FULLER'S EARTH AND ITS APPLICATION TO THE BLEACHING OF OILS.

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Fuller's Earth is a form of clay having a high absorbent power for many substances, but especially for certain colors when dissolved in oil or in water. Chemically, it is essentially an aluminum silicate having a higher combined water content than most clays, but its chemical composition may vary widely, and indeed seems to have little connection with its bleaching power.

For some years the English deposits were the only ones that furnished this material to the market, but for the last ten years the Florida beds have supplied all the earth for bleaching petroleum oils used in this country, although we are still importing some thirteen thousand tons yearly of English earth for use on oxidizable oils and those of an edible nature. For oils of this kind the Florida earth is not well suited on account of the taste imparted, fire risks and lack of bleaching power.

Occurrence.—The English earth occurs in extensive deposits underlying a broad belt of country along the southern coast and is especially prominent in the counties of Dorset, Kent and Surry. Works of some magnitude for digging, floating, drying, and grinding the earth are located about two miles from the village of Perley in Surry.

In the United States fuller's earth is widely distributed and in immense quantities. It occurs in New York at McConnellsville, in South Dakota at Fairburn, in California near Bakersfield, in Alabama, in Colorado, in Arkansas, in Florida, in Georgia, and in South Carolina. Other occurrences are known, but have been little exploited.

The California deposit is extensive, varying from fifteen to fifty feet in thickness and has been worked to some extent for use on the Pacific coast. It is said to be of fair quality, but transportation charges are prohibitive to its extended use.

By far the greater portion of the American production of fuller's earth comes from Florida and is generally supposed to be obtained in the northwestern portion near Quincy. Large amounts are, indeed, obtained from this section, but probably the greatest output is from near Palmetto on the Manatee River, where a large and well-constructed plant is in operation and is turning out the finished product at a low cost and where it can be directly loaded on to vessels. The Florida output is used almost exclusively for bleaching petroleum, although a small proportion is employed on tallows and other low grade oils and fats.

Throughout a broad belt of country extending from Northwest Florida to the neighborhood of Georgetown, S. C., the whole country is here and there dotted with deposits of fuller's earth. At Longstreet, Ga., the

strata is of great thickness, even up to forty feet, and underlies the country from near the railway at Coley's Station some three or four miles up Sheldrake creek. Its overburden varies from three to forty feet and it is underlaid by marl, which accounts for an unusually large amount of calcium carbonate shown by its analysis. Again in Wilkinson County, numerous outcrops can be found and in Twigg's county a manufacturing plant is located on an almost unlimited deposit and is turning out a few hundred tons each year. At Groveton, some fifteen miles from Augusta, another outcrop is found upon which a plant has been erected, but has ceased production, mainly owing to the fact that the earth at this point is highly charged with alum. Many deposits also occur along this belt in South Carolina. Near Aiken a deposit of earth almost exactly like that at Macon, Ga., has been discovered, but is of no great extent. At Summerville an earth closely resembling the English in color is to be found. In the region about Gaston a number of deposits occur. Also near Sumter earths of excellent bleaching qualities have been uncovered. On the banks of the Black River, near Kingstree, a deposit some twenty-five feet in thickness occurs underlying many hundreds of acres of country upon a portion of which a plant is now operating and regularly marketing earth. Throughout this southeastern belt the fuller's earth is laid down in strata of varying thickness and carries an overburden varying from nothing to many feet. The strata is itself broken up into substrata between each of which there is generally a thin vein of sand, perhaps an eighth of an inch thick and which makes the mining of the earth extremely easy as following these veins it breaks readily with a pick into tabular blocks from two to ten inches in thickness.

In northern Alabama a large deposit is being developed with prospects of any increasingly large output.

The Arkansas deposits are peculiar in nature in that as a rule they do not occur in strata, but are in pockets some of which are of unknown depth. Near Benton a deposit was worked for sometime and regularly furnished earth to the New Orleans refineries, but is now understood to be exhausted. In Saline County, near Germania, a pocket of earth occurs which is said to be of fine quality and which has been opened to a depth of eighty feet. Its lateral extent appears to be about 100 x 200 feet. A prominent firm of Chicago packers have for some years obtained a large portion of their requirements of fuller's earth from an Arkansas deposit.

