

The Use of Selective Solvents in Refining Crude Shale Oil

By William Carl Lieffers

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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 Petroleum Refining Engineering.

Signed

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ACKNOWLEDGMENTS

The author wishes to express sincere thanks to Professor James O. Ball, Head of the Petroleum Refining Department, to Professor George LeMaire, Assistant Professor, and to Professor Hugo H. Geissler, Assistant Professor, all of the Petroleum Refining Department, Colorado School of Mines.

Professor Ball gave the author guidance and encouragement throughout the work.

An especial debt of gratitude is owed Professor LeMaire who followed the work throughout, gave guidance and suggestions on all phases of the work, and proofread the final manuscript.

Professor Geissler gave many valuable suggestions both in experimental work and in the organization of this report.

For all this assistance the author expresses his grateful thanks.

INTRODUCTION

The position of the United States in recent years has changed rapidly with regard to the supply of domestic petroleum reserves and the accessibility of foreign oil. The cost of discovery of new oil deposits is continually increasing while consumption continues at a tremendous rate. The use of foreign oil to augment domestic supply offers one solution to this problem; however, reliance on foreign supply would be unwise in the event of another war. With these factors in mind Congress passed in 1944 the Synthetic Liquid Fuels Act. This Act provided for research in the production of synthetic liquid fuels from coal, the synthine process, waste farm products, and oil shale.

The United States Bureau of Mines has done considerable research on oil shale under the Synthetic Liquid Fuels Act. The Bureau has investigated mining and retorting methods extensively and has conducted some research on the properties of, and compounds in, shale oil.

From its studies, the Bureau of Mines has concluded that

at the present time the major problem in the processing of oil shale is the refining of the shale oil into desirable products, 1/. The most objectionable compounds present in shale oil are

1/ Synthetic liquid fuels, Part II, Oil from shale: U.S. Bur. Mines Rept. Inv. 4457, p. 55, Jan. 1949.

those compounds containing nitrogen and sulphur. These compounds occur in the oil in larger amounts than in natural petroleum and produce unstable odorous materials upon distillation of the crude shale oil.

The investigation presented in this report was undertaken to determine the methods and effect of refining crude shale oil by solvent extraction in order to decrease the difficulty of subsequent processing and increase the quality of products therefrom. Removal of sulphur and nitrogen compounds was a primary objective of the investigation.

Solvent refining of crude shale oil is a very different method of refining from that used heretofore on either shale oil or natural petroleum. Solvent refining methods in the petroleum industry have been applied only to the manufacture of lubricating oils and distillates. However the nature of shale oil is such that it will require some radically new refining technique to produce satisfactory products. Perhaps hydrogenation or catalytic conversion will eventually be used, but solvent refining offers a wide field of investigation in which one or several processes of merit may be found which can be applied to the shale oil refining problem.

This report contains a discussion of the composition of

shale oil, a description and the origin of the oil used, solvent evaluation tests, and detailed studies of those solvents seeming to be most effective.

COMPOSITION OF SHALE OIL

As stated in the introduction, the object of this investigation was to determine whether the use of selective solvents would be a feasible method of refining crude oil recovered by retorting oil shale. Some properties and peculiarities of shale oil will be presented to show why solvent refining of crude shale oil may be an answer to the shale oil refining problem.

The material presented here is general and is applicable to almost any shale oil. In appearance, shale oil is usually black or dark brown, although some steam retorted or slowly converted oils may possess a green cast in natural light. The odor is generally foul because of the presence of nitrogen compounds. The specific gravity of shale oil is generally quite high as compared to natural crude oil. Gravities as high as 33° A.P.I. have been reported although the more common values are from 20 to 25° A.P.I. The composition of shale oil with regard to the relative amounts of various classes of compounds present may vary over wide ranges because of the type of shale retorted; the speed, pressure, and temperature of retorting;

and the presence or absence during retorting of gases such as steam or hydrogen.

The bulk of all shale oils is made up of paraffin, naphthene, olefin, and aromatic hydrocarbons and nitrogen, sulphur, and oxygen compounds are present in smaller, varying amounts. Shale oil may be asphaltic or paraffinic depending on factors already mentioned.

The main differences between crude petroleum oil and shale oil are the large amounts of nitrogen, sulphur, and oxygen compounds present in shale oil and the high degree of unsaturation of shale oil. An analysis of a typical Colorado shale oil 2/ gives the following composition: 50% olefinic

2/ Oyle from a kind of stone: Ind. and Eng. Chemistry, vol. 40, no. 12, p. 16A, Dec. 1948.

linkages, 25% aromatics, and 25% paraffins. Analyses of Colorado shale oils given by the U.S. Bureau of Mines 3/ show

3/ Op. cit., p. 48.

paraffins and naphthenes of 27 to 33%, olefins of 43 to 49%, and aromatics of 19 to 25%. It may be seen that if only the oil shale from one particular region or formation is considered, the oil recovered from such shale varies in composition within definite limits.

NITROGEN

The presence of large amounts of nitrogen compounds represents perhaps the greatest difference between shale oil and

crude petroleum. The highest nitrogen content reported in crude oil is 0.802% in the crude from Ojai Lease, California 4/. However the nitrogen content of shale oil rarely

4/ Sachanen, A.N., The chemical constituents of petroleum, p. 376, New York, Reinhold Pub. Co., 1945.

falls below 1.0% and usually is from 1.5 to 2.0%.

