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A STUDY OF ASPHALTIC CRUDE OILS
HAVING POSITIVE OLIENSIS REACTIONS
AND
THE DEVELOPMENT OF A PROCEDURE FOR
RENDERING THE RESULTS NEGATIVE

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Refining Engineering.

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SUMMARY

The purpose of this work is to develop a method to convert crude oils having positive Oliensis tests into oils having negative Oliensis tests.

The Oliensis test is used on crude oils, as well as asphalts, to determine their non-homogeneity characteristics. In many states, crudes having positive tests are not permitted to be transported in pipelines with crudes having negative tests: Because this circumstance causes reduction in the price of the positive test crudes, a method is needed whereby the crudes can be treated at the point of production to produce negative test results.

It is known that the result of the Oliensis test depends on the amounts and properties of the asphaltenes present as well as the peptizing power of the resins present in the crude oils and asphalts.

Of the various treating methods tried, two proved to

be effective in converting positive Oliensis test crudes into negative test.

1. Treating with activated clay above room temperature.
2. Treating with 96-percent sulfuric acid.

Because of the relatively lower yield by the sulfuric acid treatment, and the destruction of the asphaltic properties, the method of treating the crudes with activated clay is more practical. Spent oil shale was found to have the same effect as activated clay. However, larger amounts of spent oil shale were needed to produce the same effect as with activated clay.

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ACKNOWLEDGMENTS

I wish to express my grateful appreciation to Professor James H. Gary, Head of the Department of Petroleum Refining Engineering, Colorado School of Mines, for suggesting the topic and for his helpful suggestions and guidance during the course of this work.

George W. LeMaire, Professor of Petroleum Refining Engineering, Colorado School of Mines, and the thesis adviser, has always given freely and obligingly of his time and his valuable ideas to direct the various phases of this problem.

Without the help of these men, this investigation could not have progressed to its present point. The author wishes to thank each of these men for their generous aid.

INTRODUCTION

This paper comprises a study of asphaltic crude oils having positive Oliensis reactions and the development of a method for rendering the results negative.

In 1933, Oliensis published the results of long research on the flocculation of some components in certain asphalts when the bitumen is dissolved or dispersed in a selected solvent. The resulting procedure, known as the "Oliensis Spot Test," has been widely used and discussed. As mentioned by the U.O.P. manual (1947, p. B-5), this test is conducted as follows:

Weigh the equivalent of 2 ml. of asphalt into a 25-ml. Erlenmeyer flask. If the asphalt does not flow readily at room temperature, gradually warm it on a hot plate until it flows over the bottom in an even layer. Cool to room temperature without rapid chilling, add exactly 10.2 ml. of naphtha that has certain specifications as (Skelly Solve-S) and weigh. Close the flask with a rubber stopper through which is inserted a 20-cm. length of 8-mm. glass tubing extending approximately 17 cm. above the stopper. Dissolve the sample carefully. To obtain

complete dispersion in 6 to 8 minutes, heat in a gently boiling water bath at first but increase this temperature by steps of 25°F in a glycerin bath if necessary. Immerse the flask up to its neck and warm for 1-minute intervals. Remove from the bath and swirl 5 seconds until dispersion is complete. Allow the flask to cool to room temperature and weigh. If there has been any loss in weight, make it up with naphtha.

Place a drop of the mixture on a No. 50 Whatman filter paper or one of similar grain. If the drop forms a brown or yellowish brown circular stain with a darker solid or annular nucleus, report the test as positive. If, however, the drop forms a uniform brown stain, defer the decision. Set the tightly stoppered flask aside at room temperature in subdued light for 24 hours. Stir the mixture vigorously until it is homogeneous and test again as above. If the stain is still a uniform brown, report "negative"; but if a dark nucleus, such as is described above, has formed, report "positive."

Example of the positive and negative Oliensis spots is shown in Figure 1.

The Oliensis test is used on crude oils as well as asphalts to predict the colloidal stability of the asphalts produced from the crudes. The spot test is commonly considered as a test for the presence of overheated or cracked material in the asphalt. Such products are considered undesirable in road building asphalts. However, positive spot tests have been obtained on asphalts from certain West Texas crude sources where the asphalt was not subjected to excessive temperatures during handling and processing or was not blended with other bitumen.

Negative Spot

Positive Spot

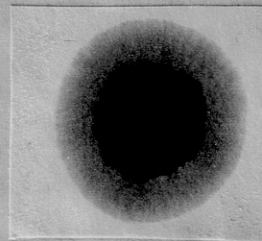
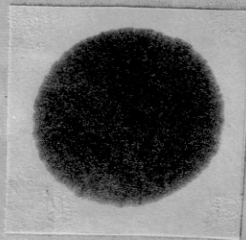


Fig. 1. Oliensis Spot Test

Consideration of the above result which is presented by Born (1937, p. 519) indicates that the Oliensis test establishes a purely arbitrary line between homogeneous and heterogeneous asphalts. According to Born, the Oliensis test, originally designed to differentiate cracked asphalts from steam-refined or vacuum-distilled asphalts, tells nothing about the characteristics of asphalts except the reaction of these asphalts to a distorted test. The data submitted by Born show that such natural asphalts can be differentiated from cracked asphalts by lowering the aniline number of the solvent used so that it is equivalent to the aniline number of the natural solvent occurring in the crude oil from which the asphalt was produced.

