UNITED STATES
DEPARTMENT OF THE INTERIOR
J. A. KRUG, SECRETARY

BUREAU OF MINES
JAMES BOYD, DIRECTOR

REPORT OF INVESTIGATIONS

A METHOD OF EVALUATING BLEACHING CLAYS

BY

DONALD W. ROSS

REPORT OF-INVESTIGATIONS

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

A METHOD OF EVALUATING BLEACHING CLAYS[1]

By Donald W. Ross[2]

CONTENTS

---

[1] The Bureau of Mines will welcome reprinting of this report, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Report of Investigations 4295."

[2] Chemical engineer, Tuscaloosa Branch, Metallurgical Division, Bureau of Mines, Southern Experiment Station, Tuscaloosa, Ala.

INTRODUCTION

Petroleum oils of widely different grades have long been clarified or decolorized by contact with fuller's earths. More recently, so-called activated clays have also been used for this purpose. Still more recently such clays have been used in the form of nodules termed "catalytic pellets." Clays of varied appearance and from different localities possess the desired bleaching qualities, but evaluation of such clays, so useful to the oil industry, has not been simple. Previous methods of identification and evaluation have largely followed procedures of production methods and were not primarily based upon the fundamental properties of the clays. Thus, a false assumption has grown up that bleaching clays probably have no common properties on which a method of comparison can be based.

Fuller's earths and activated clays have a large absorptive capacity for the color constituents of petroleum and its products. Decolorizing is accomplished by bringing the oil into intimate contact with the clay and later separating the decolorized oil from the clay with its load of absorbed coloring matter. Former practice in absorbing "color" was to use the clay as granules or in powdered form. More recent practice is to use clay pellets that are more abrasion-resistant than the granules. The oil is either filtered through a bed of clay, percolation method, or agitated on contact with the clay, contact method. Viscous oils are decolorized at an elevated temperature, so that their viscosity is lowered to the point at which thorough contact with the clay is insured. Nonhumidifying, nonoxidizing gas, such as dry steam or dry nitrogen, is used to seal such hot oil masses from the atmosphere.

Basic work on the comparison of decolorizing clays has been conducted by Dr. P. G. Nutting,[3] who also recorded the location and the geology of a large number of clay deposits. He also described the physical properties of a number of leading decolorizing clays. Although Dr. Nutting has done a monumental work, his decolorizing test lacks a high degree of accuracy because of the minute quantities of clay employed.

The object of the present investigation was to examine the common properties of absorptive clays, to correlate these properties with their bleaching capacities, and to develop a better method for evaluating them.

_____

[3] Nutting, P. G., Adsorbent clays, their distribution, properties, production, and uses. In Contributions to economic geology, 1941-42. U. S. Geol. Survey Bull. 928 (c), 1943, pp. 127-221, pl. 13.

DEVELOPMENT OF A LABORATORY METHOD

In developing a clay-testing method, existing though inadequate procedures of some apparent merit were tested on clays whose behaviors were known. The most promising leads thus obtained served as the basis for the work from which a sound testing method was developed. This stepwise procedure was accomplished by measuring the decolorizing capacities of clays having certain known properties. These decolorizing capacities were determined by modifications of the commonly known percolation and contact methods. Both methods were used at room and elevated temperatures and on air-dry clay, clay dried at various temperatures, and on both activated and unactivated materials. These experiments led to the conclusion that the decolorizing capacity of any given clay increases as its absorbed water content decreases, and vice versa. This property was tested through several cycles of wet to dry to wet. Thus, no decolorizing-capacity figure has a definite meaning unless the remaining absorbed moisture is also indicated. Freundlich[4] stated: "The ubiquitous presence (omnipresence) of water vapor implies that practically all solid surfaces of the objects around us are coated with a film of adsorbed water." He pictured adsorption as including two quantities: First, specific adsorptive power, or the amount adsorbed per square centimeter of surface; second, specific surface area, including both external and internal surface of the clay grains. Activable clays differ in compactness, the more compact clays not only absorbing and giving up moisture more slowly, but requiring more time to decolorize oil than the more friable clays. Compact clays also require more vigorous chemical treatment to bring them to maximum decolorizing capacity. A third property, defined by the term "penetrability," indicates susceptibility of being penetrated.

Adsorption of moisture and of the coloring matter of petroleum therefore, are affected by three factors: (1) specific adsorptive power, (2) specific surface, and (3) penetrability or rate of penetration. The first two are quantities that would exist at equilibrium. The third is important, because the rate of approach to equilibrium is slow and differs from clay to clay.

Brunauer, Emmett, Teller, and Love[5] have recently developed means of measuring areas of powders by use of certain liquids at temperatures near their boiling points; and, more recently, Garrison[6] used partial pressures of certain vapors at known temperatures. This latter procedure is similar

[4] Freundlich, Herbert, Colloid and capillary chemistry. Translated from the third German edition. E. P. Dutton, 1922, pp. 102-167.

[5] Brunauer, S., Emmett, P. H., Teller, E., and Love, K. S., The use of low-temperature van der Walls adsorption isotherm in determing the surface area of various adsorbents. Jour., Am. Chem. Soc., vol. 59, 1937-38, pp. 2682-2689. Adsorption of gases in multimolecular layers. Jour., Am. Chem. Soc., vol. 60, pp. 309-319. The measurement of surface area of soils and soil colloids by use of low-temperature van der Walls adsorption. Soil Science, vol. 45, pp. 57-65.

[6] Garrison, Allen D. U. S. Patent 2,375,641, issued May 8, 1945. Assigned to Texaco Development Corp.

to the one used herein for measuring water-condensing capacities of clays, in which clays are compared at constant partial water-vapor pressure at room temperature.

It will be shown that water adsorption by clays does affect adversely the decolorizing capacity of clays but is not necessarily in direct relation thereto. Hence, measurement of water-condensing capacity of clays or of surface areas is not a substitute for the measurement of oil-decolorizing capacity. For the latter, the contact method as herein altered and described is probably the simplest known procedure.

Absorbed water was found to be lost at temperatures up to 250° C., and other investigators, including C. S. Ross and P. F. Kerr,[7] have shown that smaller amounts continue to be lost at still higher temperatures but below those at which chemically combined water is liberated. In the current work on absorptive clays, for each increment of water removed, a corresponding increase in decolorizing capacity took place. This relation is apparent even when the water content is small, such as the amount removable in the temperature range 110° to 250° C. For decolorizing purposes, therefore, the problem is one of drying the clays at an optimum temperature for an optimum time, assuming that the various clays had reached equal water content. This is not exactly true but appears to be close enough for purposes of a method for identification and evaluation of decolorizing clays. The optimum conditions were found to be the drying of minus 150-mesh clay at 110° C. for 5 days.

From what precedes, it is evident that measurement of color and measurement of moisture content are of importance to this work; hence, some discussions concerning them are included.

Color Measurement

The recording of color is not simple. Kalichevsky and Stagner[8] state: "Color, as seen by the eye, involves several phenomena, the balanced recording of which is not yet entirely satisfactory." This view is further substantiated by Reinman.[9] The means used to measure color in this investigation was developed from Munsell's concept and is presented as Appendix A-1. The color scale arrived at consists of the series of shades obtained by decolorizing increasing increments of Kettleman crude oil per unit of Filtrol X clay, plotted on rectangular coordinates as ml. of oil per gram of clay versus shade (color) of oil in such manner that the plot made a straight line. Thus plotted, successive, equal increments of oil per gram of clay represent successive divisions of an arbitrary scale of color.

7/ Ross, C. S., and Kerr, P. F., The Kaolin Minerals. In Shorter Contributions to General Geology, 1930: U. S. Geo. Survey Prof. Paper 165 (e), 1931, pp. 151-180.