The series of compounds containing nitrogen which have been identified in shale oil is the nitrogen bases such as pyridines, quinolines, pyrroles, and isoquinolines. Such compounds make up only a fraction of the total nitrogen content in crude shale oil. The bulk of the nitrogen appears to be in highly complex multi- or hetero-cyclic compounds of unknown structure. These compounds have resisted all efforts to isolate them and appear to be sensitive to heat since upon distillation decomposition of these materials takes place with the appearance of nitrogen bases of the types mentioned above. The fact that the nitrogen appears in compounds which range from light pyridines to complex unknown structures sensitive to heat is one of the main difficulties in shale oil refining. The nitrogen appears in all fractions upon distillation and prevents isolation of all nitrogen-bearing compounds in one particular part of the oil. Nitrogen compounds also exhibit remarkable instability and cause distilled portions of the oil to darken on standing, deposit gums, and have foul odors. Removal of these compounds by present methods necessitates treatment of the oil with strong sulphuric acid. This is a very wasteful treatment, which also removes desirable aromatic and

unsaturated compounds together with the nitrogen compounds. To summarize their effect, nitrogen compounds are found in all distillate fractions, and contribute to unstability in color and odor, deposition of gums, and polymerization products.

SULPHUR

Sulphur compounds in shale oil cover most of the compounds found in crude oil. Mercaptans, organic sulfides, disulfides, hydrogen sulfide, thiophenes, and thiophanes have been recognized in shale oil. Investigation of sulphur compounds in shale oil has as yet been only carried out on naphtha. A recent U.S. Bureau of Mines paper 5/ states that the bulk of the

5/ Ball, J.S., Dinneen, G.U., Smith, J.R., Bailey, C.W., and Van Meter, R., Composition of Colorado shale-oil naphtha: Ind. and Eng. Chemistry, vol. 41, no. 3, p. 581-587, March, 1949.

sulphur in shale oil is in the form of thiophene homologs. The basis of this statement is the fact that approximately two thirds of the sulphur in shale oil naphthas occurs in such forms. At present it would not seem that their conclusions could be applied to shale oil as a whole from results on shale naphthas, but it is quite probable that the bulk of the sulphur is in the form of some complex heterocyclic ring structure. It is known that thiophenes are very difficult to remove or determine quantitatively. The amount of thiophenes present in shale naphthas as reported by the Bureau of Mines was determined by difference between the total sulphur present and other

forms of sulphur compounds which can be determined quantitatively. There is no known reliable determination for thiophenes in the presence of olefins. The work done in the preparation of this report has also led to the conclusion that the bulk of the sulphur is present in some complex-structured form which is difficult to remove. However, sulphur, although objectionable, is not so serious a problem as nitrogen. High sulphur crudes have been processed for many years in the petroleum industry. Crudes with sulphur contents as high as 5.0% have been reported. The sulphur content of Colorado shale oils is generally below 2.0%.

OXYGEN

Oxygen compounds also occur in shale oil in larger amounts than in crude oil. Very little data are available on these compounds, but it is known that phenol, phenol homologs, and carboxylic acids are present in the oil. As in the cases of sulphur and nitrogen compounds, only gasolines and light distillates have been investigated.

It may be concluded, therefore, that shale oil is a dark, heavy, highly unsaturated, heat-sensitive material which generally contains large amounts of nitrogen, sulphur, and oxygen compounds in all portions of the oil. The nitrogen, sulphur, and oxygen compounds in the oil are difficult to remove, and their removal is generally accompanied by large losses of desirable components. Nitrogen compounds are especially

objectionable, since they contribute to discoloration and gum deposition in all distilled fractions.

SHALE OIL INVESTIGATED

The crude shale oil used in the experimental work of this report was retorted by the Parry Process at the Golden, Colorado, Station of the U.S. Bureau of Mines early in 1945. This oil was kept in a 55-gal. barrel for $3\frac{1}{2}$ years, and it is not known how this prolonged storage affected the quality of the oil. However, in order to characterize the oil used, the sulphur content, nitrogen content, gravity, gross heating value, color, and odor were determined. In addition, a Hempel distillation conforming to A.S.T.M. procedure D 285-41 was run on the crude to determine its distillation curve. The above data are presented on Tables I and II.

PARRY RETORT

The Parry retorting method used to produce this oil is a continuous method developed by V. F. Parry and others at the Bureau of Mines Station, Golden, Colorado.

The equipment used in the Parry Process is given in Fig-

ure I. The retort as shown is set up for coal processing. Some changes were made in order to retort shale. A preheating hopper was used above the retort, the exit point for the oil vapors as shown by the arrows was raised somewhat from the position shown in the diagram, and various spent shale removal mechanisms were used at the bottom of the retort.

The retort used in this process was originally developed for the carbonization and gasification of lignite and was first operated during March 1944. The retort is a vertical, cylindrical, annular, alloy-metal type, heated externally. Heating is accomplished by burning gas at different levels of the combustion chamber in a mixture of heated products of combustion and air. When distilling noncoking materials such as shale or coal, the graded solids pass continuously into the retort from the preheating hopper. They then pass to the distillation zone where they are distilled at the desired temperature by heat passing through the walls of the retort. In one method of operation, the spent shale was removed by an inclined stoker screw immersed in a water seal.

RETORTING TESTS

Four tests were run on the retort, using different sizes of shale particles and operating techniques. It is not known from which of these tests the oil used in this report was obtained.

In test 1, $\frac{1}{2}$ x 1-in. shale particles were used with

external heating only on the retort. In test 2, $\frac{1}{2}$ x $\frac{1}{4}$ -in. particles were used with external heating as before. These two tests proved that the retort was not successful for strongly coking mahogany shales. In test 3, $\frac{1}{2}$ x 1-in. particles were used and the distillation gases were heated by recirculating them downward through the annulus. They were then drawn up through the descending column of shale to affect distillation. Test 4 used the same recirculating technique but used particles of $\frac{1}{2}$ x $\frac{1}{4}$ -in. The latter two tests proved somewhat more successful than the first two.