Pfeiffer (1950, p. 184) raised the following objections to the use of the Oliensis test in specifications:

- a. The name "test for heterogeneity" is misleading. Only the heterogeneity of the mixture of asphaltic bitumen plus kerosene is determined and it is clearly shown that the system may partly flocculate when another solvent is added.
- b. The name "test for heterogeneity" is the more to be regretted as in this way the character of a test for quality is imparted to this test, which was originally intended for identification, especially because almost all American specifications stipulate that "Asphalt shall be homogeneous." In the literature, too, there is a distinct ten-

dency to look upon the test as one for quality.

- c. The limit stated by Oliensis by no means gives a differentiation between asphaltic bitumens from normal residues and cracked residues. There are many bitumens from normal residues which do not give a negative test with the kerosene specified by Oliensis.

Many of the crude oils yield positive spot tests. Their positive spot character is an inherent property of the crude oils and is not due to cracked material. Nevertheless, in many states, the Oliensis test disqualifies these crudes as sources of asphalts for road construction because of existing laws. Segregation and diversion of such crudes to uses other than manufacture of paving material is often uneconomical. Since the Oliensis test is still valid in many states, a method is needed whereby the crudes can be treated at the point of production to remove the materials which cause the positive test.

Mallatt and Bransky (1956, p. 1) investigated the relationship between asphalt composition and the Oliensis spot test and concluded that the crude oils that yield positive-spot asphalts without cracking are usually high in sulfur content. They suggested a modified Oliensis spot test to distinguish between positive spot caused by naturally occurring bodies and positive spot caused by cracking. A blend of 35-percent xylene in n-heptane as

the solvent was found to serve this purpose.

It is well known that the stability of an asphaltene dispersion depends both on the properties of the asphaltenes (pentane insolubles) and the properties of the maltenes (pentane solubles) in which the asphaltenes are dissolved or dispersed. The Oliensis spot test is examined by Heithaus and Fink (1959, p. 353) in relation to colloidal stability as follows:

If a very small amount of a poor solvent such as normal heptane is added to an asphalt, no precipitation of asphaltenes occurs. The peptizing power of the maltenes is sufficient to keep the asphaltenes well peptized in spite of the presence of the nonsolvent. However, when the (volume) ratio of heptane to asphalt exceeds a certain value, precipitation of asphaltenes occurs unless one simultaneously adds some good solvent such as xylene to keep the system well peptized. As the dilution ratio (ratio of total volume of diluent to volume of asphalt) is increased, the proportion of xylene necessary to keep the asphaltene peptized increases--that is, the Heptane-Xylene Equivalent increase. The Heptane-Xylene Equivalent tends to reach a limiting value at high dilution.

Now in either the Oliensis test or the Heptane-Xylene Equivalent test the dilution ratio, that is, the ratio of solvent plus nonsolvent to asphalt has been chosen, as about 5. It can be seen that this ratio is so high that the test results reflect almost entirely the properties of the asphaltenes. Thus a positive Oliensis test indicates primarily that the asphaltenes are somewhat difficult to peptize. Since, as noted above, the colloidal stability or state of peptization of the system depends also on the peptizing power of the maltenes, a positive Oliensis test does not, then, neces-

sarily indicate that the undiluted asphalt is an unstable or poorly peptized system.

Heithaus and Fink (1959, p. 353) examined the Oliensis spot test to determine whether it is a valid indicator of the qualities of asphalt which are most important to good performance. Emphasis was placed on resistance to hardening and rheological properties.

It is shown that the Oliensis test is not directly related to durability, as both positive and negative asphalts may vary widely in hardening tendency. Even highly-cracked asphalts can have very low hardening tendencies. Furthermore, the rheological character of Oliensis positive asphalts is not necessarily different from that of negative materials. Age-hardening is no more pronounced in one class of asphalts than in the other.

In view of their results, Heithaus and Fink (1959, p. 353) suggested that the Oliensis test be replaced by more direct measures of asphalt quality, such as those based on viscometric measurements.

Various methods have been developed by which Oliensis positive asphalts can be rendered negative. Mallatt and Bransky (1956, p. 1) accomplished this change by increasing the amount of resins. They found that the

amount needed ranged from 5 to 30 percent and depended upon the intensity of the spot. Increasing the oil fraction while holding the amount of resins and asphaltenes constant had no effect on the spot test. Thus, it appears that the resins and not the oils show a marked effect in holding the asphaltenes in colloidal suspension when asphalt is diluted with naphtha in the spot test.

Heithaus and Fink (1956, p. 353) converted positive asphalt to negative materials when precipitating a portion of the asphaltenes by dilution of the asphalt with about 10 volumes of a light naphtha. The insolubles were then removed by centrifuging and the naphtha evaporated from the supernatant liquid under vacuum. Conversion to Oliensis negative products did not improve the quality of asphalt.

