

THE EFFECT OF LEACHING TIME, AT THE OPTIMUM  
ACID CONCENTRATION, ON THE REJUVENATION OF  
A SPENT BLEACHING CLAY

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ACID CONCENTRATION, ON THE REJUVENATION OF  
A SPENT BLEACHING CLAY

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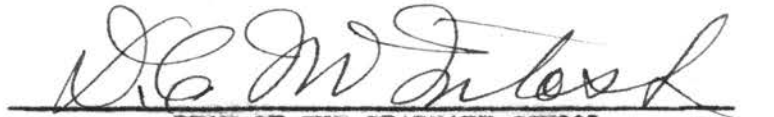
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## PREFACE

One of the phases of chemical research which has been greatly neglected is that of determining a method of correlating the bleaching power of a clay with factors which could be easily determined. It is known that leaching a contact clay restores, at least partially, its decolorizing power. It is the purpose of this paper to find the optimum conditions, of Sulfuric Acid concentration and leaching time, for restoring this decolorizing power. It should be understood that the best conditions for rejuvenation of the clay used in these experiments would not necessarily be applicable to any different system, but it is hoped the data obtained might be helpful in a rough estimation of the rejuvenation of other clays. The clay and oil is fully enough described so that the data might also be helpful in any later attempt to correlate the decolorizing power of clays with physical or chemical properties. No attempt has been made to evaluate the data obtained with economical plant operation, although there is no doubt but what conditions close to the optimum must be obtained.

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## INTRODUCTION

Some patents have been filed for the rejuvenation of bleaching clays and a small amount of material was found in periodicals and books but the best conditions for restoring the decolorizing power of clays have had but little work done on them.

The process of bleaching with the aid of an earth dates back to the time of the Chinese and Egyptians, with rapid progress being made during the middle ages (8). In the United States bleaching with clay was introduced in the industry of soap making. In 1891 John Olsen discovered a deposit of this active clay in Arkansas and in 1893 a larger deposit was found at Quincy, Florida. This marked the beginning of the commercial use of clay. At the present time the greatest use of bleaching clay is in the refining of products of petroleum distillation or cracking, as well as lubricating oils, the adsorbent earth functioning as a medium to remove or convert deleterious compounds in the oil. The chief sources of bleaching clay in the United States are in Arizona, southern California, Colorado, Florida, Georgia, Illinois and Texas. The large deposits seem almost inexhaustible. (12)

Kohlendorf<sup>1</sup> was the first to find that the leaching process is able to improve the bleaching effects of clays. His results were not good because he failed to consider all of the numerous variables, however, by leaching with 10% sulfuric acid at 100° Centigrade he was able to show that rejuvenation of a spent clay could be accomplished.

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1 D. R. P. 305, 452

Bleaching clays are used to remove suspended, colloidal, and dissolved impurities, such as carbon, coke, resinous, and asphaltic substances, especially those rich in oxygen, hydrocarbons and poor in hydrogen and coloring matter. (8) The clay also tends to increase the chemical stability and neutralize the acid treated oil without previously neutralizing with alkali and washing with water. Bleaching clay could be used to replace the acid treatment entirely, but the amount of clay necessary would make this impractical. Specifically, the clay removes acid, alkali, soap, gum, and, to some extent, sulfur. It also finds value as a catalyst to side reactions and cracking and helps in the prevention of "sludge" deposits in insulating oils.

This decolorizing power is not possessed by all clays and is dependent on the interior structure (Nutting). (23) The three chief sources of bleaching clays are recognized as: volcanic ash; certain igneous rocks that are low in silica, high in bases, and partially decomposed; and the marine secondary mineral, glauconite.

$\text{SiO}_2$  is important in the origin of these active clays and Fussteig (8) suggests the following reactions:



This feldspar is decomposed by  $\text{H}_2\text{SO}_3$  and atmospheric weathering, which results in the transformation of feldspar to Kaolin silicate according to the following equation:



During the course of many thousands of years, Kaolin Silicate went through a leaching process to form a loose and porous material. By weathering, feldspar was split up to form an insoluble substance in water, which was impregnated with ultra microscopic channels. Water



and Carbonic Acid caused great adsorption surfaces so as to make it valuable as a decolorizer. The most ideal leaching process would be one which followed that occurring naturally, but with greater speed.

Many varieties of silicates exist which have ultra microscopic channels, those having the finest channels being called zeolites, which are generally hydrated Aluminum Silicates of calcium or sodium. Zeolites, with other argillaceous earths, are classified as Fuller's Earth.

#### THEORY

According to Gibbs Law (9) when dissolved matter changes the original surface tension of a solvent, the concentration of the dissolved substance at the surface will be changed, having in consequence, a remaining solution of quite another concentration. The concentration in the solution will be changed so that the surface tension is reduced to a minimum. When the surface tension of a solvent is reduced by a dissolved substance, the latter tends to collect on the surface layer of the solution.

By adding to the solution a certain volume of solid material, the surface tension at the interface of these two phases will be lowered as the concentration of the surface tension increases. Simultaneously, the concentration of the remaining solution decreases. The surface of the solid must be great if the change of concentration is to be noticeable. The solid adsorbs the dissolved compound.

The adsorption theory of Freundlich states that  $\frac{X}{M} = KC^P$

where: X -- Units of impurities  
M -- Quantity of adsorbent used  
C--- Equilibrium concentration of the impurities in the oil.  
K and P -- Constants, depending on the nature of the adsorbent.

By converting the above equation to the logarithmic form,

$\text{Log } \frac{X}{M} = \text{Log } K + P \text{ Log } C$ , the equation becomes a straight line

when  $\frac{X}{M}$  is plotted against  $C$ .