It was found in tests 1 and 2 that a carbon-silica deposit was formed on the hot retort wall and that this deposit would have to be periodically removed in a continuous operation. It was found that at a temperature under 450 C, 200 to 300 Btu per lb of solid shale are sufficient for distillation. An average of 10 lb of shale was retorted per hr per sq ft of heated retort surface, and 75 to 80% of the potential heat was recovered as condensible oil and hydrocarbon gases. The remaining 20 to 25% of the potential heat was in the form of fixed carbon and volatile matter which could be recovered only by gasification or combustion.

The shale processed was from the Green River Formation on property of the Union Oil Company of California in the Grand Valley District of Garfield County, Colorado. The shale was of the coking mahogany type with a Fischer assay value of 56.3 to 57.4 gal. per ton. The rate of distillation during the four runs described varied from 347 to 640 lb per

hour. The recovery varied from 25.9 to 43.6 gal. per ton. Oil from these tests was sent to the Universal Oil Products Company which reported an analysis of the oil. This analysis together with analyses by the Bureau of Mines of the oils obtained from Runs 1 and 2 are presented on Table I.

The material given in this section on the Parry retort and oil obtained therefrom is from a special report of the U.S. Bureau of Mines 6/ made available through the courtesy of Mr. V. F. Parry of the Golden Station.

6/ Parry, V.F., Goodman, J.B., Wagner, E.O., Lammers, G.C., and Cook, V.A., Processing Colorado mahogany oil shale in the Parry retort: U.S. Bur. Mines Special Report C-3-69, Feb. 12, 1946.

OIL PROPERTIES

Table I gives selected properties of various shale oils. The data on oils from the fluid retort and the Union Oil Co. retort are included for comparison with the Parry oil. The application of the fluid technique to shale retorting is being studied at the present time by some of the major oil companies. The Union retort has been developed to a semi-commercial scale and seems to provide very efficient heat exchange. All oils listed on Table I were produced by continuous processes. From a study of Table I it may be seen that the oil studied in this research was somewhat lighter than other oils listed. This may be due to long storage or variation in sampling. However, its properties do not vary greatly from those of the other oils. The characterization

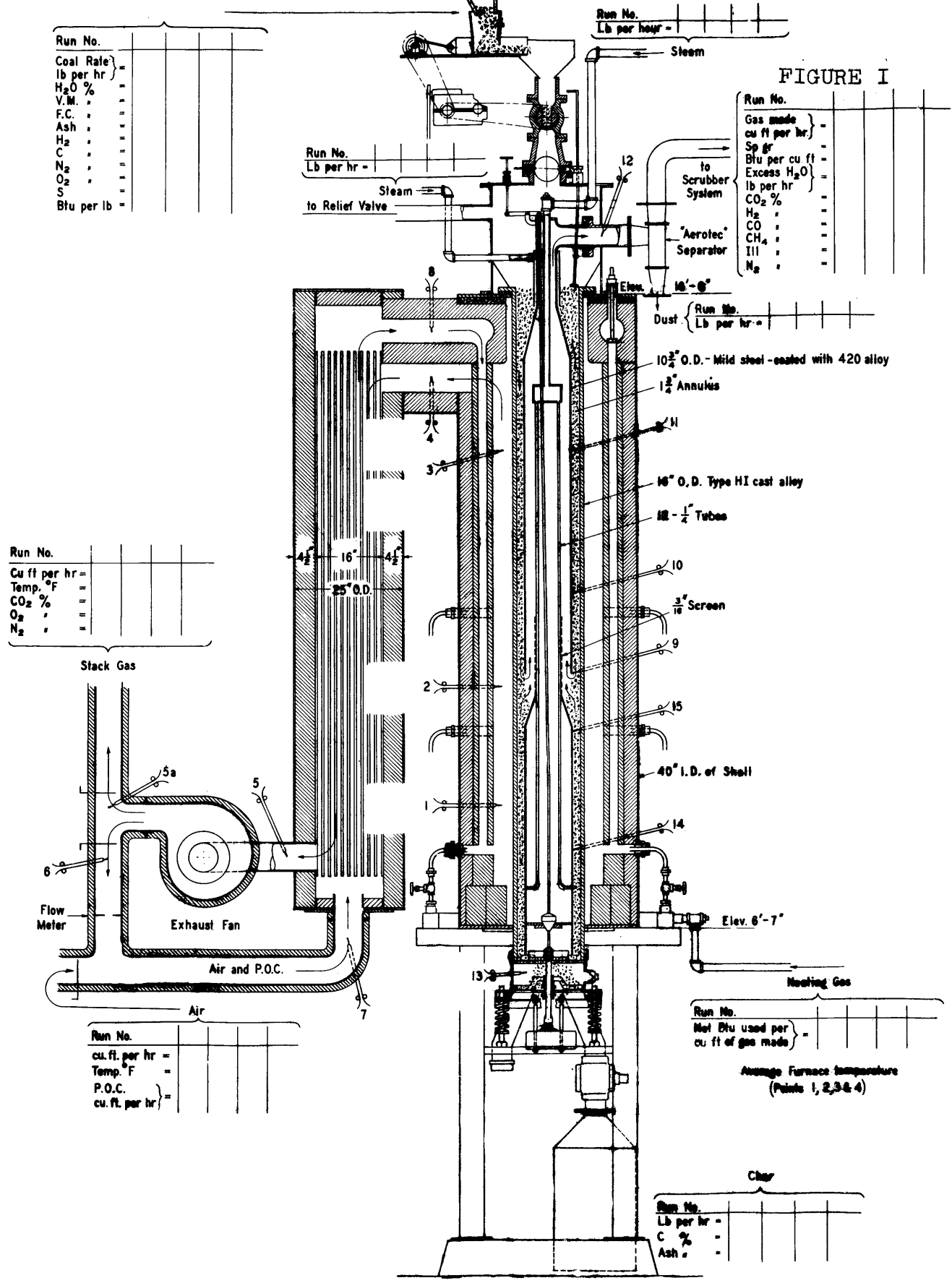


Fig. I-U.S. Bureau of Mines Pilot Plant for Carbonization and Gasification of non-caking coal - Golden, Colorado