8/ Kalichevsky, V. A., and Stagner, B. A., Chemical Refining of Petroleum: Am. Chem. Soc. Mono. 63, 1942, pp. 245-250.

9/ Reinman, Genevieve, et al, Spectrometric and Colorimetric Determination of the T.C.C.A. Standard Color Cards: Jour. of Research, National Bureau of Standards, March 1946, p. 209. R.P. 1700.

Dessicating Agents and Moisture Control

The data from this investigation have brought into prominence the wide range in amount of moisture that any given petroleum decolorizing clay can hold, depending on the humidity and temperature of the surrounding atmosphere. In view of such variation, the behaviors of desiccating agents and laboratory means of maintaining constant humidity are of great importance. Efficiency of drying agents is described in Appendix A-2. Anhydrous magnesium perchlorate, $Mg(ClO_4)_2$ (trade name dihydrite), was finally chosen as the desiccant for cooling samples of these clays. It has little effect upon the water content of clays that are dried 5 days at $110°$ C., but abstracts water from clays of appreciably higher water content.

Saturated water vapor behaves toward clay essentially as water. Berkelhamer,[10] in an exhaustive series of tests, also affirmed this point. It is common knowledge, too, that in atmospheres that are less than saturated with water vapor a state of equilibrium (apparently permanent) is reached eventually. Experiments with all clays involved in this investigation confirms this difference between the effects of saturated and unsaturated atmospheres on petroleum decolorizing clays. Therefore, means of maintaining constant humidities short of saturation were sought. The various solutions employed are given in Appendix A-3, but moist sodium chloride or a saturated solution of NaCl was selected as the most desirable. Such a solution yields 76 percent humidity at room temperature ($80°$F).

Decolorizing at Elevated Temperatures

In commercial practice petroleums such as lubricating oils are sometimes decolorized by clays at elevated temperatures. Therefore, decolorizing tests at elevated temperatures were run at $100°$ C. in a water bath and at temperatures above $100°$ C. in an oil bath. Details of the apparatus designed for this test are given in Appendix A-4. This apparatus was electrically heated, and the clay-oil mass was sealed from the atmosphere by dry steam. In the absence of steam, color was found to decrease with increase in temperature from room temperature to approximately $125°$ C. Above this range of temperature, in the absence of steam the oil darkened slightly. The presence of water in the wet steam caused the oil to darken. Moderately dry steam over a clay-oil mass that was hot enough to cause any condensed water to "flash back" into steam resulted in the oil tending to become light in color. The lowest temperature at which such satisfactory use of steam took place was approximately $125°$ C. ($257°$ F). Sealing the hot clay-oil mass away from air and cooling it before filtering was found to yield lighter colored oil than did hot filtering exposed to open air. In these hot contact tests; as in all other decolorizing tests made, decolorizing capacity decreased as liquid water in the clay-oil mixture increased. A noticeable effect of decolorizing oil by use of clay and steam at elevated temperatures was that the sparkle of the product was invariably increased by such treatment.

10/ Berkelhamer, Louis H., Rehydration Study of Clays: Jour. Am. Ceram. Soc., vol. 26, 1943, pp. 120-126.

Oil Testing

Black fluid Kettleman crude petroleum (No. 20) (the names of all materials used are listed in Appendix B-5, table 7) has served as an excellent material upon which to establish a method for measuring the capacities of clays as decolorizers of petroleum and its products. In making the tests, 4 ml. of water white benzol (i.e., 92 percent benzene) per gram of clay was added to the clay-oil mixture.

The red midcontinent lubricating oil (No. 21) used in the decolorizing experiments above 100° C. was cooled to room temperature, and its shade was determined both in undiluted condition and after being diluted with the standard amount of water-white benzol; the greenish-black Cities Service lubricating stock (No. 22) was decolorized at room temperature, and its shade was determined both undiluted and diluted with benzol. The decolorized shade undiluted closely approximated the diluted shade for both of these lubricating stocks, and all closely approximated the colors obtained with Kettleman. For all three oils used in these experiments, therefore, the benzol dilution at room temperature and the color scale established for Kettleman appear to be adequate.

Activation of Oil-Decolorizing Clays

The common method of activation by digesting the clay with a definite amount of dilute sulfuric acid for a specified period of time was used in this investigation. Although no two clays would be expected to require exactly the same treatment to develop their decolorizing capacity to a maximum, optimum conditions were established for all clays tested. The treatment finally arrived at consists in digesting (active boiling) for 1 hour 50 grams of dry clay plus 30 ml. of 95-percent, 1.84-gravity sulfuric acid, plus enough distilled water to make a total volume of 300 ml. in a 600-ml. beaker.

Dehydration of Oil-Decolorizing Clays

In use, decolorizing clays are commonly regenerated by being heated above the temperature at which they dehydrate. Therefore, a dehydration test was run on four clays, three commercial decolorizing clays, and one kaolin. As is commonly known (Nelson and Hendricks[11]/ and others), clay becomes dehydrated on being heated to 600° C. and begins to shrink and decrease in surface area at or near 700° C. The procedure followed in the experiments was to slowly approach, for several hours, a maximum temperature of 675° C. and hold that temperature for 2 hours. The decolorizing capacity of the high-magnesia Attapulgus clay (No. 1), which, according to Hendricks, is meershaum (the mineral sepiolite), was greatly increased by this dehydration treatment, whereas for the oil chemists' official clay (No. 3) and the Filtrol X (No. 8-D) commercially activated clay the increase was nominal, and the decolorizing capacity of a South Carolina secondary kaolin (No. 15) was virtually unaltered.

11/ Nelson, R. A., and Hendricks, Sterling B., Specific Surface of Some Clay Minerals, Soils, and Soil Colloids: Soil Science, vol. 56, 1943, pp. 285-296.

Chemical Nature of Clays Tested

The five types of clays used for experimentation are described as follows:

1. High-potash Ordovician clay from Minnesota. It has appreciable decolorizing capacity, both activated and unactivated.

2. High-magnesia Attapulgus clay (No. 1) is useful as a fuller's earth in unactivated condition.

3. Intermediate magnesia types from Sanders, Ariz. (Nos. 12 and 13), and Smith County, Miss. (No. 4), have a high decolorizing capacity in the activated state only.

4. High-soda type, Wyoming swelling bentonite, Volclay 300 (No. 14), is not used as a decolorizer of petroleum.

5. High-calcium, high-magnesium material Hectorite (No. 18), low in decolorizing capacity, both activated and unactivated, is not used as a decolorizer of petroleum.

Three additional types of clays, not tested in this undertaking, have been used as decolorizers: (1) Glauconites, sometimes used in activated condition, (2) very high-magnesium, low-aluminum fuller's earth (mentioned by Schroter,[12] and (3) bauxitic type material used in dehydrated form. It is highly rated because of decolorizing capacity and ability to withstand oft-repeated regeneration by heat. On account of its high alumina content, however, it has not commonly been classed with the other oil-decolorizing clays. Such a wide variety of materials of necessity involves diverse chemical composition. Recently developed crystal chemistry is apparently of great value in formulating modern concepts concerning these clays.

Concepts concerning the nature of their origin, mineral names, and chemistry are in a state of flux, and responsibility for them, therefore, will be left to the literature and to future developments. All of the commercial clays used in this investigation are thoroughly discussed in technical literature. A few leading references that contain excellent bibliographies are as follows: Ross and Hendricks[13] have recently published a comprehensive study of these clays from the crystal chemistry viewpoint; Bradley and Grim [14] have studied them by means of microscope and x-rays,

---

12/ Schroter, G. A., and Campbell, I., Geological Features of Some Deposits of Bleaching Clays: A.I.M.E. Tech. Paper 1139, Mining Technology, 1940, pp. 1-31.

13/ Ross, C. S., and Hendricks, S. B., Minerals of the Montmorillonite Group, Their Origin and Relation to Soils and Clays: U. S. Geol. Survey Prof. Paper 205 B, 1945, pp. 47-69.