Langmuir<sup>2</sup> represents the interior of the adsorbent with saturated valence and the surface with unsaturated valence. These surface valences are responsible for adsorption. Haber says adsorption is a loose chemical combination between adsorbent and adsorptive. Euchen,<sup>3</sup> Lorenz, and Lande<sup>4</sup> consider the adsorption power due to a fall of potential on the surface of the adsorbent. Gurwitch (15) believes the adsorbent attracts both the molecules of the solvent and the dissolved substances. The proportion is determined by: (1) The proportion of both molecules in the solution; and (2) by the power with which both molecules are attracted by the adsorbent. Fusteig (9) believes the adsorptive power is practically wholly dependent upon the sort of substances dissolved.

Two processes occur during decolorization: (1) an adsorption of the adsorptive, and (2) separation of the adsorptive as flocculents. One (9) clay may be a very good bleaching agent for one oil, but poor for another. This difference in bleaching power is caused by the shape of the microscopic channels in the clay.

Removal of substances such as Iron Oxide from the clay, may destroy the decolorizing property entirely (9). Some of the catalytic

2. Langmuir, Journal Am. Chem. Soc., 1918, p. 1361

3. Euchen, Zeitschr. Elektrochem. ang Phys. Chem., 1922, p. 6

4. Lorenz and Lande, Zeitschr Anorg. Allg. Chem. 1922, 125 p. 47

properties may be due to  $\text{AlCl}_3$ . Temperature does not have a great effect upon adsorption, but at a given temperature, in time a maximum decolorization is reached and then effectivity drops.

#### SURVEY OF LITERATURE

Hilpin and Schneeberger (10) reduced the nitrogen content of oil from .71% to .08% by treating an acid oil with a finely divided clay and adding caustic soda to release the free base and to neutralize the acid.

By using heated Bauxite in quantities of from 80 to 350 pounds per barrel of Kerosene the Burma Oil Company was able to reduce the sulfur content from 0.134% to 0.0202%. The clay had been ground to grains of 10-80 mesh and had been previously heated to  $600^\circ$  Centigrade. Although the temperature at which this was carried out was not given, ordinarily, contacts are carried out just below the Flash Point of the oil. When lower temperatures were used, the sulfur content was lowered to only 0.11%. Most sulfur in oils is present as  $\text{H}_2\text{S}$ , S,  $\text{RSH}$ ,  $\text{R-S-S-R}$ ,  $\text{RSR}$  and  $\text{C}_4\text{H}_4\text{S}$ . All except elementary sulfur and the mercaptans are removed by this Bauxite method.

According to Mattson (19), nearly all inert substances charge themselves negatively in water. An explanation could be accounted for by assuming the electrical forces within the oriented, interfacial layers of molecules to be such as to attract and fix the OH ions of the water while the H ions, or cations which may have displaced them, remain free, and diffuse into the surrounding water, which then assumes a corresponding positive charge. Or it may be simply assumed that the bond attaching the OH ion is more powerful or more readily attached than that attaching the H atom. It is part of a potential double bond.

Thus clay particles in water tend to surround themselves with an atmosphere of charged ions; some from their own material if any are free but supplemented by H, OH, and other ions from the water. Since the H is small and mobile while the OH tends to remain with the Silica, there is a marked tendency for H to diffuse away from the silicate particle and be replaced by other less mobile bases if these are available. In general, activation consists simply in the removal of the ions loosely held at the surface, so that in filtration other chosen ions or charged aggregates may be adsorbed and thus removed from the solution or suspension.

An active bleaching clay when placed in a hydrocarbon containing no oxygen atoms will adsorb colored ions of the unsaturated type first, but when these are not present, a good clay will break out parts of even saturated chains or rings. (23) If the clay is not completely dry, H and OH ions remain on its surface and its activity is greatly reduced, so that it adsorbs only the blackest hydrocarbon groups and passes the yellow and red fractions. If an alcohol is added to even a good petroleum, bleaching clay has almost no power to filter it. The more highly siliceous type of clay has a greater capacity for OH adsorption and combination. Also, there appears to be a selective advantage at high temperatures, which appear to give off OH more rapidly than hydrocarbons from the active surface. When contacting is done at or over 175° Centigrade complete dehydration of the clay is not essential and it is even possible to inject the clay in the form of a mud without lowering the efficiency.

According to Fussteig (12) the two factors of greatest importance in the leaching process are: (1) temperature and (2) concentration.

He believes a temperature of 100° Centigrade to 110° Centigrade gives the best results and the concentration varies widely, the maximum being concentrated when the ultra microscopic channels are very resistant to the action of the acid (12). After washing out the acid, the residue contains 75 to 80% water, which should be dried to about 30% water. Overheating should be carefully guarded against.

After leaching a clay with acid, the remaining acid probably indicates equilibrium between the acid and clay. All carbonates of the clay are destroyed after cooking the mixture. It is then diluted with water to dissolve as much of the water soluble salts as possible. Some clays even crack pure saturated paraffinic hydrocarbons, while others do not. There are certain kinds of bleaching clays that are able to oxidize the oil during the bleaching process in such a manner that the oil begins to burn. The bleaching power of some clays is increased by ignition, but that of many clays is destroyed entirely. One clay being inactive on hot crude when raw, may be highly active after acid leaching, although on cotton seed oils this action may be reversed.

Contacting by placing clay in a still has the advantage of higher efficiency but causes polymerization at the temperatures used, which is carried on catalytically by the higher unsaturated hydrocarbons. Too low a temperature decreases the efficiency because all the air from the channels is not excluded. The best temperature condition for contacting is that at which no air remains in the ultra microscopic channels and this condition must be determined experimentally for each clay. When the acid treat and clay contact are carried out simultaneously, by introducing acid and clay together, unknown hydrocarbons are formed which act catalytically and cause settling of the oil on standing. For

better efficiency, however, some acid should be present during the contact.

Baylis (3) recommends a leaching temperature of about 100° Centigrade and a leaching time of about five hours, the latter depending on the kind of clay being rejuvenated.