factor (K) given for the writer's Parry oil was obtained from a generalized correlation of A.P.I. gravity versus total heat of combustion in Btu per lb. It is believed that other characterization factors for shale oil were obtained from the 50% boiling point and the fundamental definition of the characterization factor. In the Hempel distillation of Parry oil it was found that at a temperature of about 500 F there was definite evidence of cracking as shown by a fluctuating vapor temperature and coke production in the bottom of the flask. Thus it would seem any 50% boiling point and hence any characterization factor based upon distillation data would be liable to some inaccuracy. In contrast, the two properties used by the writer to obtain K were specific gravity and total heat of combustion. Both of these properties are subject to precise determination and unless the correlation used is not applicable to shale oils, it seems that the value of K below 10.0 is the more accurate.

In Table II are given the writer's distillation data of Parry oil. The distillate was initially light yellow and had a typically foul shale-distillate odor. Upon standing 24 hours, the distillate quite typically turned deep red and deposits began to form on the sides of the container. The bottoms were black and heavy, and a coke deposit on the bottom of the distillation flask indicated that cracking had taken place.

The properties and origin of the oil as presented in this section are a basis for comparison of this oil with other shale

TABLE I

Properties of Various Shale Oils

Property	Parry (Lieffers)	^{7/} Parry (Run 1)	^{7/} Parry (Run 2)	^{7/} Parry (UOP)	^{8/} Fluid	^{9/} Union
Specific Gravity	0.9176	0.9260	0.9200	0.9230	0.9194	0.9242
A.P.I. Gravity	22.7	21.3	22.3	21.8	22.4	21.6
Nitrogen, %	1.45	----	1.8	----	----	----
Sulphur, %	0.955	0.83	1.0	0.91	0.60	1.26
Gross Heating Value, Btu/lb	18,260	----	18,420	----	----	----
Water, %	0.33	----	----	----	0.02	0.2
K	below 10.0	----	----	11.0	----	----
Fischer Assay of Raw Oil Shale, gal./ton	56.3 to 57.4	56.3 to 57.4	56.3 to 57.4	56.3 to 57.4	105*	55

* Recovery per ton of very rich Australian shale retorted.

^{7/} Idem.

^{8/} Blanding, F.H., and Roetheli, B.E., Retorting oil shale by the fluidized solids technique: Oil and Gas Jour., vol. 45, no. 41, pp. 86-88, Feb. 15, 1947.

^{9/} Reed, Homer, and Berg, Clyde, Shale and air counter-flow in new continuous retort: Petroleum Processing, vol. 3, no. 12, p. 1188, Dec. 1948.

TABLE II

Hempel Distillation of Parry Crude Shale Oil

Charge - 300 cc

Rate of Distillation - 2 to 3 cc per minute

Barometric Pressure - 620 mm Hg

Procedure - A.S.T.M. D 285-41

Volume of Crude Overhead, %	Temperature, F at 760 mm Hg
IBP	157
1	167
5	281
10	331
15	383
20	433
25	468
30	501
32	508*

* Maximum temperature. Cracking began and distillation was stopped.

Volume of distillate ----- 97 cc

Volume of bottoms ----- 190 cc

Holdup in flask, coke and gas ----- 13 cc

Gravity of bottoms A.P.I. at 60 F ----- 14.5

oils. The properties of the oil investigated are typical of shale oils. The next section of the report deals with preliminary experimental work performed with various solvents.

EXPERIMENTAL WORK

The difficulties in refining shale oils have been discussed in the previous sections. The object of this research was to produce an oil of improved quality by lowering the sulphur and nitrogen contents of the oils and by improving the color and odor of the oil.

Solvent refining offers several advantages over other refining methods. First, there is no reaction between the solvent and the oil; thus there is a minimum loss of chemicals or oil; also, there is no production of undesirable substances. Second, if a selective solvent is used for nitrogen and sulphur compounds, these compounds will be removed with no loss of unsaturated or aromatic compounds of high octane value. Third, the solvent refining of the shale oil with the removal of objectionable compounds facilitates further refining procedures such as distillation, thermal cracking, or dewaxing and improves the products from such processing. Fourth, corrosion of equipment in subsequent refining is greatly lessened.

Because solvent refining of crude oil is a new concept, principles of solvent refining as applied to light distillates are of little value. Although a general method of application may be taken from the lubricating-oil solvent refining methods, previous techniques are of limited value. Lubricating oils contain a very large percentage of desirable constituents, usually about 95%. These desirable compounds are believed to have structures of one or two aromatic rings with long paraffinic side chains which may be slightly or greatly branched. In crude oil, and especially in crude shale oil, this ratio of desirable to undesirable constituents is greatly changed. Aromatic, sulphur, nitrogen, oxygen, and complex polycyclic compounds make up the major part of the oil. Separation of solvent and oil is difficult, since much of the shale oil is soluble in the solvent. Also many of the desirable constituents in the oil are liable to be dissolved in the extract layer. Therefore, not only solvents and their effect on oil were studied but also the best methods of applying solvents with regard to amounts, temperature, and number of contacts.

EVALUATION TESTS

Evaluation tests which were used were taken from standardized procedures wherever possible. The principal tests were the determination of nitrogen and sulphur contents, gross heating value, and specific gravity. Qualitative tests

of color and odor were also used. Securing of representative samples was the most difficult part of the testing of the oils. It was found that good samples could be taken by heating the oil to 100 F in an oven and agitating the oil violently by shaking immediately before sampling. Cooling of the oil was avoided as much as possible, since even at 70 F some of the heavy materials in the oil deposited on the sides of the container and thus made the fluid part of the sample non-representative.