14/ Bradley, W. F., Grim, R. E., and Clark, W. L., A Study of Behavior of Montmorillonite Upon Wetting: Zeitsch. Kristallographie, vol. 97, 1937, pp. 216-222.

as has Paul F. Kerr;[15]/ F. H. Norton[16]/ and Grim[17]/ have studied the thermal dehydration properties of these materials; and Noll[18]/ who has studied the formation of these clays, finds the presence of magnesium particularly advantageous. (See also Appendix A-5.)

Chemical analyses were made on 31 samples in the present investigation. Twelve of these are commercial decolorizing clays, one a commercial South Carolina secondary kaolin, two halloysites, one Volclay 300, a Wyoming swelling bentonite, and one is the high-lime, high-magnesia material Hectorite. The others are previously unproved materials, which were found to vary widely in decolorizing capacity. As shown in table 7, the analyses of each clay were made on unactivated clay (labeled A in table 7), acid extract (labeled B in table 7), and activated residue (labeled C in table 7). For comparative purposes, B and C of table 7 were calculated to percentage of unactivated clay. The residue C was also calculated to 100 percent. For representative analyses, see Appendix B-5. The results obtained from the activations and analyses show that: 1. Copious effervescence, on addition of acid to the clay, indicates the presence of carbonates. 2. Where present in commercial decolorizing clays, up to 3 percent lime (CaO) is removed in solution by the sulfuric acid. 3. In the presence of sufficient acid any large percentage of lime left in the residuum is present as calcium sulfate, $CaSO_4$. The indications are that on first being formed, this calcium sulfate may be anhydrous or present partly as hemihydrate. On standing, it undoubtedly goes over into the dihydrate gypsum. 4. Titania present is but little affected by the activation. Sulfates of magnesium, aluminum, sodium, and potassium are readily washed from the residuum. 5. Decolorizing by clays is apparently a matter of surface chemistry. If this be true, relations that may exist between chemical composition and decolorizing capacity might not be readily evident. Analyses of two high-class decolorizing clays show wide variation in their chemical compositions. Attapulgus (No. 1) fuller's earth showed the greatest decolorizing capacity of any of the fuller's earths tested, and Smith County, Miss., clay (No. 4-C) activated 1 hour showed the greatest decolorizing capacity of any of the activated clays tested. Their compositions are shown as Appendix B-5, table 7. 6. Examination of the composition of the filtrates suggests the possibility that removal of such materials as alumina and soda has not only increased surface area per gram, but also may have increased specific adsorptive power per square centimeter of surfaces. 7. The findings of Noll,[18]/ linked with the high-magnesium content of

15/ Kerr, P. F., and Cameron, Eugene L., Fuller's Earth of Bentonitic Origin from Teckachapi Pass, California: Am. Mineralogist, vol. 21, 1937, p. 230.

16/ Norton, F. H., Critical Study of the Differential Thermal Method for the Identification of Clay Minerals: Jour. Am. Ceram. Soc., vol. 22, 1939, pp. 54-63.

17/ Grim, R. E., and Rowland, R. A., Differential Thermal Analyses of Clay Minerals and Other Hydrous Minerals: Am. Mineralogist, vol. 127, Pt. 1, 1942, pp. 746-761; Pt. 2, 1942, pp. 801-818.

18/ Noll, W., Economic Geology Supplement to vol. XXXII, Nov. 5, 1937, pp. 607-761; Geophysical Laboratory Paper 937, Geo. W. Morey and Earl Ingerson, Reference 155. Also, Arbeiten uber die Synthesis und natürliche Bildung der Jonminerale: Hannoverische Hochschulgemeinschaft, Pt. 17, 1940, pp. 1-2.

Attapulgus (No. 1) fuller's earth, 9.63 percent MgO, and the intermediate magnesium contents of the activable Sanders, 5.98 percent MgO, and Smith County, 5.03 percent MgO, suggest that the magnesium content may in some manner be connected with large surface area per unit weight of clay, and may thus indirectly connect decolorizing capacity with chemical composition. This lead was not followed.

In identification work on decolorizing clays, chemical analysis of the unactivated clay in conjunction with decolorizing tests has frequently been illuminating; but as no direct relation was found between chemical composition and decolorizing capacity, chemical analysis is not used as a procedure of the method.

THE METHOD

In review, the above step-by-step established the following: 1. In all decolorizing tests in this investigation, whether made at room temperature or at elevated temperature, decolorizing capacity of any given sample was found to decrease as liquid water in the clay-oil mixture increased. Because this relation exists, the decolorizing capacities of absorptive clays can be compared on samples that are dried to substantially constant weight at 110° C. 2. The common method of activation (by digestion with dilute sulfuric acid) serves as activation means in such a method. 3. The amount of water condensed by a clay in constant humidity at room temperature serves to identify further its type. During the hundreds of determinations made in this investigation, the procedures have been repeated and reexamined, hence appear to be basically sound. A detailed description of the method follows.

Detailed Statement of the Method

Dry the clay test sample and grind it to 0.6 percent on 150 mesh. Then, for a period of 5 days, dry this ground clay at 110° C. In a layer not over half an inch thick place one 10-gram [19] portion of the dry clay in a humidity of 76 percent (enclosed space over moist sodium chloride provides a humidity of 76 percent at room temperature) for a period of 5 days; remove and weigh. The grams gained in weight is the percentage gain in weight caused by condensation of moisture in the clay. Place another 10-gram portion of the dry clay in a 125 ml. Erlenmeyer flask. To this add 1 ml. of black Kettleman crude petroleum (64 percent volatile at 65° C.) and 40 ml. of water-white benzol. Stopper the flask and shake this clay-oil-benzol mixture every 10 minutes for 2 hours. Filter a portion of the supernatant liquid into a 3 ml. test tube through a filter paper that is suitable for medium- to fine-grained precipitates, and stopper. Record the shade of filtrate obtained and return filtrate to the Erlenmeyer. Add an additional 1 ml. of Kettleman oil, shake, let stand, etc. Repeat the process with

---

19/ A convenient method of avoiding errors in weighing, which are caused by moisture absorption, is to dry beakers at 110° C. for each portion of clay in a test, weigh approximately 10 grams of the 150-mesh clays into each of the beakers. Make the final 5-day drying in them, and finally correct the weights of clay in each to exactly 10 grams by adding similarly dried clay.

successive additions of 1 ml. of Kettleman oil until the shade of the filtrate exceeds shade 9. Plot the shades against ml. of oil per gram of clay, average the values obtained at shades 3, 4, 5, 6, 7, 8, and 9, and use this as the value of shade 6. Compare the moisture-condensing and decolorizing values obtained with those of clays of known value. Representative values are presented following this method. It is advisable to run simultaneously parallel tests on proved commercial clays.

For activation purpose, pour 30 ml. of concentrated sulfuric acid, 95 percent H_2SO_4, gravity 1.84, into 200 ml. of distilled water in a 600-ml. beaker. Add slowly 50 grams of the 150-mesh clay that is dry at 110° C. and increase the total volume to approximately 300 ml. Heat to boiling point (stir to avoid bumping until the clay is boiling actively), and boil for 1 hour, keeping the volume substantially constant by addition of distilled water as is needed. If effervescence is copious on addition of clay, determine the percentage of lime present and add sufficient additional sulfuric acid to satisfy approximately the lime content. After the mixture has boiled 1 hour, decant the supernatant liquid while it is hot. Repeat the decantation five times, filling the beaker to the 300 ml. point for each decantation. Then pour the residue on a filter paper and wash 6 times with distilled water. Dry the residue as above (5 days at 110° C.), weigh it, and place it in a weighing bottle for use in chemical analysis, etc. If the first filtrate is cloudy, return it to the filter paper until it comes through clear. Subtract the dry weight from 50 grams and multiply the difference by 2. The result is the percentage weight loss caused by activation. Test this activated material for decolorizing capacity by the above method.