Belden and Kelley (5) give the following procedure for activating a spent clay; after the clay has been washed free of excess oil with a suitable solvent it should be treated with a solution of acid in water for a sufficient time to allow the acid to fully react with the clay, washing the treated clay to remove the water soluble impurities, and heating the washed clay to drive off the water.

Pfaff and Siewecke (25) rejuvenated bleaching clay by using 30% Sulfuric Acid at a temperature of the boiling point of the acid which was 105° Centigrade. They also recommend Sulfuric Acid as the most economical acid for this purpose.

Some methods of rejuvenation do not use the acid leach but depend on a good solvent to remove the oil from the spent clay. Lemmon (18) uses such a method and recommends solvents such as the following:

1. Naphtha 25%, alcohol 10% and Benzol 65%
2. Naphtha 50%, alcohol 5% and Benzol 45%
3. Naphtha 75%, alcohol 5% and Benzol 20%

The results obtained by these are inferior to the leaching process but might have an advantage economically.

Huber (16) believes an acid concentration of 7 to 35% with leaching time of from 1 to 3 hours gives the best results. The temperature used was 90° Centigrade and a liquid-solid ratio of 2 to 1 apparently gave the best results. Enough liquid should be used to give

the mixture adequate fluidity for thorough agitation.

Baylis (2) prefers a 12 to 20% sulfuric acid solution and treats the clay from 2 to 10 hours at a temperature of 80° to 95° Centigrade. In washing the leached clay, an ordinary tap water greatly reduces its decolorizing power because of the cations in the water which are readily adsorbed. Repeated leachings do not materially destroy the effectiveness of the clay.

Kobayashi and Yamamoto (17) found an acid concentration of 15% used at a temperature of 105 to 110° Centigrade and a liquid-clay ratio of 2 to 1 heated from 3 to 5 hours gave good rejuvenation. A Japanese acid clay was used in their experiments.

Burghardt (6) recommends a leaching time of from 2 to 3 hours at 105° Centigrade. He also believes the amount of acid used depends on its concentration. Separation of the oil from the clay can be made very satisfactorily by filtering through paper.

In general only the results of adsorption of the colors from a single oil by different amounts of adsorbent can be grouped together (24). The conditions are not those of a simple solution of a solute in a simple solvent and comparisons of color alone are inadequate. In studying the bleaching of oils, even with the same clay, different factors of the oil must be taken into account. Such things as type, color, acidity, temperature, kind of color and source of oil on a particular oil must, in plant practice, be studied separately.

It is the purpose of this work to determine the effect of the leaching time on the rejuvenation of a spent bleaching clay at the optimum condition of acid concentration. This was accomplished by first finding the best acid concentration and then determining the

effects of time on this leaching action. By rejuvenation, as used here, is meant the ability to remove color rather than all the effects the clay might have on the oil.



## EXPERIMENTAL

In brief the procedure used in these experiments was as follows:

1. Contact natural clay and oil.
2. Wash excess oil from clay with Stoddard Solvent.
3. Leaching the clay with acid.
4. Washing the clay.
5. Drying the clay.
6. Contact the rejuvenated clay.
7. Determine the Tag Robinson color of the contacted oil.

Throughout the experiments the same oil and clay were used. The oil, furnished through the courtesy of the Continental Oil Company, was a mixture from the Oklahoma City, Lucein and Crescent fields. The Pale Oil had been dewaxed by the Barisol Process and gave the following tests as received from the refinery.

Gravity-----23.4  
 Flash Point-----465° Fahrenheit  
 Fire Point-----535° Fahrenheit  
 Viscosity at 100-690 to 730° Fahrenheit  
 Cold Test----- -6° Fahrenheit

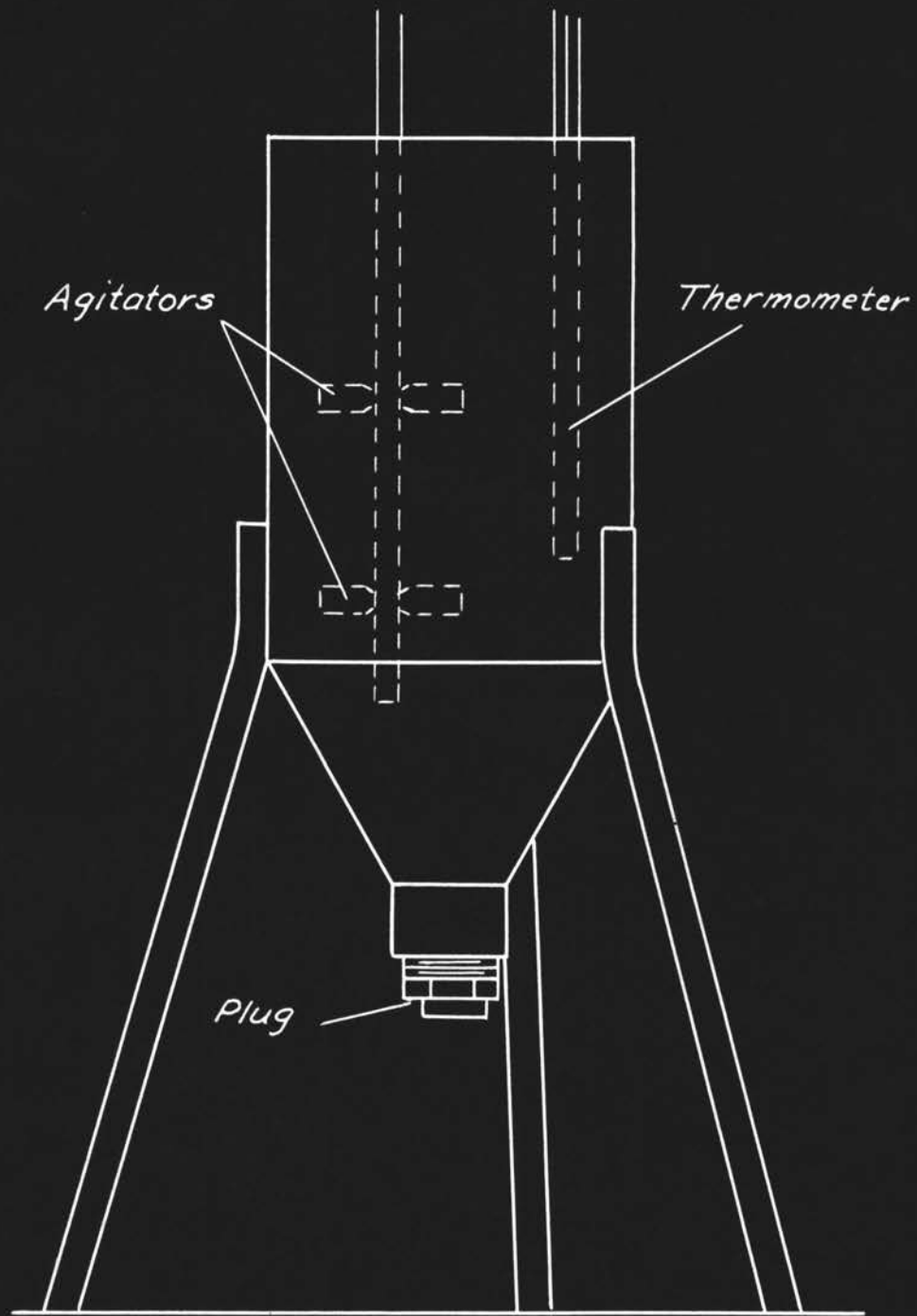
The clay used was a product of the Floridin Company and is known as their grade XXV. It also is commonly known as Fuller's Earth and is of grain size so that 90% of it passes through a 100 mesh screen. The analysis of the clay was as follows:

SiO <sub>2</sub>	62.83%
Al <sub>2</sub> O <sub>3</sub>	10.35%
Fe <sub>2</sub> O <sub>3</sub>	2.45%
CaO	2.43%

MgO	3.12%
K <sub>2</sub> O	0.74%
Na <sub>2</sub> O	0.20%
H <sub>2</sub> O (combined water)	7.72%
Moisture (Mechanically held)	6.41%

In order to obtain an oil which could be used as a standard for this work, and which did not contain too great an amount of coloring matter to make clay treatment impractical the dewaxed oil was first acid treated with Sulfuric Acid. The acid treating unit, as shown in Figure I, permitted batch treatments of 2000 milliliters. The treatment consisted of two parts. First, 2000 milliliters of the oil was treated with 10 milliliters of 94% Sulfuric Acid at a temperature of 46° Centigrade. The oil-acid mixture was agitated at 1750 R.P.M. for 15 minutes and then allowed to settle 30 minutes before the sludge was removed through the plug at the bottom of the unit. In the second stage, 15 milliliters of 94% Sulfuric Acid was agitated with the remaining 1750 milliliters of oil for 20 minutes, at the same rate and temperature. After settling 30 minutes, the sludge was removed as before and the oil was allowed to settle over night at 25° to 35° Centigrade. This process was repeated until enough standard oil was obtained to carry out the experiments. All these batches were mixed and kept in the cold to prevent any further settling of sludge. The standard oil showed a Tag Robinson color number of 1.8.

The Tag Robinson Colorimeter is widely used in the petroleum industry for obtaining colors of oil. In operating this machine, reflected light passing through a layer of oil is matched in color against the same light through a standard disc. Each machine is equipped with three color



*Figure 1*  
*Acidizing Unit*

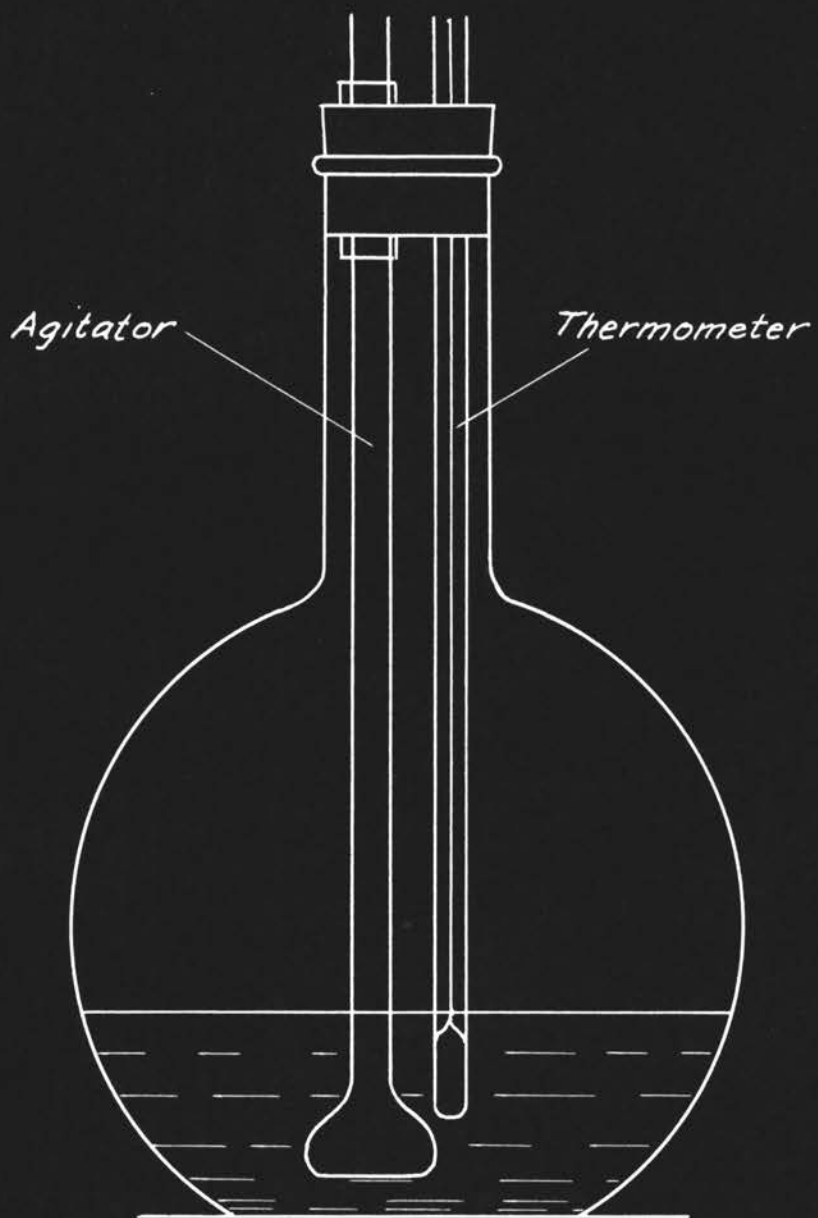
discs so that a wide range of color can be determined. In using disc number 2, the number 8 is added to the scale reading while in using disc 3, sixteen is added. By such a system the color range is divided into 24 whole numbers, the largest being the lightest color and the smaller numbers the darker colors. The accuracy with which the machine was read was probably  $\pm 0.1$ .