Nellensteyn (1937, p. 79) found that the asphaltenes go into solution if a diluent having certain surface tension is added to the light naphtha solution. Nellensteyn's surface-tension rule has been defined as follows:

When mixing asphaltic bitumen with liquids, which are totally miscible with the medium and the protective bodies of this bitumen, flocculation occurs when the liquid has a surface-tension below 24 dynes per cm. at 25°C; if the surface-tension is higher than 26 dynes per cm., total peptization takes place, while in the intermediate zone of 24 to 26 dynes per cm., flocculation or peptization depends upon the more or

less stable character of the micelle.

This rule has been confirmed by the following facts:

1. Some reagents are characterized by their immiscibility with the oily medium and protective bodies combined with a high surface-tension. These cannot peptize on account of their immiscibility.
2. Other reagents (true flocculents) are characterized by their complete miscibility with the medium and the protective bodies, but their low surface-tension leads to partial or complete insolubility.
3. Combination of the two types of reagents can be completely peptizing, if they are mutually miscible. This must be ascribed to the fact that the immiscibility of the first reagent is corrected by the second, whereas the low surface-tension of the second is corrected by the first.

The following examples of combination are given by Nellensteyn (1937, p. 79): Aniline - ether; Benzyl alcohol - gasoline; O-nitroanisol - ether.

EXPERIMENTAL WORK

Component Analysis

For determination of the material that makes the asphalt have a positive Oliensis test, one asphalt sample is separated into its components according to the following procedure:

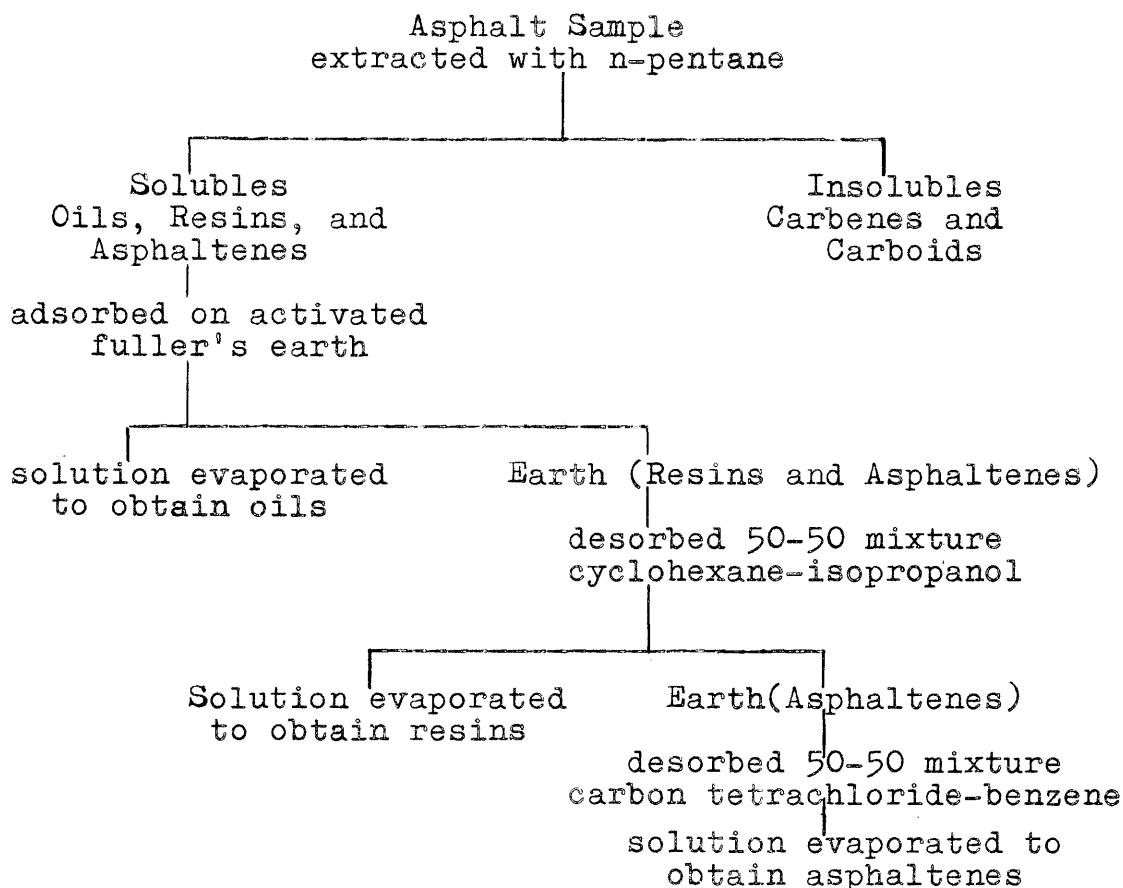
About 25 g of the sample is weighed in the extracting thimble and extracted with about 250 ml of normal pentane in a Soxhlet apparatus. The extraction is continued until the liquid coming down from the extractor becomes colorless. The insolubles that remain in the extraction thimble contain carbenes and carboids. The solution in the flask contains oils, resins, and asphaltenes.

The above solution is transferred to a beaker and freshly activated fuller's earth is added. The mixture is shaken intermittently and allowed to settle overnight. The pentane layer will become clear when the adsorption

is complete. Then the mixture is filtered and the filtrate is heated in a water bath to evaporate the solvent, leaving only the oils.