Auxiliary Aids to Identification

Several other tests are helpful as preliminary and auxiliary aids to identification:

1. As numerous authors have noted, many decolorizing clays have a waxen luster in the earth-moist condition.

2. The amount of water held by air-dry clay necessarily varies with the humidity of the atmosphere. For atmospheric humidities of 20 to 70 percent and a room temperature of approximately 80° F., the moisture contents of the clays used in this investigation, have kept within or near the following limits: Fuller's earths, 8 to 12 percent; raw activable clays, 17 to 25 percent; South Carolina kaolin (No. 15), 0.5 to 2.5 percent.

3. In proportion, as clay decolorizes Kettleman oil, the clay turns black. On the other hand, clays of negligible decolorizing capacity change but little in color upon being mixed with it. These facts are particularly evident on filtering the oil from the clay.

4. The amount of calcium carbonate in a sample can be approximated roughly by the amount of effervescence caused by putting an excess of acid on a small amount of the clay sample.

DECOLORIZING CAPACITY VALUES

Representative commercial decolorizing clays are Attapulgus (No. 1), fuller's earth, and Filtrol X (No. 8-D) commercially activated clay. The decolorizing test measures the clays' capacities as decolorizers, whereas moisture regained in 5 days in 76 percent humidity aids in identification of the type of the clay. The decolorizing capacities of these two clays, measured in ml. of Kettleman crude, 64 percent volatile at 65° C., required per gram of clay to produce shade 6 in the decolorized oil was found to be 0.5 ml./g. for Attapulgus fuller's earth and 0.75 ml./g for Filtrol X commercially activated clay. Their percentage moisture regains for 5 days in 76 percent humidity at 80° F. were 12.7 percent for Attapulgus and 15.4 percent for Filtrol X. Moisture regains of other clays simultaneously treated were official Oil Chemists' clay (No. 3) 13.5 percent, and Smith County clay unactivated (No. 4) 18.0 percent. Wyoming swelling bentonite, Volclay 300 (No. 14), not used as a decolorizer of oil, regained but 9.8 percent.

SUPPORTING DATA

Knowledge of the effects of common desiccants upon decolorizing clays was needed. Data on this subject are presented as Appendix B-1, table 3. The relation of moisture in clay to oil-decolorizing capacity at temperatures of 26.7° C. (80° F.) to 250° C. is shown as Appendix B-2, table 4. In this table decolorizing capacity is shown to increase with decrease in moisture content of the clay. The relation of moisture content to decolorizing capacity is shown in Appendix B-3, table 5. The effects upon decolorizing capacities of clays caused by heating to 675° C. are shown in Appendix B-4, table 6. Chemical analyses of unactivated clays, acid extracts, and activated residue are presented in Appendix B-5, table 7. Table 7 also serves as a list of the materials tested in this investigation.

SUGGESTED FURTHER WORK

During testing of phenomena for use in the method, other avenues for future research appeared. For all clays studied, the decolorizing capacity of activated clays was found to be high if moisture-condensing capacity of the unactivated clay was high. Furthermore, the moisture-condensing capacity of kaolin (No. 15) was low, and acid activation did not increase it appreciably. Conceivably, an activation treatment that would selectively dissolve part of the alumina, or water and alumina, from kaolin, possibly ammonium bisulfate, might serve to increase its water-absorptive capacity and also its decolorizing capacity. Similar means of activation might serve to remove part of the potash contents of potash-bearing absorptive clays and thus increase their absorptive capacities. Based upon the findings of Noll[18] concerning the magnesia content of such clays and of the magnesium contents of Attapulgus (No. 1), Sanders (Nos. 12 and 13), and Smith County (No. 4) clays, development of other means of activation appears to offer promise. In consideration of such investigations, the primary assumptions are that the starting materials should be cheap and that the resultant product should be capable of being formed into abrasion-resistant catalytic pellets. Two types of attack on magnesium activation are suggested.

1. Meerschaum (sepiolite), 2 MgO 3 SiO$_2$ 2H$_2$O, might be made under controlled conditions, washed free of soluble salts, and the resulting meerschaum dehydrated. A first approach to this problem might be to coprecipitate sodium silicate in dilute solution with a soluble magnesium salt, such as magnesium chloride plus ammonium chloride, followed by washing and dehydrating the residue. Such preliminary work might be followed by application of results to naturally occurring materials.

2. A magnesium silicate might be made by displacement of another alkaline earth from its silicate by magnesium, possibly by heating granulated blast-furnace slag or Portland cement with a strong acid magnesium compound such as magnesium ammonium chloride plus ammonium chloride. The calcining treatment might be followed by digestion with magnesium ammonium chloride water solution to dissolve soluble products; the residue might be washed and dehydrated. (See C. C. Winding, U. S. patent 2, 364,015 (1944)).

Once a mode of formation of meerschaum or other suitable silicon-magnesium or silicon-magnesium-aluminum complex is developed, its application to high-magnesia, high-alumina, or other clays might prove feasible. The calcination and hydrochloric acid digestion of Hectorite (No. 18 E to G), from which lime was removed and magnesia remained in the residue, suggests that high-calcium, high-magnesium clays or dolomite used in accordance with the Chesny patents[20] might serve as a source of magnesium; and in conjunction with chlorine, as from discard calcium-chloride of the ammonium-soda process or other source, magnesium chloride might be obtained in accordance with the Pike[21] patent. In this connection, Elkington British patent[22] 530,048 treats of reactive magnesium oxide produced by steam expansion of magnesia.

SUMMARY

Presented above are the detailed procedures of a method for identification and evaluation of natural clays for use as decolorizers in refining petroleum and its products.

The results of this investigation have shown that any given clay increases in decolorizing capacity as its absorbed water content decreases, and vice versa. As a result of following this phenomenon through several cycles of wet to dry to wet clay, the conclusion was drawn that no decolorizing-value figure has a definite meaning unless the absorbed moisture content is indicated.

20/ Chesny, Heinz H., French patent 827,065 (1938) and U. S. patent 2,089,339, August 10, 1937.

21/ Pike, R. D., Production of Magnesium Chloride from Calcium Chloride and Dolomite: U. S. patent 2,357,130 August 29, 1944, assigned to Harbison Walker Refractories Co.

22/ Elkington, Frank, Reactive Magnesium Oxide: British patent 530,048, December 4, 1940.

The decolorizing capacities of various clays were measured by modification of the commonly known percolation and contact methods at room temperature and at elevated temperatures on air-dry clay, on clay dried at various temperatures, and on dehydrated clay in their activated and unactivated states. Moisture contents of the clays were measured under all these conditions.

In atmospheric humidities of 20 to 70 percent at room temperature of approximately 80° F., the moisture contents of the clays used in this undertaking have kept within or near the following limits: fuller's earth, 8 to 12 percent; raw activable clays, 17 to 25 percent; South Carolina kaolin, 0.5 to 2.5 percent.

The above development led to the conclusion that the decolorizing capacities of absorptive clays can be compared on samples that are dry to substantially constant weight at 110° C., and that the amount of water condensed by a clay in constant humidity at room temperature aids in its identification as an oil decolorizer.

The common method of activation by digestion with dilute sulfuric acid was the means of activation used in this work. Chemical analyses of the unactivated clays, acid extracts, and activated residues were made.

A detailed statement of the method arrived at was presented.

Suggestions were made for further research on the activation of such clays.