The clay was dried at  $105^{\circ}$  Centigrade to constant weight so that a uniform moisture content was present in each batch. By preliminary experiments it was found that a good bleach could be obtained in contacting the oil and clay for 25 minutes at  $200^{\circ}$  to  $205^{\circ}$  Centigrade. Agitation during contact was carried out at 525 R.P.M., this speed giving thorough enough mixing so that the clay did not settle to the bottom. It was further found that under the above conditions 11 grams of the natural clay contacted with 100 milliliters of oil gave a Tag Robinson color number of 8.5. This ratio of clay and oil was chosen since the color obtained was apparently that of many commercial oils. Care should be taken in contacting, that the vessel be large enough to allow for foaming. Ordinarily the ratio of the volume of the vessel to the volume of oil should be 2.5 to 1<sup>5</sup>. If the clay has been thoroughly dried before introducing into the oil there is practically no foaming for the Fuller's Earth used. Figure II shows the contacting unit.

After contacting, the clay was separated from the oil by filtration through Sargents Pure White 38 Centimeter Filters. One hour after introducing the clay-oil mixture on the filter, the oil was usually

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5. Much of the information on acid treating and contacting was obtained from reports by Research Chemist, Atkinson to the Continental Oil Company and will not be used as specific references.



*Figure 2*  
*Contact Unit*

fairly well drained and the color was determined. Since color is harmed by age, this is important that the color be read at equal time intervals after each contact. After allowing the oil to drain well, the excess oil was washed out by five 50 milliliter portions of Stoddard Solvent, and the clay was allowed to dry in the atmosphere.

In rejuvenating the clay, care was taken to remove all the spent clay from the filter into a 50 milliliter beaker. To this clay the concentrations of acid were added until a liquid-clay ratio of 20:11 was obtained. This mixture was then placed in a water bath and heated at 100° Centigrade for 2 hours and 15 minutes. At the beginning of the leach, the mixture was agitated rapidly until the foaming period was completed. Part of the oil then came to the surface. During this leaching period the mixture was agitated every 25 minutes until it appeared homogeneous. After leaching, the action of the acid was stopped with water. After settling an hour, the system had divided into three layers: the clay at the bottom; the supernatant liquid in the middle and a small layer of oil which had been removed from the clay channels, at the top. By decantation, this oil was removed, and the clay and supernatant liquid were separated by filtration through filter paper. The clay was washed with distilled water until the filtrate was free of acid. The use of hard water here, destroys the bleaching power of the clay. This washing usually required from 4 to 5 hours.

The clay was then placed in the oven and dried at 115° Centigrade for 3 hours. The time and temperature here again are important because it is very easy to overheat, thereby breaking down the interior structure of the clay. Huber (16) says a temperature of 150° Centigrade is not too high but the author found that for the clay used in these experiments,

a temperature above 125<sup>o</sup> Centigrade decreased the decolorizing power of the clay.

The rejuvenated clay was then again contacted at the same conditions as described for the natural clay, and the color determined one hour after removing from the contacting unit. This method gives a direct comparison of the bleaching power of the rejuvenated clay on a basis of the natural clay. Since all of the oil is not removed in the leaching process, the bleaching power of the clay, on a basis of the rejuvenated clay, would be less.

The above procedure was followed for concentrations of Sulfuric Acid of 1, 3, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, and 30% (Table I) and it was found that by plotting the concentration of acid in percent against the Tag Robinson color number a smooth curve was obtained with a maximum decolorization at an acid concentration of from 7 to 9% Sulfuric Acid with an indicated maximum at 8% acid (Figure 3). The same procedure was followed with Hydrochloric Acid but due to experimental difficulties the amount of time which would be required prohibited an extensive study on the effect of concentration of this acid. From the data obtained, however, it seems likely that this acid would rejuvenate the clay better than did the Sulfuric Acid.