Properties.—Fuller's earth varies greatly in its properties and no two deposits seem to be exactly alike. It is generally of a light brownish or grayish color, but may be any intermediate shade or white, cream, yellow, pink, or even black. Its specific gravity varies from about 1.75 to 2.5. It sometimes falls to powder when placed in water and does not generally

show plasticity. These properties are not by any means general, however, and the majority of Southern samples retain their shape in water. Some earths are hard like rock, while others will break down almost like kaolin with the slightest pressure. The Southern earths are almost generally very acid in reaction by the regular methods used in testing soils for acidity, still they contain no acid. The property is simply one of absorption or adsorption, as Cameron has shown to be the case with many clays. (*Bull.*, 30, *Bureau of Soils*). This so-called "acidity" is a direct measure for their absorptive capacity for such bases as lime, but is by no means proportional to their power to extract colors from solution in oil. This "acidity" varies from next to nothing in the Longstreet earth to a point where it requires 1.5 per cent. of calcium oxide to "neutralize" it in some smaller deposits. While this absorption power is not proportional to the power of bleaching oils it is directly proportional to the effect which many of these earths have of imparting a rancid or oxidized odor to edible oils. Earths which do give a very rancid odor to such oils have no such effect upon them if first treated with lime water until they no longer react acid to litmus or give an acid filtrate when shaken up with salt. Unfortunately, however, they lose their bleaching power at the same time, and this is undoubtedly the reason why earths rich in lime are never among the best bleachers. By partly "neutralizing" with lime the effect on the odor can be removed much more rapidly than the bleaching power departs, but this varies with the temperature at which the bleaching is done. If earths which show this strong "acidity" are suspended in water and subjected to the action of the electric current they act like negatively charged colloids, slowly migrating to the positive electrode, and it is this property which accounts for their yielding an acid filtrate when shaken up with salt solution and their absorption of azo colors from oil solution changing them at once to the same shade as if they had combined directly with a true acid.

Some deposits of fuller's earth yield a prepared product which in some way greatly hastens the oxidation by the air of oils with which it is mixed, and this action is so rapid and violent that the contents of filter presses have been known to burst into flame immediately on being opened to the air. This property is, of course, fatal to the use of that particular earth to bleach an oxidizable oil.

Most samples of fuller's earth when dry and unground adhere strongly to the tongue owing to their rapid absorption of water into their pores.

The reason why fuller's earth bleaches oils has not been understood. The subject has been little discussed, but there have been two opinions extant, one that the change was of a chemical nature, and the other that it was simply the mechanical entangling of *suspended* coloring matter. Neither is correct, for the true reason is one of simple absorption, or ad-

sorption, the whole subject of which has been so admirably reviewed by Cameron (*Bull.*, **30**, *Bureau of Soils*). The effect of this absorption for colors is distinctly different in oil from that in water solution and will, of course, differ with every solvent used. That it is, however, a simple absorption action is readily shown by the fact that a fuller's earth which has taken up all the color it will readily hold yields almost all this color to alcohol after the adhering oil has first been extracted with ether or gasoline. The earth thereby regains most of its bleaching power, but not all for the reason that certain organic products still firmly adhere.

Uses.—Fuller's earth was first used to remove grease from woolen cloth in the process of shrinkage or fulling by means of moisture and heat and it is to this use that it owes its name. In smaller quantities it is used in the drug trade as an absorbent powder similar to "talcum powder," and is much more efficient. Mixed with glycerol it is sold as a well known proprietary medicine used for external application. The one great and important use, however, is for the bleaching and decolorizing of oils, fats and greases.

Production.—According to the reports to the United States Geological Survey (*Mineral Resources*, 1904, p. 1121) there were 29,400 short tons of fuller's earth produced in the United States in 1904. Much the larger part of this came from Florida and was used in the refining of petroleum. No figures are available as to the American production of earth to be used in bleaching animal and vegetable oils but, from private information, the American output for 1906 can not be far from about 2,500 tons for Arkansas, 1,000 tons for California, 400 tons for Georgia, and 100 tons for South Carolina. In the present year the Arkansas output will be much reduced owing to the abandonment of work by two of the chief producers, while the South Carolina output promises to increase and Alabama may enter the field as a prominent producer.