The fuller's earth as obtained above is transferred to a Soxhlet apparatus and desorbed with fifty-fifty mixture of cyclohexane and isopropyl alcohol. The solution is then heated and the solvent evaporated to obtain the resins.

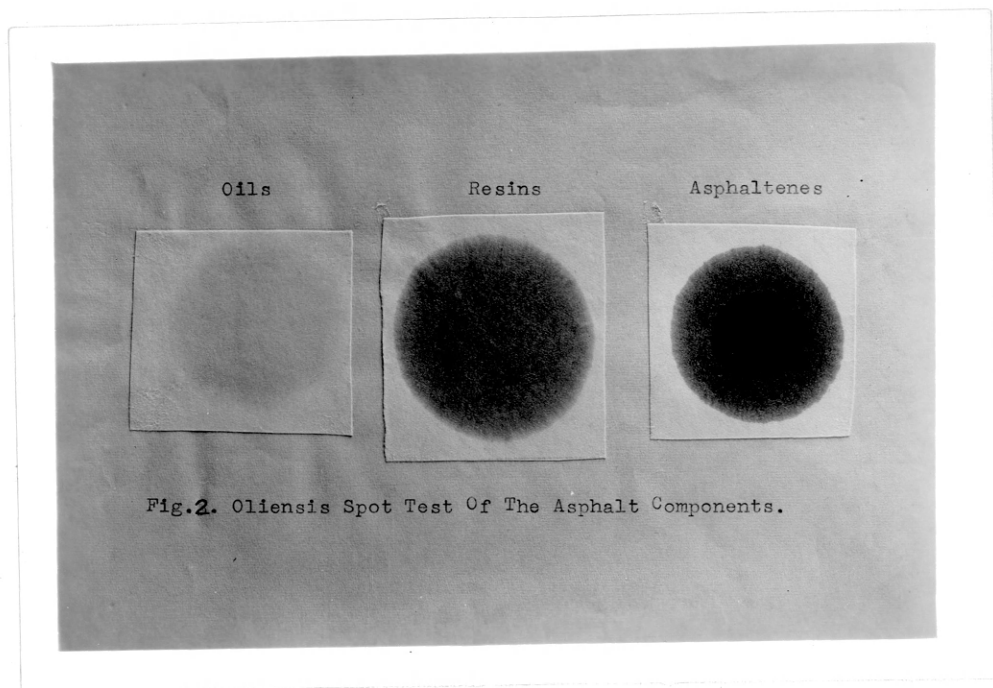
To obtain the asphaltenes, the fuller's earth from the last step is now desorbed with a fifty-fifty mixture of carbon tetrachloride and benzene solution. The asphaltenes component is recovered by evaporating the solvent. This procedure is illustrated by the following diagram:



After the sample was analyzed, an Oliensis test is made on each of the three asphalt components. The oils and the resins gave negative spot test; whereas the asphaltenes produced a positive test-as shown in Figure 2.

General Methods of Converting the Positive Oliensis Crudes Into Negative.

The factors influencing the result of the Oliensis test are the amount and properties of the asphaltenes and



the peptizing power of the maltenes. Therefore, the positive spot-test crude oil could be converted into negative spot-test crude by two general methods discussed in this thesis.

1. Increasing the peptizing power of the maltenes.

A limited number of organic solvents were added to the positive spot-test crude in different amounts to as much as 10-percent by volume and the spot test was made on the mixture. The following organic compounds were tried without getting any effect in converting the positive spot-test crude into the negative:

benzene		cyclo hexanol
toluene		wax
xylene		aniline
n-butyl benzene		methyl aniline
cyclohexane		pyridine
carbon tetrachloride		triethanol amine
chloroform		phenol
chlorex		o-chlorophenol
acetone		grease
methyl ethyl ketone		fatty acids
γ -butyro lactone		n-butyl lactate
methanol		ether
i-propanol	n-butanol	furfural

2. Partial removal of the asphaltenes. The crude oil samples used were: (1) Kewanee crude—from Grass Creek, Wyoming, having API gravity of 32.2 and Positive Oliensis test; (2) Gebo Embar crude—from Thermopolis, Wyoming, having API gravity of 28.0 and Positive Oliensis test; (3) Synthetic crude having API gravity of 25.2 and Positive Oliensis test. This sample was made as follows:

lube oil	80 percent
kerosene	10 percent
Visbreaker Tar	10 percent

The following experiments were made on the above three samples:

A. Treatment with Sulfuric Acid.

Sulfuric acid of different concentrations (6, 12, 24, 48, and 96 percent) were tried. The only effective concentration was found to be 96 percent.