APPENDIXES

A-1. Color

The following quotation from Kalichevsky[8] serves to describe Munsell's concept: "It is then possible to describe any color in terms of its three attributes, which are defined by the Americal Optical Society as follows: Brilliance (value) is that attribute of any color which may be classed as equivalent to some member of a series of grays ranging between black and white. Hue is that attribute of certain colors which differs characteristically from the gray of the same brilliance (value) and which permits them to be classed as reddish, yellowish, greenish, or bluish. Saturation (chroma) (intensity of hue) is the attribute of all colors possessing a hue which determines the degree of difference from gray of the same brilliance." Colors in the range from black to white are referred to as shades. A further subdivision of this is to refer to colors of brilliance from medium gray to white as tints.

Difference in light-colored portions of oil obtained by decolorizing black Kettleman crude petroleum were found to be readily distinguishable by the eye over a wide range from water-white to medium amber. In darker portions, the color was found to be increasingly masked and more difficult to read. Slight differences in color were found to be readable by comparing the

colors of the oils in test tubes of approximately equal diameter surrounded on three sides by a white background, such as a towel, in light from the north sky. Thus viewed, the diameter of the test tube became a negligible factor. No special equipment was needed. In exploring the indicativeness of such oil-color comparisons an arbitrary scale was set up for recording results. For this purpose, the colors produced from Kettleman crude petroleum over the range from "water white" through "nearly opaque" were divided into 40 shades and fractions of a shade. These divisions were so spaced that "shade" plotted against ml. of Kettleman per gram of Filtrol X clay (No. 8-D), dried at 105° C. for 5 days, resulted in a straight line plot. The values used in this plot were: 0.1/g. produced shade 0.5; 0.2, 1.5; 0.3, 2.5; 0.4, 3.5; 0.5, 4.5; 0.6, 5.5; 0.7, 6.5; 0.8, 7.5; 0.9, 8.5; 1.0, 9.5; 1.1, 10.5; 1.5, 14.5. That is, a constant ratio was arbitrarily set up between ml. of Kettleman oil per gram of Filtrol X clay and the quantity termed shade. This ratio closely approximated the average of determined Kettleman-Filtrol X values plotted according to the divisions given below for colors from "water white" to "nearly opaque." This color scale, plotted as a straight line for Filtrol X, also resulted in approximately straight-line plots for other clays. Conversely, where a light shade and a dark shade were determined and plotted for a clay and a straight line was drawn through the two points it closely approximated the positions of intermediate determined shades. The colors of the divisions were found to be approximately as follows: "Water white" divides into tints 0 to 4; "greenish yellow," 4 to 8; "light amber," 8 to 20; "medium amber," 20 to 28; "dark amber" shades, 28 to 32; "dark reddish amber," 32 to 36; "nearly opaque,"36 to 40. By use of this arbitrary scale, it was possible to designate decolorizing capacities thus: 0.3, 5, in which 0.3 indicates the fraction of a ml. of oil-treated per gram of clay, and 5 represents the shade of the treated oil. The amount of oil decolorized by a given clay to shade 6 was used as a single figure to express decolorizing capacity. A highly accurate value for shade 6 was obtained by averaging the values obtained for shades 3 to 9, inclusive.

Quoting again from Kalichevsky and Stagner:[8] "It is usually desirable to evaluate the efficiency of an adsorbent in terms of a standard adsorbent by determing the relative amounts of the two required to refine a certain oil." In the present undertaking, Filtrol X was the standard clay and Kettleman crude the standard oil. This means of color comparison is perhaps better suited for comparing the wide range of oil-color shades of this undertaking than would be one of the devices commonly used for commercial grading of petroleum by color, as each of them tends to be suited to some specific purpose other than the comparing of true color values over a wide range. Kalichevsky and Ramsey[23] show a chart in which percentage transmissions of light through a violet filter and a red filter for a series of oil (color) fractions obtained by varying the oil-clay ratio are plotted in terms of Tagliabue Robinson scale of color. The machine that they recommended for this purpose is sold under the name Hellige-Diller photoelectric colorimeter. Plotting percentage transmission of light through the above

23/ Kalichevsky, V. A., and Ramsey, J. W.: Jour., Ind. Eng. Chem., vol. 25, 1933, p. 691.

series of Kettleman-Filtrol X colors in conjunction with the violet and red filters of the above machine would, of course, serve to calibrate it in terms of the above arbitrary straight-line color scale used in this investigation.

A-2. Efficiency of Drying Agents

TABLE 1. - The efficiency of drying agents[1]

Drying agent	Mg. of residual water per liter of air
A trap at - 194° C.	1.6×10^{-23}
Phosphorus pentoxide, P_2O_5	Less than 0.00002
Anhydrous magnesium perchlorate, $Mg(ClO_4)_2$	Less than 0.0005
Magnesium perchlorate hydrate, $Mg(ClO_4)_2.3H_2O$	Less than 0.002
Anhydrous alumina, Al_2O_3	0.003
Sulfuric acid (100%), H_2SO_4	0.003
Calcium chloride, porous granular, $CaCl_2$	0.14 to 0.25
Calcium chloride, fused	0.36
Sulfuric acid (95%) (concentrated, sp. gr. 1.84) H_2SO_4 + Aq.	0.3

[1] Table 1 is from International Critical Tables, vol. III, 1928, p. 385.

A reflux condenser using liquid air as the cooling medium is the most efficient desiccant (water trap) known. The common drying agents, however, are more readily available and convenient to handle. Phosphorus pentoxide is undoubtedly the best of the chemical reagents for water. It is tacky and hard to handle, however, and suffers the great disadvantage of becoming rapidly glazed with a coating of metaphosphoric acid, HPO_3, so that only a fraction of the material is ever used. Magnesium perchlorate (porous granular; trade name Dihydrite) is as good as phosphorous pentoxide, is porous and easy to handle, and, in addition, will absorb up to 60 percent of its weight of water without reduction in efficiency. It is prepared by dehydration in a high-vacuum at temperatures up to 250° C. For large-scale drying the material can be regenerated to advantage. Aluminum oxide for drying purposes is prepared by ignition of the hydrate to 500° C. (trade name Hydralo). It supposedly will absorb 15 to 20 percent of its weight of water. It can be reactivated by drying at 175° C., and reactivation may be repeated indefinitely. Sulfuric acid (100%) is a very efficient dehydrating agent, but because it is a corrosive liquid, its use in desiccators has the disadvantage of causing vessels kept over it to become coated with sulfuric acid. Ninety-five percent sulfuric acid drops rapidly in dehydrating efficiency with decrease in acid content. Its specific gravity is greater than that of water; hence, a film of dilute acid supposedly forms on the upper acid surface, requiring frequent stirring of the acid if maximum dehydrating efficiency is to be maintained. Calcium chloride is a cheap, fairly efficient drying agent. It has the disadvantage of becoming gummy; its pores become sealed, and its efficiency is thereby greatly reduced.

A-3. Laboratory Methods for Maintaining Constant Humidity

The following including table 2, is from International Critical Tables, vol. I, 1926, p. 67: "In considering laboratory methods for maintaining constant humidity, it is known that a saturated aqueous solution in contact with an excess of a definite solid phase at a given temperature will maintain a constant humidity within a closed space around it."

TABLE 2. - Constant humidities over aqueous solutions

Substance	Temperature, °C.	Humidity, percent
Sodium bichromate, $Na_2Cr_2O_7 \cdot H_2O$	20	52
Magnesium chloride, $MgCl_2 \cdot 6H_2O$	20	34
	30	32
Sodium chloride	0	78
	20	76
	40	75
	60	74
	100	73.5

The saturated solution is commonly heavier than water. Therefore, formation of a film of dilute solution on its upper surface was avoided by having a portion of the solid phase project up through the liquid surface. In this work all substances of table 2 were tested extensively at room temperature, approximately 80° F., and sodium chloride, which yields 76 percent saturation at room temperature (80° F.), was selected as the agent for maintaining constant humidity. Although this condition represents an appreciable amount of water vapor in the atmosphere, yet under no conditions did water condense on the container and frip into the sample, as is frequently the case with saturated atmospheres even in carefully temperature-regulated rooms.