Mining and Preparation.—Fuller's earth is worked much the same as any clay bank. First the overburden must be removed with pick and shovel and then the clay dug in much the same manner, perhaps shaking up the bank now and then with an easily placed charge of dynamite. At times the steam shovel may be used to decided advantage. The lumps of earth must next be dried so as to contain about four or five per cent. of moisture. This may be done under sheds, as is the custom with kaolin, but on the large scale the kiln, or rotary dryer, is found to be more economical. If artificial dryers are employed, it is highly important that a temperature but little above the boiling point of water be used, as removal of the constitutionally held water seems to lessen the bleaching power for animal and vegetable oils. Indirect firing of rotary dryers is ordinarily used for the earth should not be mixed with any solid products

of combustion, but when petroleum can be obtained, as is the case with some of the rotary dryers used in Florida, direct firing has many advantages, the hottest part of the dryer being the point where the moist earth enters.

When dry the earth must be ground and perhaps bolted. The grinding is usually done in burr mills, or in ball mills, and the degree of fineness is regulated by the purpose for which the earth is to be used. For heavy petroleums the particles must be coarse grained and the earth must therefore be bolted to about twenty to fifty mesh. For cotton seed, lard and many other oils, it must be used in a very finely ground state. For this purpose a large American consumer grinds the imported English earth to pass a 130-mesh sieve. The imported ground English earth, on the other hand, appears not to have been bolted, but almost entirely passes a 100-mesh sieve. The earth grinds easily and, if previously screened from loosely adhering sand, is not especially destructive to the burr stones. One South Carolina company working on an unusually hard earth uses mills which have emery cutting faces.

APPLICATION TO THE BLEACHING OF OILS.

Petroleum.—The bleaching of petroleum is distinctly different in its mode of procedure and in the kind of earth to be used from the method used with other oils. The Florida earth appears to be the best earth so far discovered, while the English is much inferior for this purpose. Here too the presence of notable amounts of lime in the earth is said to be deleterious in its action.

The application is extremely simple and consists in allowing the oil to flow down through columns of earth much the same as a sugar solution is decolorized by bone black. Here, too, the first portions of oil passing are almost colorless and then gradually grow darker until the earth has absorbed all the color it will remove. The earth can be revivified by burning off the adhering petroleum in rotary kilns much as bone black is recovered to be used again. The rather high heat to which the earth is thus subjected does not seem to injure its bleaching power for petroleum oils, where it would be utterly fatal to its use on animal and vegetable oils and fats.

The degree of fineness to which the earth is ground depends upon the viscosity of the oil to be bleached. The heavier oils require a very coarsely grained earth, while the lighter oils can use an earth as finely ground as 124-mesh.

Animal and Vegetable Oils.—The method used in treating oils of this character is distinctly different from that used on mineral oils and consists essentially in heating the oil by indirect steam to some given temperature, adding the finely ground earth, stirring for some two or three minutes, and then running the hot oil immediately through filter presses

to remove the earth. The temperature used varies with the kind of oil and with the views of the individual refiner, but is generally a few degrees below the boiling point of water, although a much lower temperature is sometimes employed. The amount of earth used also varies with the kind of oil and with the characteristic properties of the special sample, for different lots of the same variety of oil vary greatly in the amount of earth required to bleach them to a standard shade. Lard and lard oil generally require about 1 per cent. of earth. Cotton seed oil ordinarily requires 5 per cent., while certain dark tallows and greases require much more. The amount used on cotton seed oil varies greatly, however, both with the particular lot of oil and in the practice of the refiner. Following the bleaching process cotton seed oil is generally treated by a special refining process to improve the taste and odor. One of the items of success in modern refining is to carefully select for bleaching those lots of oil which require the least earth for not only is the cost of material saved, but also the amount of oil which is thrown away in the spent earth is proportionally less. In spite of this fact, as high as 10 per cent. of earth is sometimes used on cotton seed oil, although this would be considered very poor practice on the part of most refiners. A large per cent. is required, however, to reach a certain standard grade of color, if a low temperature is used, and this low temperature is thought by some to sufficiently improve the flavor and odor of the oils to warrant the increased cost of its use. In selecting the oils to be bleached or in comparing different samples of fuller's earth, they are usually first tested in the laboratory by simply heating 200 cc. of the oil to the temperature taken, ordinarily 100°, adding a definite quantity of earth, stirring steadily for three minutes while the temperature is maintained and filtering as quickly as possible. The oil is run into a 120 cc. oil bottle, placed in a colorimeter and the color standardized with the red and yellow glasses of the Lovibond scale. In these laboratory tests 6 per cent. of earth is ordinarily used on cotton seed oil and 1 per cent. on lard and lard oil.

While lard and cotton seed oil refineries are the chief users of fuller's earth it is also used on castor, linseed, cocoanut and other oils, and on tallow and greases.