Procedure: Sulfuric acid was added drop by drop from a pipette to the crude with constant stirring. Then the mixture was left for a few hours to allow the sludge to settle. The supernatant liquid was then decanted to a separatory funnel, washed with water several times to remove the residual sulfuric acid, and then an Oliensis test was made on the treated oil. After treatment, the color of the crude changed from dark brown to green and

the density was lowered. The minimum amount of sulfuric acid required, the API gravity of the treated crudes, and the yield percent were determined as shown in Table I, below:

Table I. Sulfuric Acid Treatment of Crude Oils

Sample	Original API	Min. amount H ₂ SO ₄		Yield percent	Treated API
		vol. percent	lb/bbl		
Kewanee	32.2	1	6.45	85	33.0
Gebo Embar	28.0	5	32.20	72	30.0
Synthetic	25.2	1	6.45	75	26.5

Figure 3 shows the pictures of the spot tests before and after the sulfuric acid treatment of the crude samples mentioned above.

The vigorous sulfuric acid action on the crudes reacted with most of the asphalt components, destroying the asphaltic properties. Therefore, this process does not appear to be practical, as shown from the low yield-percent in Table I.

B. Treatment with Activated Clay (Fuller's Earth).

The crude oil samples were first treated with clay at room temperature without any effect. Then it was found that activated clay is effective at higher temperatures in adsorbing the materials that cause the positive

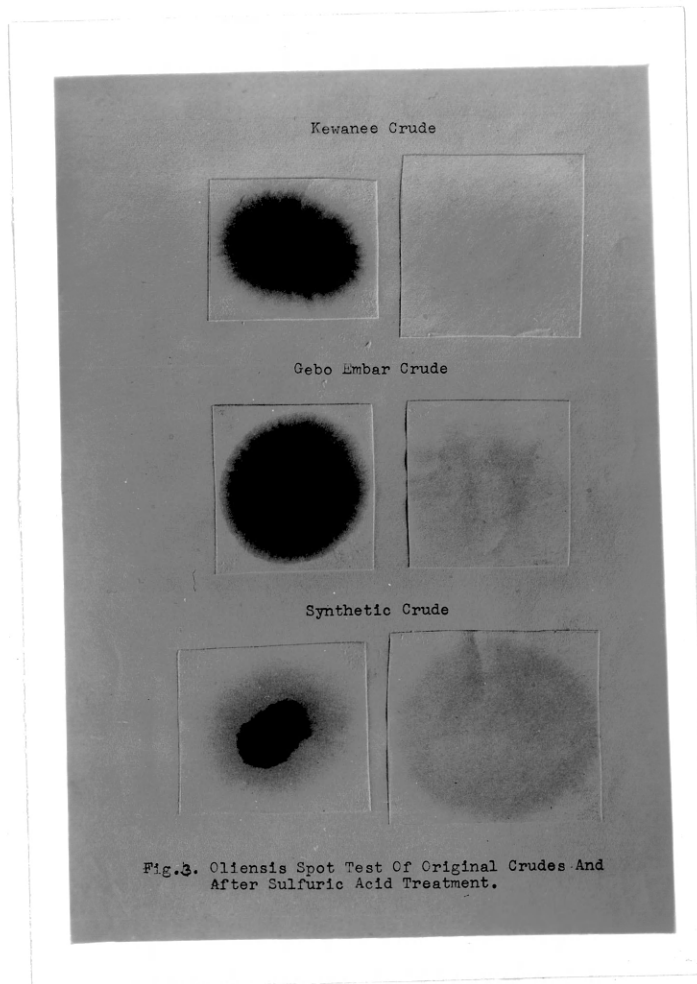


Fig.3. Oliensis Spot Test Of Original Crudes And After Sulfuric Acid Treatment.

Oliensis test.

Procedure: A certain amount of activated clay is added to 100 ml of the crude in a round-bottom, 3-neck flask of 500-ml capacity. The mixture is heated by means of a hot plate under a reflux condenser. The temperature is controlled and the time of heating is fixed in each run. After cooling, the mixture is filtered through a coarse filter paper and an Oliensis test is made on the filtrate.

Evaluation of the Process Variables.

The clay sample used in the experiments is 30- to 60-mesh fuller's earth having slightly acid reaction (pH = 6). For this specific kind of clay, the variables that affect the process are the temperature, the amount of clay used, and the time of treatment.

1. Effect of Temperature:

With a fixed amount of clay and time of treatment, the effect of temperature could be evaluated. Ten grams of clay was added to 100 ml of the crude and heated for one hour. The temperature was varied for each run, within the range of 300° to 500° F. With an increase in temperature the efficiency of the clay for adsorption was increased until reaching a certain temperature above which the clay became less effective. The optimum

temperature varies with the kind of crude oil used. Generally, the more viscous the oil, the higher the temperature required.

2. Effect of Amount of Clay:

The temperature and the time of treatment were fixed for this experiment while varying the amount of clay used. Amounts of clay ranging from zero to 20 g per 100 ml crude were tried. It was found that the greater the amount of clay used, the better the result within the experimental limits. The minimum amount of clay required to change the positive spot test to negative was determined for each sample.

3. Time of Treatment:

A time range from 5 minutes to 2 hours was used. The minimum time needed was determined at the optimum temperature and amount of clay required for each sample.

The optimum conditions for each sample are listed in Table II, below:

Table II. Optimum Conditions for Activated Clay Treatment of Crude Oils

Sample	Temperature °F	Amount of Clay		Time min
		g/100 ml	lb/bbl	
Kewanee	450	4	14	30
Gebo Embar	425	4	14	15

The spot test at the above conditions is shown in Figure 4.

