard, and conversely a reading of 25+2 indicates that the sample tests 2 full points darker red than the standard.

Table No. 2

Type of oil	Foreign clay	Domestic clay	Our clay
Palm oil	5Y−2.6R	25Y−6.0R	5Y−2.5R
Tallow	10Y−4.5R	10Y−6.3R	5Y−3.9R
Raw linseed oil	10Y−3.0R	10Y−5.6R	5Y−3.5R
Soy bean oil	5Y−4.0R	10Y−5.2R	5Y−4.5R
Linseed oil (refined)	5Y−3.9R	5Y−5.3R	5Y−3.8R

These figures also are based on the Lovibond scale and the lower the number of yellow and/or red, the more efficient the clay.

The superiority of our bleaching clay is demonstrated equally forcefully when comparisons are made of filtration rates. The average filtration rate of our clay on lubricating oil of a given type was 2½ minutes whereas the average filtration rate of one of the best known domestic clays on the same oil was 10½ minutes.

All of the foregoing tests were run on clays adapted for contact filtration. It is practically useless to make tests on percolation clays as none of the treated clays heretofore known are suitable at all for percolation, since because of their powdery form they pack almost immediately and prevent the free flow of oil therethrough.

From the foregoing description of preferred forms of our process, apparatus for practicing that process, and products of said process, it will be seen that we have provided a novel and improved bleaching clay and method and means for producing it. While we have gone into considerable detail in discussing various theories of clay structure and treatment, it has been for the purpose of assisting those skilled in the art to properly understand and practice our invention, and is not meant as a limitation of the scope of our invention or to preclude the use of suitable equivalent means and steps in its performance. It is to be understood that the embodiments herein given are merely illustrative of the broad principles of our invention as defined by the appended claims.

We claim as our invention:

1. The process of producing a highly active acid treated fuller's earth or clay which includes: mixing a quantity of unground hydrous aluminum silicate and a strong mineral acid with

sufficient water to make a readily flowable pulp therefrom; heating said mixture under pressure with substantially no agitation thereof, whereby the natural grain size of the silicate particles is preserved; washing the treated mixture to remove free acid and soluble salts therefrom; and drying said washed silicate.

2. A process as defined in claim 1 in which the pressure maintained during treating is above 30 pounds per square inch.

3. A process as defined in claim 1 in which the pressure maintained during treating is above 30 pounds per square inch and the temperature is above 250° F.

4. The process of producing a highly active acid treated fuller's earth or clay which includes: adding a strong mineral acid to a quantity of hot water; then adding an amount of unground hydrous aluminum silicate to said acid water mixture to form a flowable pulp; heating said mixture under pressure with substantially no agitation thereof, whereby the natural grain size of the silicate is preserved; washing said mixture with hot water to remove free acid and soluble salts therefrom; and drying said washed silicate.

5. A method as defined in claim 4 in which the pressure maintained during treating is above 30 pounds per square inch.

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