Nitrogen

The nitrogen content of the oils was determined by the Kjehdahl-Gunning method. The Bureau of Mines 10/ states that

10/ Op. cit. (Synthetic liquid fuels), p. 50.

nitrogen determination of shale oil is difficult. Reported values by different methods and by different laboratories give results which vary 60% from the mean. The Bureau recommends the Kjehdahl macro- or the Dumas micro-methods. The composition and amount of catalyst used appear to be major factors in the accuracy and reproducibility of the Kjehdahl method. In all work of this investigation four granules of Hengar selenium catalyst were used to digest a two to three-gram sample of oil. It was found that approximately 40 ml of 93% sulphuric acid were sufficient to complete the digestion to a clear green solution. A maximum variation of results of 7% from the mean value was found, and usually variations were within 5%.

Sulphur

Sulphur content was determined by A.S.T.M. Method D 129-44, Sulphur in Petroleum Oils by Bomb Method. A Parr oxygen bomb was used for the combustion of approximately a one-gram sample of oil. The sulphur was determined gravimetrically by precipitation as barium sulfate. Precision of the results were within the limits of the method as specified by the A.S.T.M.

Heating Value

Gross heating value was determined by the Parr instrument mentioned above by the procedure specified by the manufacturer of the instrument.

Color

Colors or casts of the oils under natural and ultraviolet light were determined. Both colors are a good qualitative indication of the degree of refining. Ultraviolet light proved very useful in solvent extraction work because separations invisible in ordinary light are easily detected under this light and because the color of the oil gives some indication of the materials present. Table III gives a summary of the colors produced under natural and ultraviolet light by some of the compounds present in oil.

TABLE III

Colors of Organic Materials Under Various Lights

Material	Color	
	Natural Light	Ultraviolet Light
Paraffins and low molecular weight naphthenes and aromatics	Green	Blue
Higher molecular weight naphthenes and poly ring structures	Blue	Green
Unsaturated high molecular weight compounds	Brown or Greenish-brown	Lemon yellow
Resins and cokes of extremely complex structure and high specific gravity and molecular weight	Black	Black or Brown

Note: A polar additive such as a lubricating oil additive will impart a blue color to an oil under ultraviolet light.

CONCENTRATION OF NITROGEN AND SULPHUR BY DISTILLATION

The first step in studying the shale oil was to determine whether an appreciable portion of the nitrogen and sulphur compounds could be concentrated in any particular fraction of the oil by distillation. It was also desired to study the products obtained by distillation and note their stability or gum-forming tendencies. Two distillations were performed on the shale oil. Both distillations were carried out as prescribed by A.S.T.M. Method D 285-41, Distillation of Crude Petroleum.

The first distillation was continued until a vapor temperature of 300 F was reached. This temperature corrected for barometric pressure was 313 F. A Hempel distillation flask was used with jack chain in the neck of the flask to provide a refluxing surface. The overhead product amounted to 10% of the charge to the distilling flask. The distillate was yellowish and foul smelling. The specific gravity of the distillate was 0.74 at 17.0 C. In order to evaluate the effectiveness of the distillation in concentrating sulphur and nitrogen in the fraction, determinations were made on the distillate, and the remainder of the oil left in the flask. The distillate had a sulphur content of 0.796% and a nitrogen content of 0.072%. The bottoms contained 1.023% sulphur and 1.485% nitrogen. The specific gravity of the bottoms was 0.9396 at 60 F.

From a study of the results above, it is evident that no

appreciable concentration of undesirable constituents occurred by removing a portion of the lighter components from the oil. The distillate did not contain an appreciable amount of nitrogen, but the sulphur content was large. It is not known whether the sulphur and nitrogen present caused the subsequent darkening, but after 24 hours the distillate turned reddish, and after several weeks the color was deep red and there were some deposits of gums on the sides of the container. This reaction is typical of shale oil distillates. 11/ It was

11/ Laspe, W. E., The use of solid adsorbents and selective solvents in refining shale gasoline: Colorado School of Mines Thesis, p. 31, 1948.

concluded therefore that removal of all light hydrocarbons up to a temperature of 300 F did not concentrate any considerable portion of the sulphur and nitrogen compounds either in the distillate or the bottoms. In order to evaluate the effect of further removal of light components, a second distillation was conducted.

The second distillation was continued to a vapor temperature of 400 F (415 F corrected for barometric pressure). As in the first distillation, a Hempel flask and jack chain were used and the same A.S.T.M. method was followed. The overhead product amounted to 20.4% of the charge to the distilling flask. The appearance of the freshly distilled product was similar to that of the product from the first distillation. The specific gravity of the distillate was 0.7942 at 60 F. As in the first distillation, sulphur and nitrogen contents were determined on the distillate and bottoms. The distillate

had a sulphur content of 1.067% and a nitrogen content of 0.360%. The bottoms contained 0.885% sulphur and 1.72% nitrogen. The specific gravity of the bottoms was 0.9567 at 60 F.

From a study of the above results it may be seen that a considerable portion of nitrogen and sulphur appeared in both the distillate and bottoms. There was not sufficient concentration in either portion of the oil to warrant the use of this method to isolate these types of compounds. Certain trends, however, may be seen from the results. Sulphur content tends to become higher in the distillate than in the bottoms. This would lead to the conclusion that a large part of the sulphur occurs in lower boiling forms. This conclusion seems to be borne out by the findings of the Bureau of Mines, which reports the bulk of the sulphur in the form of thiophenes. In contrast to the sulphur, nitrogen content of the distillate increases but not significantly. The bulk of the nitrogen appears in the bottoms, a fact which leads to the conclusion that most of the nitrogen is in the form of complex heavy-molecular-weight compounds of unknown structure. Selective solvents should be effective in removing such compounds.

From the results of the two distillations, the isolation of nitrogen and sulphur compounds by distillation did not appear promising, and no further work was done on this subject.