It was found that the density of the treated crudes at the conditions mentioned above was higher than that of the originals as shown in Table III, because of some vapor loss of the lighter constituents during the process.

Table III. Activated Clay Treatment of Crude Oils

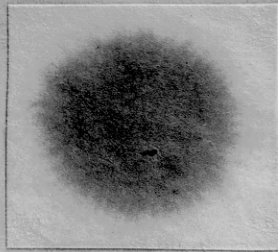
Sample	Original API	Treated API
Kewanee	32.2	29.0
Gebo Embar	28.0	25.8

The activated clay treatment of crude oils is found to be more economical than the sulfuric acid treatment because of the higher yield by the former process and more practical since the asphaltic properties are retained.

It should be known that the synthetic crude could be converted to negative spot test (Fig. 5) by just filtering through Whatman filter paper No. 50. This unusual behavior indicates that the cause of the positive spot test in this particular case is due to some suspended materials, e.g., carbenes and carboids.

Filtration through Whatman filter paper No. 50 was tried for the other two samples without getting any effect.

Kewance Crude



Gebo Embar Crude

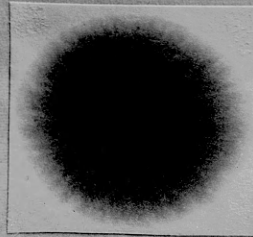


Fig.4. Oliensis Spot Test Of The Crudes After Clay Treatment.

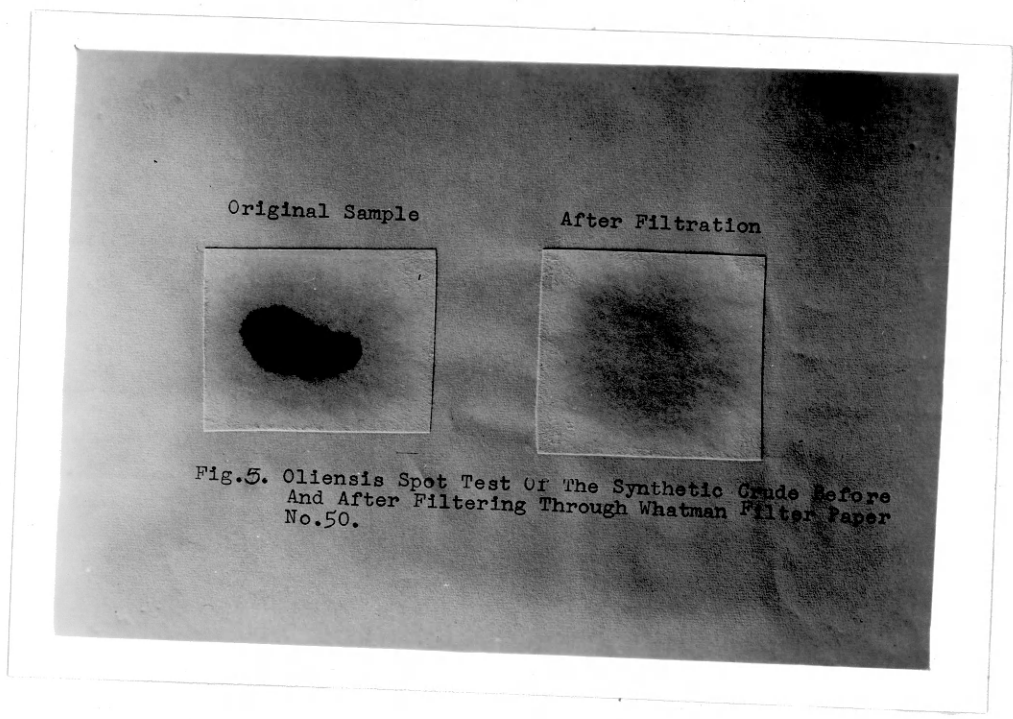


Fig.5. Oliensis Spot Test Of The Synthetic Grade Before
And After Filtering Through Whatman Filter Paper
No.50.

C. Treatment with Spent Oil Shale.

The spent oil shale used in this experiment had a slightly alkaline reaction (pH = 8). Treatment with spent shale was tried at room temperature without any effect. As in the case of activated clay, it was found that spent oil shale was effective at higher temperatures. However, the adsorbing capacity of spent shale was lower than that of clay because of the presence of many impurities and inert materials. Ten grams of spent shale was needed for every 100 ml of crude oil compared with four grams of clay.

DISCUSSIONA. Adsorption by Fuller's Earth and Activated Clays:

Fuller's earth is used for bleaching, deodorizing, clarifying, dehydrating, or neutralizing mineral, vegetable, and animal oils, fats, and greases. Petroleum products so treated are bright stocks, cylinder stocks, long-residuum or blending stocks, neutral and spindle oils, transformer and cable oils, paraffin wax, petrolatum, petroleum jelly, kerosene, gasoline, and refined oils. The author found in his investigation that fuller's earth is also effective on crude oils in removing the impurities that cause the positive Oliensis test.