The optimum concentration was found in order to determine the optimum time for the leaching action. These experiments were carried on similarly to those on determining the optimum concentration but the leaching time was varied instead of the acid concentration. The effect of leaching time was determined for the three optimum acid concentrations of 7, 8, and 9% Sulfuric Acid (Table II). It was found that smooth curves were obtained again and there was a maximum leaching time as well

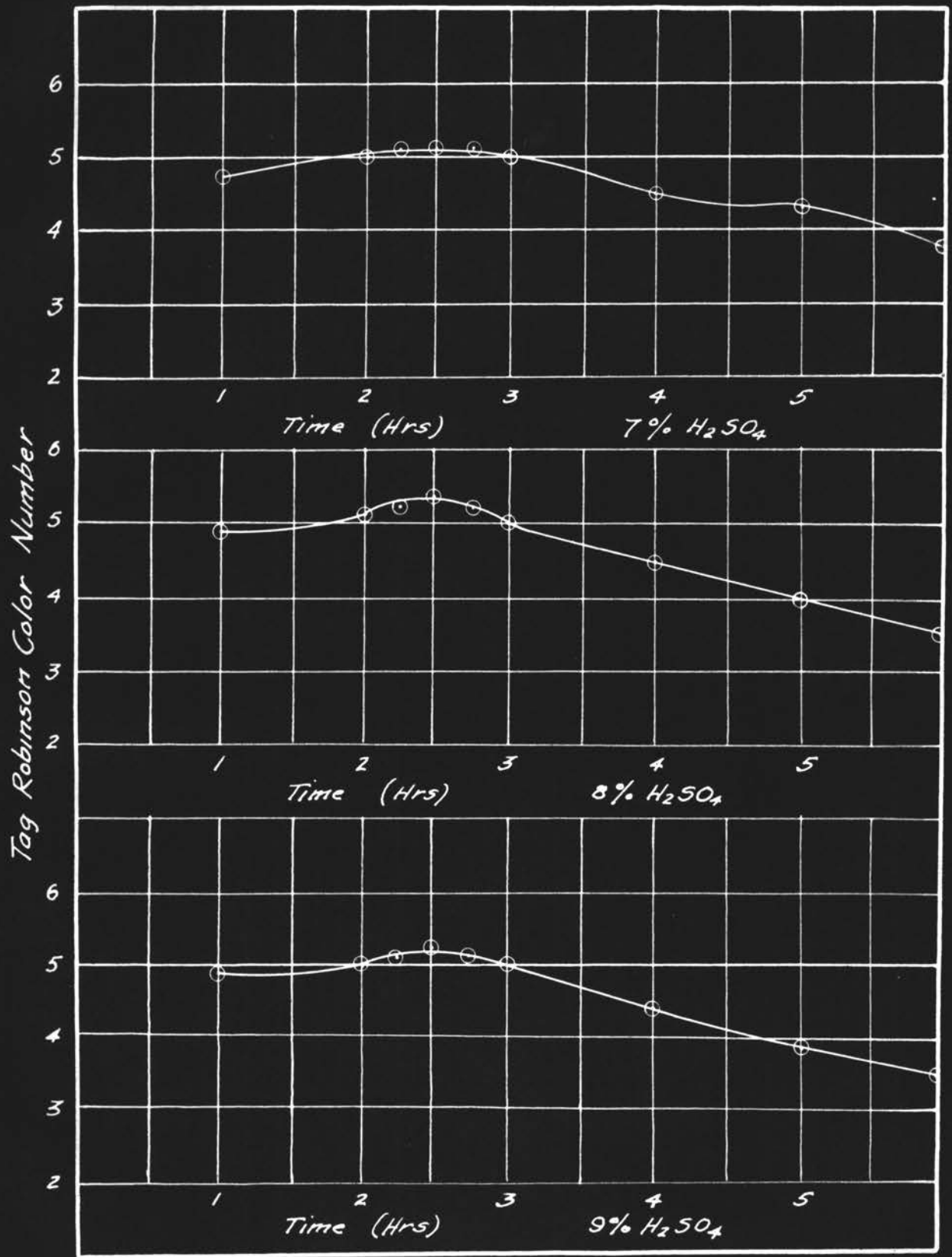


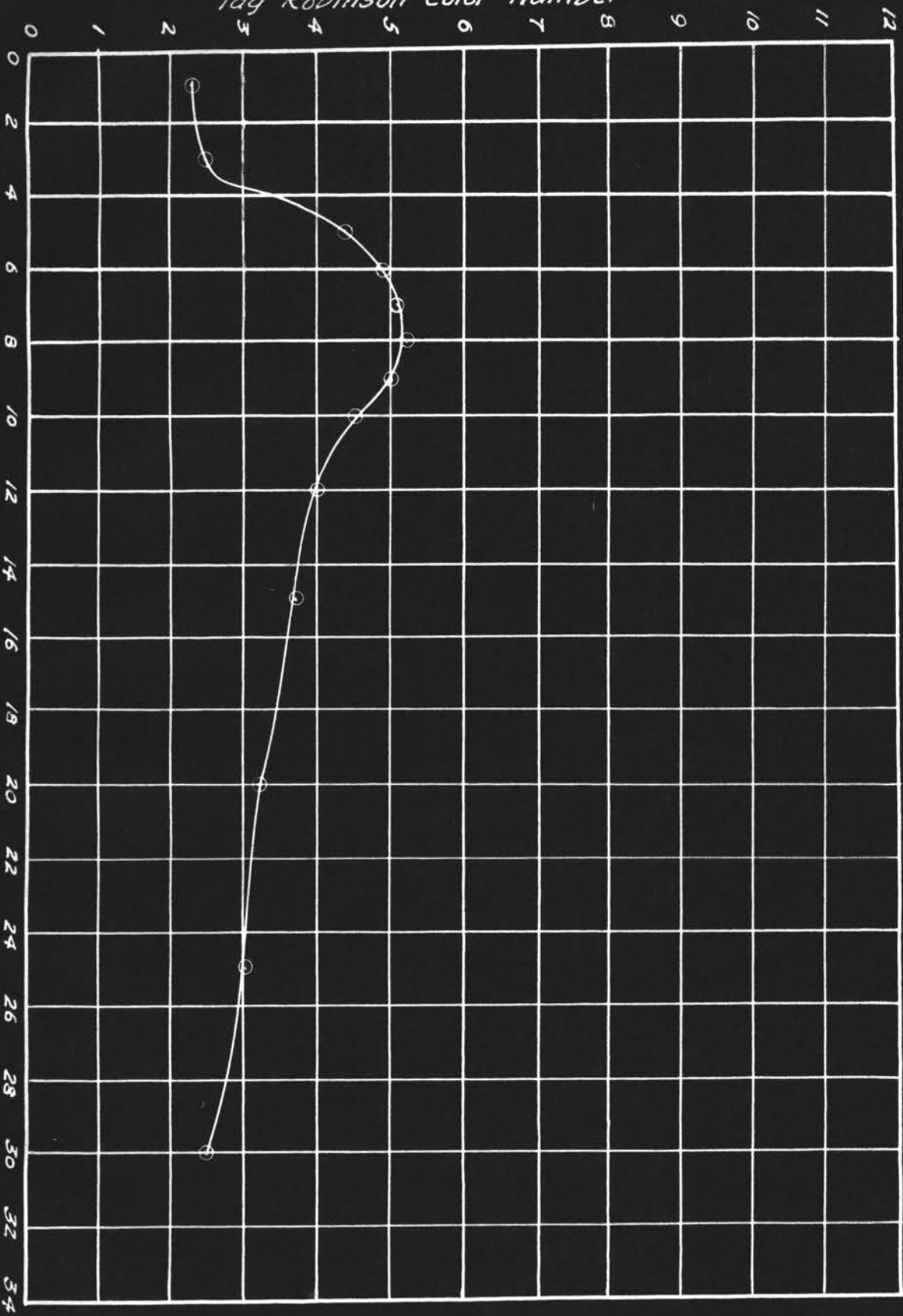
Figure 3  
 The effect of leaching time on the rejuvenation of  
 a spent bleaching clay