The relationship between "percentage humidity" and relative humidity is given as follows by Perry:[25] "Percentage humidity is the quotient of the number of pounds of water vapor carried by 1 pound dry air at any temperature, divided by the number of pounds of vapor which 1 pound of dry air would carry were it completely saturated at the same temperature. Percentage relative humidity is the quotient of the partial pressure of water vapor at any temperature divided by the partial pressure if saturated at that temperature."

A-4. Oil-Bath Apparatus for Hot Contact

Apparatus and Procedure

The clay-oil mixtures were heated above 100° C. in a 500 ml. spherical, ring-neck, pyrex glass flask, immersed to the neck in a high point tempering oil. The oil was contained in a stainless-steel cylindrical can. An electrical heating unit was coiled around the lower two-thirds of the can. This position of the coil insured heating of the oil in the lower part of the can without overheating it at its upper surface. The entire assemblage was

[25] Perry, John H. (editor in chief): Chemical Engineers' Handbook, 1934, p. 691.

packed in powdered keiselguhr (diatomite) in an iron can of such dimensions that the keiselguhr insulation was not less than 3 inches thick on the sides and bottom. The top of the assembly was covered by three 3/8-inch layers of asbestos faced with metal. All parts of the lid structure were merely fitted together and were removable, so that the apparatus could be disassembled and reassembled with a minimum of labor. For quick handling of the flask, the lid of the inner can was built semi-permanently around its neck. Electrically driven stirrers operated through the lid, one in the oil bath and the other in the clay-oil sample charge. A thermometer with its bulb in the sample charge completed the apparatus proper. The electric heating unit was No. J.S. 9605, steel-sheath, oil-immersion, safe working temperature 750° F., E. H. Wiegand Co. Chromolox catalogue No. 42. It was a flexible element, approximately 1/4 x 96 inches in size, intended for 230 volts A.C. and 3,000-watt capacity; however, 220 volts A.C. was used. The electrical input was controlled by a stack voltage controller (Variac). A voltage of 35, as shown on the Variac, served to maintain a temperature of approximately 150° C. in the flask. Seventy volts was the maximum used even for the most rapid heating of the unit. Wet steam was provided by an electrically heated laboratory steam boiler. Suitable adjustment of the electrical input provided a steady flow of steam. Dry steam was provided by passing wet steam through a copper coil heated by a Bunsen burner. From the coil to the sample flask the conduit was insulated with asbestos cord. This equipment for decolorizing at elevated temperatures proved very satisfactory in use. With it, accurate control of temperature was simple. This equipment was designed solely for development of the test method. It should be suited to commercial testing, however, up to the temperature limit of the oil bath. The oil bath consisted of E. F. Houghton & Co.'s tempering oil No. 80, flash temperature 630° F., fire temperature 710° F.

A-5. Other Bureau of Mines Work on These Clays

The Tuscaloosa station of the Bureau of Mines maintains samples of many leading clays, among which are most of the leading oil decolorizing clays. This collection of clays might suitably be termed a library of clay samples. The clays used in the present work were drawn from this library of clays. Other studies, pertinent to the present work, made from this library of clay samples follow: 1. William W. Goode, Jr.,[26] working on a cooperative agreement between the Federal Bureau of Mines and the College of Engineering of the University of Alabama, made a study of control tests in the contact process of decolorizing edible oils. The results of this work were submitted as a thesis in partial fulfillment of the requirements for the degree of Master of Science. S. J. Broderick and E. S. Hertzog served as the Bureau's representatives in this work. Nine commercial fuller's earths, including official fuller's earth for 1941, were tested against cottonseed oil, and results were compared in terms of Lovebond colored glasses. 2. E. R. Todd,[27]

26/ Goode, William W., A Study of Control Tests in the Contact Process of Decolorizing Edible Oils: University of Alabama Library, Masters Thesis, Class T 378, Book G 613S, 1941.

27/ Todd, Edwin Richard, The Properties of Bleaching Clays: University of Alabama Library, Masters Thesis, Class T 378, Book T 566p. 1942

working on a similar cooperative agreement for a masters thesis, with E. S. Hertzog as Bureau representative, made a study of the properties of bleaching clays. Ten clays were used, ranging from commercial bleaching clays to Wyoming swelling bentonites and ceramic clays. These clays were tested both in unactivated and activated condition and, in addition, a study of the effects of base exchange was made. In that work the clays were tested against cottonseed oil in accordance with the method used by Goode,[26] and in addition were tested against petroleum: (1) Nabob red oil at elevated temperature by the contact method, and (2) Kettleman crude at room temperature by the percolation method, using the Nutting form of this test. Resulting oil colors were compared by light transmission on a photoelectric colorimeter and by the use of Lovebond color glasses. As commercial bleaching clays were included in the tests, comparisons of the various clays were based on these. An outstanding feature of that work is the fine lot of chemical analyses that it contains.

Berkelhamer[10] ran an extensive set of moisture-absorption tests of clays in humid atmospheres. His tests cover a large proportion of the materials contained in the Bureau's library of clays and include most of its decolorizing clays.

X-ray analyses and petrographic microscopic examinations of the clays showed a slight change in the refractory indices, and movement in the X-ray lines, in the case of several of the activated clays. This might indicate some change in the lattice structure of the basal clay mineral. Further work in this direction might be well worth while.

Appendix B-1

TABLE 3. - Effects of drying agents on clays

Changes in moisture content of clays during 84 days of controlled humidity at 78° to 80° F.

Humidity control substances	Days from start	Attapulgus (1) fuller's earth, unactivated				Official Am. Oil Chem. (3) fuller's earth				Filtrol X (8-D) comm. activated clay			
		Moisture	% shade[1]	Moisture	% shade	Moisture	% shade	Moisture	% shade	Moisture	% shade	Moisture	% shade
Start.............	0	10.62		0.0		11.69		0.0		19.05		0.0	
Magnesium[2] Perchlorate Mg (ClO4)2	5	6.26		4.75		7.61		4.26		15.87		3.43	
	32	2.79		2.32		2.18		2.02		7.72		1.30	
	61	0.66		0.99		1.05		1.12		5.49		0.59	
	84	0.66	(3.5)	0.66	(3.25)	1.05	(5.5)	1.12	(5.35)	5.00	(0.50)	0.59	(0.35)
Con. sulfuric acid, 95% H2SO4, sp. gr. 1.84....	5	6.62		2.44		6.10		1.57		11.43		1.79	
	32	3.49		2.33		3.62		0.89		6.43		1.07	
	61	1.92		0.76		2.93		0.56		5.49		1.55	
	84	1.48	(3.5)	0.76	(3.25)	2.71	(5.75)	0.56	(5.35)	5.13	(0.5)	1.07	(0.35)
Granulated calcium chloride, CaCl2..........	5	6.29		2.54		7.12		1.45		12.04		2.15	
	32	4.95		2.99		4.64		1.45		9.08		1.79	
	61	4.27		2.99		4.18		1.45		8.21		2.03	
	84	4.62	(4.5)	2.99	(4.0)	5.08	(7.0)	1.45	(7.0)	8.71	(1.5)	2.15	(0.5)
Moist magnesium chloride (34% humidity at 20° C.)......	5									21.80		10.53	
	32									22.54		13.16	
	61									22.05		13.64	
	84									22.54	(5.75)	14.47	(5.0)

1/ Shade produced by 0.1 ml. Kettleman crude oil per gram of clay.
2/ The samples in the confined atmosphere over any one agent were together in one vessel.