Fuller's earth is described as a hydrous aluminum silicate, the chemical composition of which may be too variable to afford a means of identification. The silicates that form fuller's earth are present as the minerals attapulgite and montmorillonite.

Many of the properties of the finished fuller's earth vary with the source and are affected by the mesh-

size range and residual-water content. The bulk density usually falls between 28 to 45 lb per cu ft. Lower bulk densities are correlated with high adsorptive power, finer states of division, low water content, and extrusion in processing. True densities, affected only by the mineral composition and thermal history, fall between 2.4 to 2.6 g per cc.

The chief property of fuller's earth is its adsorptive power. During the drying step, water is driven off, leaving particles full of submicroscopic pores. In these pores the great area of active adsorptive surface is probably developed. The more active grades of fuller's earth develop 60- to 70-percent porosity and surface areas of 120 to 140 sq m per g.

Fuller's earth usually has a pH in the range 6.5 to 7.5. Although neutral or nearly so, it may act as a powerful neutralizing agent for strong acids. This mechanism appears to be largely the result of selective adsorption. Fuller's earth is relatively inert chemically, but may exert catalytic effects.

Mantell (1951, p. 53) mentions that the action of earths from different localities is often quite specific. Oils from different oil fields also require specific treatment, bleaching well with some clays and poorly with

others. The same clay may be very effective with one oil and less efficient with another oil from a different source. The most important variables are temperature; time; pH; amount of the adsorbent; and concentration and type of the material to be adsorbed.

With a raise in the temperature of treatment, the adsorption power increases until it reaches a maximum, when it starts to decrease with further increase in temperature. Comparatively high temperatures seem to be favorable for the adsorption of impurities from oils (perhaps because of increased adsorption capacity of the impurities through the removal of adsorbed gas or vapors, or because of decreased viscosity, increased diffusion, or because of increased catalytic action at elevated temperature). At excessively high temperature, the adsorption power becomes low because of the decrease in the saturation value and the oxidation of the oils and some other chemical reactions.

The time of treatment required for the mixture of oil and clay to reach to equilibrium (saturation value) decreased with the increase in temperature. Therefore, the optimum temperature is chosen by balancing between the maximum adsorption power and the minimum time required. Generally, the more viscous the crude oil, the

higher the temperature needed.

The capacity of an adsorbent for an adsorbate is directly proportional to the concentration of the latter in the solution. As the concentration of adsorbate decreases, there is a progressive and corresponding decrease in the amount of the adsorbate taken up by a unit weight of the adsorbent. Freundlich represents the quantitative relation between the adsorbate and the adsorbent at constant temperature by the following equation:

$$X/m = KC^n$$

where: X = amount of adsorbate removed,

m = amount of adsorbent used,

C = concentration of residual adsorbate,

K and n are constants.

A plot of log. X/m vs. log. C produced a straight-line curve with a slope equal to n and intercept equal to log. K.

It should be known that the Freundlich equation is applicable only for low concentration of adsorbate.

Acid-treated clays of the proper type are much more efficient adsorbing agents than most varieties of fuller's earth or bleaching clays. However, it is more expensive than fuller's earth and the spent clay cannot be reactivated for reuse.

Two types of impurities may reduce the adsorbing power of earths--inert matter such as quartz, which merely dilutes, and impurities such as iron sulfides, calcium carbonate, or soluble salts, which may reduce the original adsorptive power when the adsorbent is heated to "temper" or "reactivate" it.

B. Proposed Continuous Process for Treating Crude Oils.

Figure 6 shows the flow diagram of a continuous process by which crude oils could be treated at the point of production to remove the impurities that cause the oil to have a positive Oliensis test. The incoming crude oil is passed through a heat exchanger countercurrently with the treated hot crude oil. Then the oil is heated further to the desired temperature by means of a tubular furnace. After that, the hot oil is passed through a flash evaporator, which is maintained at a lower pressure than the tubular furnace, to remove the highly volatile components of the crude. The advantage of this step is to lower the pressure of the oil that passed through the adsorption tanks, thereby reducing the initial cost of these tanks.

The adsorption tanks, steel cylinders with conical bottoms, are fitted with suitable filtering screens and filled with coarse earth. The crude oil is passed down-