Although America furnishes all of the fuller's earth used on pertoleum it supplies but a small portion of that used on edible oils. The English earth is considered superior to any American earth yet marketed for this purpose, and in 1905 was imported to the amount of 12,981 tons, of which 1,502 tons were in lump. The ground earth was invoiced at $8.11 per ton, while the unground earth was valued at $7.61 per ton. To these prices should be added the duty of $3.00 and $1.50, respectively. The quoted market price of the ground earth is some four dollars per ton higher.

Many attempts have been made to develop American deposits and to supplant the English earth and many failures have resulted. Up to the present no American product has been put on the market which, in the opinion of the trade, is equal to the English earth.

For a fuller's earth to supplant the English earth in American practice, it must have the following properties given in the order of their importance.

1st. It must bleach as well as the English.
2nd. It must not cause the color of the oil to revert.
3rd. It must filter well.
4th. It must absorb no more oil than the English.
5th. It must not catch fire when removed from the presses.
6th. It must give no permanent taste or odor.

To find all these qualities in one earth is no easy matter and all American earths put on the market have failed in one or more particulars, although the writer is confident that the fault has not always been inherent in the earth itself and there is no really good reason why a pound of earth should be imported.

Most American earths do not bleach as well as the English, but a number of deposits do, and the writer has had samples from three deposits that bleach decidedly better. The extent of the bleaching power is, of course, the first requisite. As before stated this bleaching power can be much lessened by the addition of lime water to the earth. On the other hand, every attempt to treat the earth so as to increase the bleaching power has met with failure.

The question of color reversion is deemed important by certain refiners and these claim that with certain American earths the color tends to come back to cotton seed oil in the treatment after bleaching. This is a quality inherent in the earth, and if extensive would be fatal to its use.

If the earth does not filter well, much time is lost, the filter presses become clogged, the oil is in contact with the earth longer than it should be and oil is mechanically lost. The difficulty is due to slimes and depends on the way the earth breaks down under the action of the mills. Fine grinding is essential to the full bleaching action, but certain earths can be ground, even to 200-mesh without forming slimes, owing to their peculiar cleavage, while others if ground fine enough to bleach properly will completely choke the presses. This is not due to the chemical composition of the earth as some have supposed, but rather to its mechanical condition.

Absorption of oil is not altogether a quality of the earth, for even with the English the amount left behind varies greatly with conditions and with the thoroughness with which the presses are blown out with steam. The amount left behind in the best practice is about 10 per cent., while the

average will probably be from fifteen to twenty. Samples of spent English earth have been sent to the writer containing as high as twenty-four per cent. of oil and it can be seen at once that this is no small part of the cost of the process. American earths are reported to generally absorb too much oil. The reason is really the same as causes difficult filtration, for where slimes are formed they hold much oil mechanically.

As has already been stated certain fuller's earths cause a very vigorous oxidation to take place in the oil with which they are saturated on exposure to air. The action is so intense that the mass sometimes catches fire as soon as the presses are opened. At other times it takes place later in the waste piles of spent earth. The English earth is without this trouble and this property if well marked would naturally condemn any material. No reason can be assigned why one earth should have this property more than another. The fact simply remains and must always be reckoned with.

Most American earths give a decided taste and rancid or oxidized odor to oils, and this increases with the temperature used. With lard or lard oil this is a serious matter, but in the practice of most cottonseed oil refiners a subsequent treatment removes the taste and odor imparted by the earth. This action is in some way connected with the "acidity" of the earth and can be entirely overcome by neutralizing this absorptive power with lime although, as before stated, the bleaching power, unfortunately, goes at the same time.

Besides these difficulties which must be met before an American earth can become successful, there is another within the refinery, and this is due to the fact that the workmen are always prejudiced against any new earth and any special change in their measures or methods. They accordingly lay all difficulties which may arise in the refining process to the innovation and condemn the earth to their superiors.

In spite of all these facts it is the opinion of the writer that imports of English earth will show a great falling off before many years are past.

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NOTES.

Note: A Modification of the Tannin-Salt Method for Separating Proteoses and Peptones.—Some criticism has been raised in regard to the Tannin-salt method for separating proteoses and peptones from the simple amino bodies as worked out by Bigelow and Cook[1]. The principal criticism is in the fact that in the Kjeldahl digestion when sulphuric acid is added to the filtrate of the tannin-salt precipitate and heat is applied, serious foaming takes place which often results in loss of sample.

[1] This Journal, 28, 1485.