SOLVENT EVALUATION

In order to evaluate the effect of various solvent and to

determine which should be used for detailed studies, a large number of solvents were contacted with shale oil. The solvents studied fell under three headings: pure solvents, disolvent mixtures, and trisolvent mixtures. Also, some chemicals were used on the crude shale oil which reacted with the oil. Compounds which reacted with the oil were not studied in detail. The solvents used for detailed study were those which offered promise from the preliminary investigations and which gave no indication of reaction with the oil.

To be successfully used in refining oils, a solvent must have four properties. First, the solvent must be immiscible with a large part of the oil in order that a separation into two layers will occur. Secondly, the solvent must exhibit selective solvent preference for either the desirable or undesirable portion of the oil. Third, the density of the solvent must be such that a separation into two or more layers is effected. Fourth, the solvent must have some property or properties which can be used to separate the solvent from the oil it has extracted and also to recover the solvent which has entered the refined-oil phase. The usual cost of solvents is so great that it is not economic to allow any appreciable amount of solvent to be lost from the system. The four qualities, immiscibility, selective properties, suitable density, and recovery properties, must be kept in mind at all times while working with solvents.

The procedure used in the preliminary testing of solvents was to contact 50 cc of oil at room temperature with an equal

volume of solvent. The separation tendency of the solvents was noted, as were the colors of the layers formed.

Pure Solvents

The first tests on solvents were made by contacting many solvents with crude shale oil and noting those which seemed to extract some materials from the oil. A summary of the work performed is given in Table IV. Except for dilution naphtha, a ratio of 1:1 of oil to solvent was used.

Results: From a study of Table IV it may be seen that very few of the solvents separated themselves from the oil, probably because of the large amounts of aromatics, resins, and asphalt present in the crude shale oil. Since most of the solvents used in the petroleum industry show a preferential solubility for such components, it is reasonable to assume that if the concentration of these compounds reaches a large value, the solvent will become miscible with the oil. Several solvents, such as phenol, chlorex, cresol, and aniline used in the manufacture of lubricating oils, gave no separations. That is, these solvents when mixed with the shale oil were above their critical solution temperatures.

Only eight solvents separated from the oil, and of these eight, one, ethyl acetate, appeared to react with some of the oil. Of the seven remaining, four showed only slight extraction as shown by the green or yellow color of the solvent layer. Two solvents showed promise of being effective. The first of these, furfural, extracted some dark material

from the oil. Furfural is an excellent solvent for asphaltic and resinous material and is widely used for its solvent powers in the petroleum industry. The second of these solvents was dilution naphtha. For the work in this report, the product of the Phillips Petroleum Company was used. This material has a very low distillation range, the end-point being about 250 F. By the addition of a large amount of this material to the oil, a large part of the asphalt in the crude was precipitated. Dilution naphtha may be thought of as a solvent which works exactly opposite to other solvents. The usual solvent dissolves the undesirable compounds and carries them from the system, whereas naphtha dissolves almost all the oil and carries the desirable compounds from the system, leaving the undesirable ones.

The third solvent which appeared to extract some material from the oil was a mixture of phenol and 20% water. It was found, however, that a large part of the phenol remained in the oil and that the bulk of the solvent layer consisted of the water. The oil phase extracted phenol from the water solution instead of phenol extracting components from the oil. The addition of such a large amount of water to the solvent increased the polarity so that extraction was not effective.

Conclusions: The first conclusion was that mechanical handling of crude shale oil is difficult because the oil is very viscous and heavy, producing difficult, slow separations of solvent and oil. The oil has a noticeable tendency to emulsify. These effects could of course be somewhat lessened

TABLE IV

Crude Shale Oil Contacted With Pure Solvents

at 75 F

Solvent	Ratio Oil to Solvent	Phases	Cast of Oil Layer	Cast of Solvent Layer
None	-----	1	Black	-----
Acetic Acid	1:1	1	"	-----
Acetic Anhydride	1:1	1	"	-----
Acetophenone	1:1	1	"	-----
Aniline	1:1	1	"	-----
Benzaldehyde	1:1	1	"	-----
Chlorex	1:1	1	"	-----
Cresol	1:1	1	"	-----
Dioxane	1:1	1	"	-----
Ethylaceto- acetate	1:1	2 (Reaction)	Brown	Brown
Ethylene glycol	1:1	2	"	Green
Formaldehyde	1:1	2	Black	"
Formic Acid	1:1	1	"	-----
Furfural	1:1	2	Brown	Black
Glycerine	1:1	2	Black	Yellow
Methyl ethyl ketone	1:1	1	Black	-----
Nitrobenzene	1:1	1	"	-----
Nitromethane	1:1	1	"	-----
Paraldehyde	1:1	1	"	-----
Phenol*	1:1	1	"	-----
Phenol and 10% water*	1:1	1	"	-----
Phenol and 20% water*	1:1	2	Brown	Brown
Water	1:1	2	Black	Yellow
Dilution Naphtha	1:3	2	Green	Black Asphalt Precipitate

* Used at a temperature of 110 F.

by an increase in temperature, which would reduce the viscosity of the oil.

Studies of the solvent extraction of shale oil by pure solvents lead to the conclusion that two solvents offered promise. These were furfural and dilution naphtha. Dilution naphtha represents a class of compounds which show promise as solvents: light paraffin hydrocarbons of preferably not over five carbon atoms in the molecule.

Centrifuge Tests: The next tests were performed to determine the effect of centrifuging crude shale oil in order to remove any heavy asphalt, coke, shale dust, or water present in the oil. It was also desired to evaluate the effect of the addition of dilution naphtha to the oil in the precipitation of asphalt.

Three tests were performed: on crude shale oil, on shale oil diluted with naphtha, and on shale oil diluted with benzene. The method used in these tests was that prescribed by A.S.T.M. Method D 96-40, Water and Sediment in Petroleum Products by Means of Centrifuge.