Appendix B-2

TABLE 4. - Relation of moisture in clay to oil-decolorizing capacity at 26.7° C. (80°F.) to 250°C.[1]

Clay No.	Preparation treatment, °C.	Activated 1 hour			Unactivated		
		Percentage moisture loss	Decolorizing capacity Ml./g.	Decolorizing capacity Shade	Percentage moisture loss	Decolorizing capacity Ml./g.	Decolorizing capacity Shade
1[2]	Moist at 26.7		0.2	18		0.2	23
	Dry at 105	11.60	.2	8	10.54	.2	7
	160	1.75	.75	22	0.32	.2	7
	250	1.52	1.0	28	3.33	.3	5
3	26.7		.2	12		.2	26
	105	15.93	.2	1	12.11	.2	7
	250	4.73	.75	6	1.89	.75	3/36
4	26.7		.2	3/24		.2	2/32
	105	21.70	.2	1	20.26	.2	13
	160	1.31	1.0	9	1.69	.3	16
	250	1.05	1.0	8	0.58	.3	13
8	26.7		.5	18			
			.75	3/26			
	105	16.74	.5	7			
			.75	12			
	160	.77	.75	10			
	250	.33	.75	9			
14	26.7		.1	9		.1	26
	105	12.86	.1	3	8.23	.1	6
	160	.96			.14	.3	3/32
	250	.48				.3	3/25
15	26.7		.1	12		.1	13
	105	.4	.1	8	.4	.1	11
	250	1.17	.1	7	.26	.1	8

1/ The 26.7° C. (80°F) samples were in an atmosphere of 76 percent humidity (over NaCl) for 5 days or more before being tested. The percentage moisture losses are from next preceding temperature to the temperature indicated. The decolorizing tests were made on clays dry at the temperature indicated.

2/ See Table 7 for names of clays.

3/ Approximate.

2366

Appendix B-3

TABLE 5. - Illustrates the relation of moisture content to decolorizing capacity of clays

	Days in 76% humidity	Activated 1 hour			Unactivated		
		Clay Moisture percent	Oil Ml. oil /g. clay	Shade of oil	Clay Moisture percent	Oil Ml. oil /g. clay	Shade of oil
Attapulgus (1) fuller's earth.....A[1]	18	14.58	0.2	18	13.7	0.2	23
dry at 105° C.....................B[2]		0.0	.2	8	0.0	.2	7
Oil Chem. Official fuller's earth (3) somewhat activable.....A	66	21.75	.2	12	18.27	.2	26
dry at 105° C....................B		.0	.2	1	-	-	-
Filtrol X comm. activated (8-D)...A	42				26.29	.2	21
dry at 105°C.....................B					.0	.2	1.25
Smith County, Miss. (4) activable.A	18	23.72	.2	24	23.3	.2	32
dry at 105° C....................B		.0	.2	1	.0	.2	13
Sanders, Arizona (12) activable...A	63				24.76	.2	32
dry at 105° C....................B					.0	.2	12
Volclay (14) Wyoming swelling bentonite....................A	18	16.58	.1	9	(8 da.) 13.94	.1	23
dry at 105° C....................B		.0	.1	3	.0	.1	13
R. T. Vanderbilt (15) S. C. secondary kaolin................A	66	1.81	.1	12	.9	.1	13
dry at 105° C....................B		.0	.1	8	.0	.1	11

1/ A= Moist in 76% humidity at 80° F.
2/ B= Dry per arbitrary standard of dryness: 5 days at 110° C.

Appendix B-4

TABLE 6. - Effects upon decolorizing capacities of clays caused by heating to 675° C.

Part A. - Data of decolorizing

Ratio Ml. Kettleman crude petroleum per gram of clay	Clay Dry at 105° C.				Clay dehydrated at 675° C.			
	Secondary S.C. kaolin No. 15	Attapulgus fuller's earth No.1	Oil Chem. fuller's earth No.3	Comm. activated Filtrol X No. 8-D	Kaolin No. 15	Attapulgus fuller's earth No.1	Oil Chem. fuller's earth No.3	Comm. activated Filtrol X, No.8-D
(0.1)	4.0	2.0	1.0	0.5	4.5	2.25	2.5	0.5
(.2)	6.75	3.0	6.75	2.0	7.0	3.5	5.0	2.5
(.3)	8.0	4.0	7.0	2.5	8.0	3.75	6.75	2.75
(.4)	12.0	6.0	18.0	3.75	12.0	4.0	8.0	3.75
(.5)	20.0	6.25	18.0	4.5	20.0	4.5	11.0	4.25
(.7)		8.0		6.75		6.5		6.75
(.9)		11.0		7.25		7.25		7.50
(1.1)		17.0		9.00		8.0		10.0
(1.5)				13.0		12.0		14.0

Part B. - Effect upon decolorizing capacity caused by heating clays to 675° C.
Percentage regain in weight in 76% humidity at room temperatures 78° to 80° F.

	Percent loss in weight on being heated from 105° C. to 675° C.	Clay previously dry at 105° C.	Clay previously heated to 675° C.			Ratios of oil decolorizing capacities at shade 6 heated at 675° C. Dry at 105° C.
		5 days	3 days	5 days	9 days	
S. C. kaolin (15)........	12.75	-	1.03	0.69	0.69	1.0
Attapulgus (1)..........	8.40	12.7	6.9	8.44	8.44	1.33
Off. Oil Chem. (3)......	4.35	13.5	4.49	5.33	5.64	1.20
Filtrol X, commercially activated (8-D)........	5.6	15.4	7.07	8.54	9.07	.97

Appendix B-5

TABLE 7. - <u>Chemical analyses of clays used, including unactivated clays, material dissolved on activation, and activated residues</u>[1]

		SiO_2	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Oxides	Ign.
1-A	Attapulgus[2]...........	59.53	3.47	0.49	11.58	2.31	9.63	0.25	0.35	87.61	11.66
1-B	filtrate................	.26	2.04	.03	5.95	2.11	4.98	.16	.09	15.62	
1-C	residue................	59.27	1.43	.46	5.63	.20	4.65	.09	.26	71.99	
1-D	100% residue..........	73.19	1.78	.56	7.22	0.15	5.30	.03	.27	88.50	11.50
2-A	Florindin.............	57.42	3.06	.49	11.15	3.96	9.14	.29	.47	85.98	14.02
2-B	filtrate..............	.32	1.85	.03	6.10	3.17	5.18	.27	.05	16.97	
2-C	residue..............	57.10	1.21	.46	5.05	.79	3.96	.03	.41	69.01	
2-D	100% residue......:...	72.36	1.97	.58	7.69	.15	5.62	.40	.34	89.11	10.89
3-A	Oil Chemists Clay.....	59.17	6.53	.69	14.57	3.45	3.39	.37	.40	88.57	11.43
3-B	filtrate..............	.34	2.91	.03	3.30	2.29	.94	.20	.31	10.43	
3-C	residue...............	58.82	3.62	.67	11.27	1.15	2.45	.17	.10	78.25	
3-D	100% residue[3]........	65.98	5.60	.69	13.48	1.59	2.84	.46	.24	90.88	7.17
4-A	Smith County, Miss....	58.39	4.49	.24	19.76	2.19	5.03	.02	.11	90.23	9.77
4-B	filtrate; 1 hour......	.54	2.89	.01	7.97	2.11	2.55	.02	.10	16.19	
4-C	residue...............	57.85	1.60	.23	11.79	.08	2.48	tr	.01	74.04	
4-D	100% residue..........	70.85	2.41	.27	14.34	.05	3.48	tr	.13	91.53	8.47
5-A	Itawamba 15 ft........	58.81	6.63	.86	20.50	1.50	2.76	.45	.22	91.73	8.27
5-B	filtrate, 1 hour......	.46	2.58	.01	5.02	1.47	1.31	.06	.07	10.98	
5-C	residue...............	58.34	4.05	.85	15.48	.03	1.45	.39	.16	80.75	
5-D	100% residue..........	66.40	4.69	.94	17.30	.08	1.68	.34	.39	91.82	8.18
6-A	Itawamba top 1 ft.....	58.45	6.41	0.85	21.81	0.96	2.85	0.55	0.08	91.96	8.04
6-B	filtrate..............	.36	3.37	.02	7.17	.85	1.35	.02	.03	13.17	
6-C	residue...............	58.08	3.05	.83	14.64	.11	1.50	.52	.06	78.79	
6-D	100% residue..........	69.13	4.07	.96	15.97	.13	1.15	.32	.08	91.81	8.19

See footnotes at end of table.