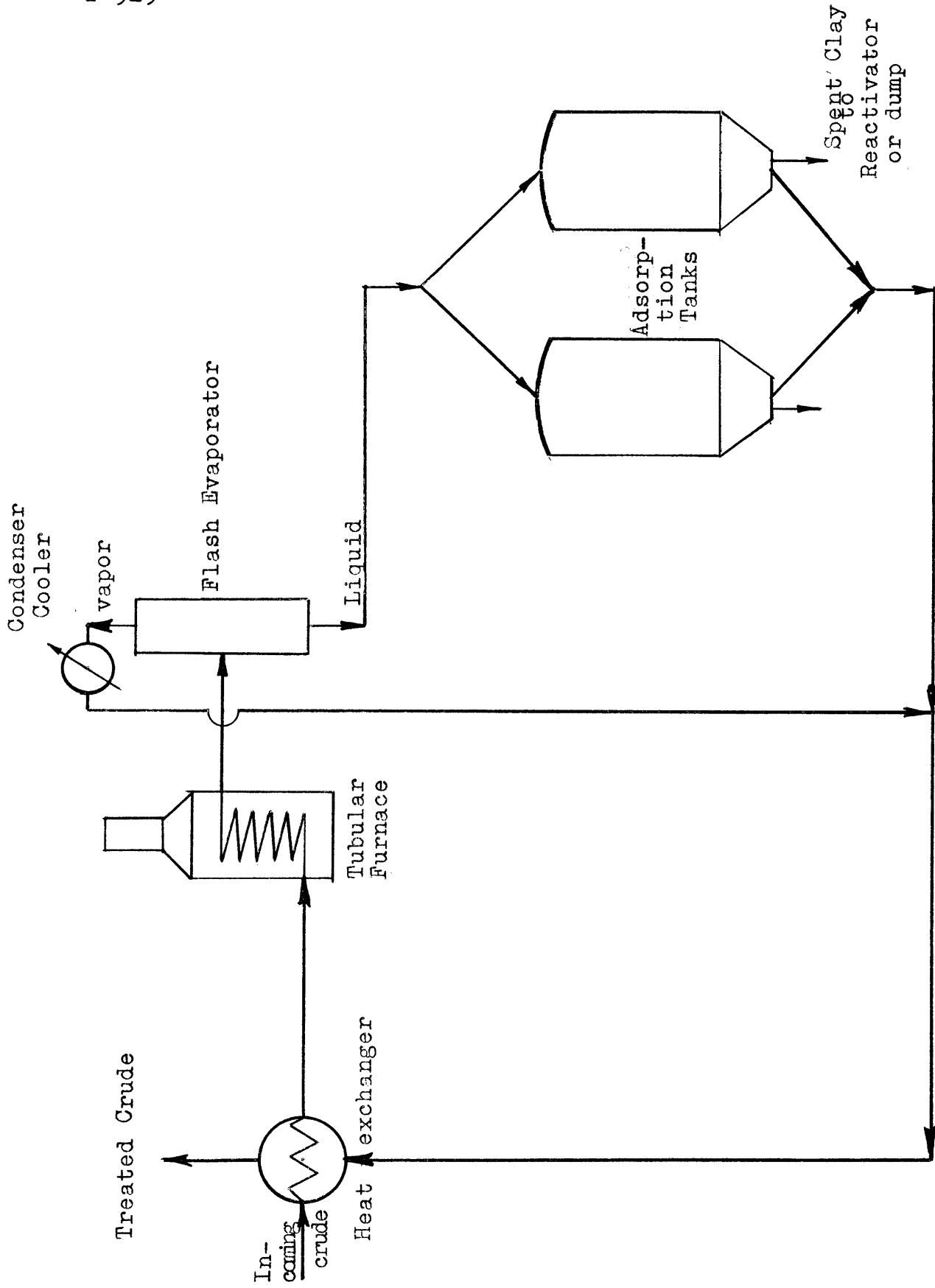


Fig. 6. Flow Diagram of Suggested Continuous Clay-Treating Process of Crude Oils.

ward (gravity flow) through one of the adsorption tanks. When the earth becomes spent, the flow of crude is diverted to the second tank. When the second tank is used, the spent earth from the first tank is revived by burning it in a furnace (not shown). Since the use of the adsorption tanks is alternative, the process could be maintained continuously. The vapors from the flash evaporator are condensed and mixed with the treated oil, and the mixture is passed through a heat exchanger to preheat the incoming crude oil.

C. Suggested Further Study.

The author found two methods to convert the positive Oliensis results into negative results with respect to crude oil: (1) treatment of the crude oil with sulfuric acid, and (2) treatment with activated clay.

Other methods are possible and those mentioned below are believed to be promising:

1. Additives that have a high peptizing power for asphaltenes and the more complex molecules should be tried. Using an additive consisting of a mixture of organic compounds as suggested by Nellensteyn might prove more effective than using a single compound.

2. Pentane was found to be effective in precipitating the impurities which are believed to cause the crude oil to have a positive spot test. It is known that the lower the molecular weight of the paraffin, the higher the flocculating power towards such impurities. Therefore, using lower paraffins is recommended, especially propane, ethane, and methane. This process requires low temperature and high pressure.
3. Negative spot-test crude oil could be used to dilute the positive-spot crude oil in sufficient amount to result in a negative quality blend.

CONCLUSIONS

In this investigation, two methods were found to be effective in converting the positive Oliensis crudes into negative Oliensis materials:

1. Treatment with 96-percent sulfuric acid.
2. Treatment with activated clays above room temperature.

The action of the 96-percent sulfuric acid on the crudes is vigorous, resulting in the destruction of the asphalt component and a relatively low yield of the treated materials. Clays adsorb the impurities that cause the crudes to have positive Oliensis test. This method of treatment is more economic than the first method because of the lower cost of the clays to the sulfuric acid and the higher percent yield of the usable materials. Spent oil shale was found to have the same effect as that of activated clay. However, the adsorp-

tion power of spent shale is less than that of activated clay, so a larger amount is needed to produce the same result.

A continuous clay-treating process of crude oils is suggested to be used at the point of production of the crudes.

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