The first of the centrifuge tests was made on crude shale oil. After centrifuging, 1.4% by volume of sediment had been collected in the bottom of the centrifuge tube. This sediment under ultraviolet light appeared a loose, brownish, non-asphaltic material. This sediment was probably coke, shale dust, and water.

The second test, made on shale oil plus naphtha in a 1:2 ratio respectively, produced 6% black, tarry, and

asphaltic sludge. It is of interest that about four times as much sediment was precipitated with naphtha as with shale oil alone.

To evaluate the effect on the shale oil, of a substance which is known to have good solvent powers for asphalt, a mixture of one part of shale oil to two parts of benzene was centrifuged as before. The sediment produced was 1.65% of the shale oil by volume. The type of sediment was similar to that produced from the crude oil itself. The only effect of the benzene was to increase slightly the amount of sediment. This fact tends to substantiate the theory that the sediment from this test and the first test was mainly coke, carbon, fine shale dust, and water. Such materials are insoluble in benzene. The effect of the benzene seems to have been the lowering of the oil viscosity and solvent action on the film of asphalt around suspended particles, which allowed more fine material to settle out during the centrifuging process. If a decrease had occurred in the amount of sediment in the centrifuge test using benzene as compared to the sediment from crude shale oil, part of the sediment would probably have been asphalt.

The conclusions to be drawn from the centrifuge tests are that the addition of naphtha to shale oil causes a considerable amount of gummy, tarry, asphaltic material to be precipitated; the water and sediment content of the shale oil is 1.4%, or about one-fourth of the amount precipitated with naphtha; and benzene has no effect on the type and amount of deposit except slightly to increase the amount

because of reduction in the oil viscosity and solvent effect on asphalt.

Two Solvents

After the study of single solvents, investigation was made of the effect of a two-solvent mixture on the crude oil. The work can be divided into two sections: the first deals with the use of two solvents, one of which is a highly polar material such as water or methyl alcohol; the second with the use of two solvents, one of which is dilution naphtha.

Polar Materials: The first part of the work using polar solvents is presented in Table V. The polar material dissolves the selective solvent and because of its immiscibility with the oil, permits a separation to take place between the oil and the mixture of solvents. Saturated solutions or 1:1 solutions of solvent to oil were used in the tests.

Results: All mixtures tried gave separations. However, by a study of Table IV it can be seen that none proved very effective. Formic acid and water was the only mixture which appeared to extract any material, but the presence of reaction products discouraged further work.

Conclusions: The conclusion from the work described in this section is that the use of any appreciable amount of water to adjust the polarity of the solvent is not successful. If water or similar mediums are used, their amounts should be kept as low as possible, preferably below 10% by volume.

TABLE V

Use of Polar Medium in Solvent Extraction
at 75 F

Solvent	Ratio Oil to Solvent	No. of Phases	Color of Oil	Color of Solvent
Acetamide and water	1:1	2	Black	Yellow
Acetanilide and water	"	"	"	"
Benzoic acid and methanol	"	"	"	"
Formic acid and water	"	"	"	Brown (some ppt.)
Hydroquinone and water	"	"	"	Yellow
B-Naphthol and water	"	"	"	"
Oxalic acid and water	"	"	"	Blue
Resorcinol and water	"	"	"	Yellow
Salicylic acid and methanol	"	"	"	Blue
Sodium acetate and water	"	"	"	Yellow
Stearic acid and water	"	"	"	Blue
Tartaric acid and water	"	"	"	Blue
Thymol and water	"	"	"	Yellow

Dilution Naphtha: The next study used dilution naphtha with various solvents. The dilution naphtha dissolved all of the oil; and the solvents, if immiscible with naphtha, formed a second layer which contained some of the shale oil. The ratio of naphtha to oil was 3:1 in all cases. The use of naphtha had three distinct advantages: (1) the oil was diluted to such an extent that it was very fluid and easy to handle, (2) the addition of naphtha precipitated from 7 to 12% by volume of the oil as asphalt, and (3) the addition of such a large amount of paraffin-type compounds produced an oil mixture in which several of the solvents were insoluble, whereas no separation could be obtained by using the same solvents with undiluted shale oil.

Results: A summary of the results obtained is given in Table VI. It can be seen that four solvents gave encouraging results: furfural, aniline, nitromethane, and phenol plus 5% water. Pyridine plus water gave a separation but from the color of the extract layer, results were not promising.

Conclusions: Conclusions from tests in this section were that the use of two solvents, one being dilution naphtha, proved promising. Separation of solvents and oil was easier than in previous tests. The solvents such as furfural, phenol, aniline, and nitromethane which gave separations, are known to have been used as selective solvents for undesirable compounds in lubricating oils and light distillates in the petroleum industry. The use of dilution

TABLE VI

Solvent Treatment of a Mixture of Shale Oil
and Dilution Naphtha

Solvent	Ratio Oil- Naphtha to Solvent	No. of Phases	Oil Color	Solvent Color
Aniline	1:3	2	Green	Black
Benzaldehyde	"	1	Brown- green	-----
Chlorex	"	1	"	-----
Cresol	"	1	"	-----
Furfural	"	2	Green	Black
Nitrobenzene	"	1	Brown- green	-----
Nitromethane	"	2	"	Black
Phenol*	"	1	"	-----
Phenol and 5% water*	"	2	Green	Black
Pyridine	"	1	Brown- green	-----
Pyridine plus 10% water	"	2	Green	Green

* Used at 110 F in contrast to other solvents used at 75 F.

naphtha as one solvent precipitates a large part of the asphalt present in the crude oil.

Three Solvents

Only two groups of three-solvent mixtures were studied: dilution naphtha, phenol, and methyl alcohol and pentachlorophenol, dilution naphtha, and methyl alcohol. A 3:1 mixture of naphtha to oil was treated with an equal volume of the solvents noted above. A 30.8% solution of phenol in methyl alcohol was used, and a 10% solution of pentachlorophenol was used.