- 23 -

TABLE 7. - Chemical analyses of clays used, including unactivated clays, material dissolved on activation, and activated residues[1/] (cont'd.)

		SiO_2	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Oxides	Ign.
7-D	Amory, Miss. 100% residue...............	67.19	2.90	.91	18.42	.20	1.85	.34	.17	91.98	8.02
8-D	Filtrol X comm. act....	62.35	1.17	.32	15.34	.78	4.12	.04	.11	84.23	15.77
9-D	Special Filtrol.........	63.82	2.60	.54	14.23	1.05	2.61	.45	.45	85.75	14.25
10-D	Super Filtrol..........	66.69	3.32	.64	14.69	1.49	2.97	.51	.43	90.74	9.26
11-A	Gen. Reduction Co......	69.85	3.87	.60	12.50	1.23	1.90	.55	.39	90.89	9.11
12-A	Sanders, Arizona 1....	60.57	1.65	.04	17.94	3.63	5.98	tr	.15	89.96	10.04
13-A	Sanders, Arizona 2....	62.08	1.77	.10	17.30	3.27	5.65	.04	.28	90.49	9.51
14-A	Volclay 300............	62.85	4.12	.22	20.93	.66	2.65	.53	2.14	94.10	5.90
14-B	filtrate, 1 hour.......	.62	.71	tr	2.67	.61	.65	.08	2.10	7.44	
14-C	residue................	62.23	3.41	.22	18.27	.05	2.00	.44	.04	86.66	
14-D	100% residue..........	67.24	3.80	.21	18.89	.07	2.24	.36	.26	93.07	6.93
15-A	R.T.V., S.C. kaolin....	45.53	.33	1.31	37.43	.10	.03	.05	.21	84.99	15.01
15-B	filtrate, 1 hour.......	.36	.06	tr	1.79	.10	.03	tr	.02	2.36	
15-C	residue................	45.18	.27	1.31	35.64	tr	tr	.05	.19	82.64	
15-D	100% residue..........	45.63	.29	1.52	38.51	.02	tr	.27	tr	86.24	13.76
16-A	Indiana W. Halloysite.	34.68	.07	.05	43.74	.18	.12	.03	.12	78.99	21.01
16-B	filtrate...............	.92	.05	.02	18.54	.11	.05	.01	.04	19.74	
16-C	residue................	33.77	.02	.04	25.20	.06	.07	.02	.07	59.25	
16-D	100% residue..........	46.14	.03	tr	35.51	.03	.07	.03	.11	81.92	18.08
17-A	Indiana B. halloysite.	33.26	26.32	0.83	20.93	0.58	1.47	0.93	0.28	84.60	15.40
17-B	filtrate...............	.25	16.47	.05	7.17	.11	.55	.03	.01	24.64	
17-C	residue................	33.01	9.86	.78	13.76	.47	.91	.90	.27	59.96	
17-D	100% residue..........	53.24	6.84	1.09	23.01	.33	1.36	.83	.15	86.85	13.15

See footnotes at end of table.

TABLE 7. - <u>Chemical analyses of clays used, including unactivated clays, material dissolved on activation, and activated residues</u>[1] (Cont'd.)

		SiO_2	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Oxides	Ign.
18-A	Hectorite[2]...........	31.80	.20	.08	.15	28.18	13.12	.12	1.11	74.80	25.20
18-B	filtrate.............	.32	.08	.01	.11	3.12	13.05	.05	1.03	17.77	
18-C	residue.............	31.48	.12	.08	.04	25.05	.07	.07	.12	57.03	
18-D	100% residue[3].......	31.82	.20	.02	.23	25.11	.16	.10	.14	57.78	4.05
18-E	filtrate Hectorite HCL activated.......	.16	.01	.01	tr	19.37	.28	.02	.87	20.62	
18-F	residue	31.64	.19	.07	.15	8.90	12.85	.10	.28	54.18	
18-G	100% residue.........	45.71	tr	.04	.21	15.15	20.20	.15	.43	81.99	18.11
19-A	S.E.M. 436 Ord.[2]....	48.58	6.42	.82	20.39	5.32	2.46	6.53	.53	91.05	5.81
19-B	filtrate, 1 hour.....	.46	2.29	tr	3.86	3.95	.60	.76	.10	12.02	
19-C	residue.............	48.12	4.13	.82	16.53	1.37	1.86	5.77	.43	79.03	4.81
19-D	100% residue[3].......	56.02	3.84	1.05	19.94	1.82	2.10	7.64	.08	92.49	5.63

CO_2: 1-A = 0.73; 18-A = 20.81; 19-A = 3.14
SO_3: 3-D = 1.95; 18-D = 38.17; 19-D = 1.88

20   Kettleman crude petroleum.- This is black fluid crude petroleum. It has been largely used by Dr. P. G. Nutting in decolorizing tests with clay. Its description is: Well No. 584,226, a neutral black California oil of $40.3°$ gravity. It is 64 percent volatile at 65° C.

21   Humble Oil & Refining Co., Houston, Tex.- This is a sample of Mid-continent red, partially refined viscous petroleum ready for treatment with clay. Its description is: 200 vis. at 100°F. red oil approximately 62.3 Y.I. Sample identification No. SX-2570 MD 1594.

22   Cities Service Oil Co., Refining Division, Ponca City, Okla., Nov. 13, 1945.- This is a sample of black (greenish-black in thin layers), partly refined, viscous petroleum ready for treatment with clay. Its description is: 150-160 vis. acid oil bright stock.

1/ A= unactivated clay; B= material extracted during activation and washing, calculated to percentage of unactivated clay; C- activated residue calculated to percentage unactivated clay; D- activated residue calculated to 100 percent.

2/ CO_2 determined (see end of table).

3/ SO_3 determined (see end of table).

ACKNOWLEDGMENTS

This report is one of many on various aspects of the Federal Bureau of Mines program toward the more effective utilization of our mineral resources.

Investigations of our mineral resources are conducted by the Mining Branch, L. B. Moon, chief, and by the Metallurgical Branch, O. C. Ralston, chief. The scope of this report falls within the province of the Metallurgical Branch, whose activities embrace the separation of difficultly beneficiated ores, production of metals from domestic deposits, exploration of ore reserves, recovery of secondary metals, and improvements of present industrial metallurgical practice. Both metallic and nonmetallic materials are included.

This investigation was carried on at the Southern Experiment Station, Tuscaloosa, Ala., under the general supervision of H. G. Iverson, chief, Tuscaloosa Division, Metallurgical Branch, and under the direct supervision of T. A. Klinefelter, in charge of the Clay Section. The work was also done in cooperation with the University of Alabama.

The investigation is a part of a general project on bleaching clays used by the oil industry, and the groundwork was provided by previous investigators, Dr. S. J. Broderick, W. W. Goode, Jr., E. S. Hertzog, E. R. Todd, and T. A. Klinefelter. X-ray analyses were made by E. E. Creitz and petrographic examinations by Dr. T. N. McVay. Chemical analyses were conducted by E. S. Hertzog and Dr. Robert Hodges. Mechanical and electrical equipment was constructed under the supervision of G. T. Adams, general shop foreman.

Thanks are due to the Humble Oil & Refining Co. and to the Cities Service Co. for cooperation in providing some of the oils.