as a maximum leaching acid concentration (Figure 4)

L. L. Davis (7) in treating lubricating oils with clay found the reciprocal of the Tag Robinson color was a satisfactory measure of the impurities. Because of the different types of impurities in oils, it is very difficult to determine the amount of impurities removed. Removal of one color might improve the Tag Robinson color much more than removal of another, so the color improvement as found in these experiments are merely relative as based on Tag Robinson Colorimeter readings.

Tag Robinson Color Number



The effect of acid concentration on the reactivation of a spent bleaching clau

TABLE I

The effect of acid concentration on clay rejuvenation

Sample No.	Grams Natural Clay to Contact 100 ml. of Oil	Color of Oil after Contact	Leaching; acid Concentration in percent	Final Color after Rejuvenation
1	11	8.5	1	2.2
2	11	8.5	1	2.3
3	11	8.5	3	2.5
4	11	8.5	3	2.5
5	11	8.5	5	4.4
6	11	8.5	5	4.3
7	11	8.5	6	4.9
8	11	8.5	6	4.8
9	11	8.5	7	5.0
10	11	8.5	7	5.1
11	11	8.5	8	5.2
12	11	8.5	8	5.2
13	11	8.5	9	5.0
14	11	8.5	9	5.0
15	11	8.5	10	4.5
16	11	8.5	10	4.6
17	11	8.5	12	4.0
18	11	8.5	12	4.0
19	11	8.5	15	3.7
20	11	8.5	15	3.7
21	11	8.5	20	3.1
22	11	8.5	20	3.2
23	11	8.5	25	3.0
24	11	8.5	25	3.0
25	11	8.5	30	2.5
26	11	8.5	30	2.6
27	11	8.5	3	2.5
28	11	8.5	5	4.4
29	11	8.5	6	4.9
30	11	8.5	7	5.1
31	11	8.5	8	5.2
32	11	8.5	9	5.0
33	11	8.5	10	4.5
34	11	8.5	12	4.0

TABLE II

The effect of leaching time on the rejuvenation of a clay

Sample No.	Grams Natural Clay to contact 100 ml. of Oil	Color of Oil after Contact	Leaching Time (Hr.)	Final Color after Rejuvenation
1	11	8.5	1	4.9
2	11	8.5	1	4.8
3	11	8.5	2	5.1
4	11	8.5	2	5.0
5	11	8.5	2.25	5.2
6	11	8.5	2.25	5.2
7	11	8.5	2.50	5.3
8	11	8.5	2.50	5.3
9	11	8.5	2.75	5.2
10	11	8.5	2.75	5.1
11	11	8.5	3	5.0
12	11	8.5	3	5.0
13	11	8.5	4	4.5
14	11	8.5	4	4.6
15	11	8.5	5	4.0
16	11	8.5	5	4.1
17	11	8.5	6	3.6
18	11	8.5	6	3.5
7% Acid				
19	11	8.5	1	4.8
20	11	8.5	1	4.8
21	11	8.5	2	5.0
22	11	8.5	2	5.0
23	11	8.5	2.25	5.1
24	11	8.5	2.25	5.1
25	11	8.5	2.50	5.1
26	11	8.5	2.50	5.1
27	11	8.5	2.75	5.1
28	11	8.5	2.75	5.1
29	11	8.5	3	5.0
30	11	8.5	3	5.0
31	11	8.5	4	4.5
32	11	8.5	4	4.6
33	11	8.5	5	4.3
34	11	8.5	5	4.3
35	11	8.5	6	3.8
36	11	8.5	6	3.8

TABLE II (Cont'd.)

The effect of leaching time on the rejuvenation of a clay

Sample No. 9% Acid	Grams Natural Clay to contact 100 ml. of Oil	Color of Oil after Contact	Leaching Time (Hr.)	Final Color after Rejuvenation
37	11	8.5	1	4.9
38	11	8.5	1	4.8
39	11	8.5	2	5.0
40	11	8.5	2	5.0
41	11	8.5	2.25	5.1
42	11	8.5	2.25	5.1
43	11	8.5	2.50	5.2
44	11	8.5	2.50	5.2
45	11	8.5	2.75	5.1
46	11	8.5	2.75	5.1
47	11	8.5	3	5.0
48	11	8.5	3	5.0
49	11	8.5	4	4.4
50	11	8.5	4	4.4
51	11	8.5	5	3.9
52	11	8.5	5	3.9
53	11	8.5	6	3.5
54	11	8.5	6	3.5

## SUMMARY AND CONCLUSIONS

- I. Throughout these experiments the following variables were kept constant:
- A. Leaching Temperature-----100° Centigrade
  - B. Contacting Temperature-----200-205° Centigrade
  - C. Drying temperature after the acid leach---115° Centigrade
  - D. Contacting Time -----25 minutes
  - E. Time between contact and color reading-----1 hour.
  - F. Time of drying the rejuvenated clay-----2.5 hours.
  - G. Time of leaching in the determination of the optimum concentration-----2 hours, 15 minutes.
  - H. Agitation during the leaching period-----25 minute intervals until a homogeneous mixture was obtained.
  - I. Naphtha wash after contacting the natural clay with 250 milliliters of Naphtha in 50 milliliter portions.
  - J. Weight of natural clay used-----11 grams.
  - K. Color readings made with Tag Robinson Colorimeter, using the white reflector and a 100 watt incandescent bulb.
  - L. Acid Clay Ratio-----20 grams of liquid per 11 grams of clay.
- II. The optimum rejuvenation of the bleaching clay used with the particular oil described took place at a concentration of from 7% to 9% sulfuric acid, the clay showing a maximum decolorizing power when treated with 8% acid.
- III. At a concentration from 7% to 9% sulfuric acid, the best leaching time was 2 hours and 30 minutes.
- IV. The curves obtained by plotting concentration of acid against color, and leaching time against color were smooth and showed a maximum point.

- V. Leaching the clay with hydrochloric acid did not give a smooth curve and the data was not reproduceable.
- VI. A spent clay can be revived by the acid leach to again successfully bleach an oil.
- VII. A natural clay which bleached an oil having a Tag Robinson color of 1.8 to a color of 8.5 after rejuvenation bleached the same oil to a color of 5.3.
- VIII. Other variables such as temperature, liquid-clay ratio and drying temperature probably would show maximum values which could be determined.
- IX. This work might also be extended to the use of different acids and salts or to the solvent method of rejuvenating the spent clay.

## BIBLIOGRAPHY

1. Bancroft, W. B.  
Applied Colloid Chemistry, 71-149, Second Edition  
McGraw-Hill Book Company, 1926
2. Baylis, Walter S.  
Reactivated Adsorbents and Method of Making Same.  
U. S. 1,810,155 June 16, 1931
3. Baylis, Walter S.  
Activated Clay and the Method of Producing Same.  
U. S. 1,819,496 August 18, 1931
4. Baylis, Walter S.  
Process of Making a Decolorizing Clay  
U. S. 1,781,265 November 11, 1930
5. Beldon, Daniel S. and Kelly, William  
Method of Preparing Absorbent Low in Salts and Free from Acid.  
U. S. 1,980,569 November 13, 1934
6. Burghardt, O.  
Activated Bleaching Clays.  
Ind. Eng. Chem. 23, 800-802
7. Davis, L. L.  
Ref. Nat. Gaso. Mfr.  
March, 1928, 90.
8. Fussteig, Rafael  
Bleaching Clays.  
Part I., Petro. Engr. February 1938, 98
9. Fussteig, Rafael  
Bleaching Clays.  
Part II., Petro. Engr. March, 1937, 64
10. Fussteig, Rafael  
Bleaching Clays.  
Part III., Petro. Engr. September, 1937, 58.
11. Fussteig, Rafael  
Bleaching Clays.  
Part IV., Petro. Engr. October, 1937, 85.
12. Fussteig, Rafael  
Bleaching Clays.  
Part V., Petro. Engr. December, 1937, 64
13. Fussteig, Rafael  
Bleaching Clays.  
Part VI., Petro. Engr. January, 1938, 80.



14. Fussteig, Rafael  
Bleaching Clays  
Part VII., Petro. Engr. March, 1938 70
15. Gurwitsch, Leo  
The Scientific Principles of Petroleum Technology.  
D. Van Nostrand Company, 1927
16. Huber, Frederick  
Method of Activating Clay.  
U. S. 1,926,148 September 12, 1933
17. Kobayashi, Kiuhei and Yamamoto Ken-ichi  
Activated Clay.  
I. The Optimum Condition for Preparing Activated Clay and the  
Characteristic Decolorizing Curve.  
J. Soc. Chem. Ind, Japan 27, Suppl. binding 181-2, 1934
18. Lemmon, Norman E.  
Revivifying Spent Fuller's Earth.  
U. S. 1,805,178 May 12, 1931
19. Mattson, Sante  
The Laws of Soil Colloidal Behavior, V.  
Soil Science 31 319 1931
20. Minerals Yearbook, 1937
21. Morrell, Jacques C.  
Treatment of Adsorbent Earths  
U. S. 1,844,476
22. Nelson, W. L.  
Petroleum Refinery Engineering, Edition I.  
McGraw-Hill Book Company 540-543, 1936
23. Nutting, P. G.  
The Bleaching Clays.  
Circular 3, U. S. Dept. of Interior Geological Survey
24. Perry, John H.  
Chem. Engr. Handbook, Edition I.  
McGraw-Hill Book Company 1052-1071
25. Pfaff, Johann Konrad, Burgdorf, Kreis, and Siewecke, Adolf  
Separation of Oil from Bleaching Clay.  
U. S. 1,827,165 October 13, 1931
26. Potter, John Seward  
Process of Treating Clays to Adapt them for Decolorizing and  
Deoderizing Oils.  
U. S. 1,649,366 November 15, 1927

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