Results: The phenol and methyl alcohol layer was black and seemed to extract some objectionable compounds. The pentachlorophenol and methyl alcohol layer was blue-brown and extraction was not great. Methyl alcohol was used as a solvent medium since its polarity is much lower than that of water but is still sufficient to produce a separation between the oil and solvent mixture. Also alcohol is able to dissolve much more phenol and pentachlorophenol than water. After 24 hours it was noted that the treated oil from the pentachlorophenol mixture had turned black. This was interesting because the oil had a definite greenish cast before refining. A similar effect was also noted with the use of hydrochloric acid. It is believed that perhaps the chlorine ion is the cause of rapid polymerization and darkening of the oil.

Conclusions: A mixture of phenol and methyl alcohol offers some promise as a solvent when used on a diluted

shale oil solution. The complexity of the action of three solvents is so great, however, that each mixture would constitute an extensive, individual problem for study. Therefore very little further work was done with three-solvent mixtures.

Reaction Compounds

The fourth section of preliminary work was on reaction solvents; that is, those compounds which when mixed with shale oil reacted with the oil. The compounds studied were three different acids: sulphuric, hydrochloric, and mixed alkane sulfonic acids, manufactured by the Standard Oil Company of Indiana.

Results: A summary of results is given on Table VII. The first acid studied was sulphuric acid.

Two different treatments with sulphuric acid were made. The first was on the crude oil itself. Difficulty in separation was encountered because of emulsification. This difficulty was noted whenever crude shale oil was treated. Sulphuric acid definitely reacted with the oil, since an acid sludge was produced. Extraction took place, for the acid layer was brown. The odor of the oil was greatly improved. The acid layer was separated and the oil removed from it by the addition of sodium carbonate. The oil was black and had a pyridinic odor. It is known that the light nitrogen bases are soluble in dilute mineral acids.

The second treatment with sulphuric acid was made on a

TABLE VII

Acid Treatment of Shale Oil

Acid	Ratio Acid to Oil	Notes
10% Sulphuric	1:1 (crude)	Acid sludge formed, acid heat noticeable, acid layer brown with extracted material, bad emulsion of oil and acid.
10% Sulphuric	1:1 (diluted sample)	Same effect as above except emulsion was easily broken.
10% Hydrochloric	1:1 (crude)	Same effect as first 10% sulphuric acid treatment.
10% Hydrochloric	1:1 (diluted sample)	Same effect as second 10% sulphuric acid treatment. Darkening of oil noted after 24 hours.
Methane and Ethane Sulfonic Acid	1:26 *	Sludge formed, reaction not so violent as sulphuric acid, no emulsions, odor improved, action was extraction plus reaction.

* Overall on total diluted samples used. Shale oil was diluted 3:1 with dilution naphtha, that is, one part shale oil to three parts of dilution naphtha.

naphtha-shale oil mixture containing three volumes of naphtha to one volume of shale oil. Sludge was again produced, odor was improved, extraction was evident in the acid layer, and the separation of oil and acid was rapid and clear cut.

From these two treatments with sulphuric acid it was evident that the sulphuric acid reacted with the oil, that the acid extracted some pyridinic-type compounds, that treatment of crude oil with acid would present great difficulty due to emulsification, and that the treatment of diluted shale oil reduced greatly the tendency of oil and acid to emulsify.

Two treatments with hydrochloric acid were made which were exactly similar to those with sulphuric acid. In both, the physical behavior of the mixtures was similar to that in the corresponding treatments with sulphuric acid. The only difference noted between sulphuric and hydrochloric acids was that after about 24 hours, oil treated with hydrochloric acid had turned from green to black. This effect was noted in the treatment with pentachlorophenol and might be attributed to the presence of the chloride ion.

The last acid used was a mixture of methyl and ethyl sulfonic acids, furnished by the Standard Oil Company of Indiana. They are known to have solvent powers for nitrogen and sulphur compounds and are less harsh in their action than sulphuric acid. These acids were used on diluted shale oil. An original treatment of one volume of acids to two volumes of the usual 3:1 diluted oil was used. The acid layer

was used to treat successive portions of oil until by color and odor of the oil the acid sludge or layer seemed to be ineffective. It was found that definite reaction took place, for a considerable amount of heavy acid sludge was formed, and that one volume of pure acids would treat about eight volumes of crude shale oil before becoming ineffective. Since the action of these acids involved reaction with the oil, no further studies were made.

Conclusions: Several conclusions can be drawn from the acid tests described. All the acids used reacted to some extent with the oil. Sulphuric and hydrochloric acids reacted more violently than sulfonic acids. Emulsion tendency of crude shale oil with aqueous acids is great, but this tendency can be lowered by the use of diluted samples of oil. Hydrochloric acid is less satisfactory than sulphuric acid in acid treatment because of darkening of hydrochloric-acid-treated oil after a short period of time. Since the main object of this report is an investigation of non-reaction solvent-extraction processes, no further work was done with acids except as described under the section "DETAILED STUDIES".

Conclusions of Initial Studies

The preliminary studies which have been described established several important facts. First, shale oil used in solvent extraction at a temperature of about 75 F was very difficult to handle and emulsified readily. Second, the only solvent which offered promise with crude shale oil was

furfural. Third, the use of dilution naphtha as a second solvent greatly improved the results of solvent extraction, handling of the oil mixture, separation of solvents and oil, and emulsion tendency of the oil. In addition, the naphtha removed a large part of the asphalt present in the oil. Fourth, the chloride ion may produce darkening of the oil. Fifth, all acids studied reacted with the oil to produce acid sludge, even when used as dilute aqueous solutions. Sixth, the solvents which offer promise are furfural, furfural-naphtha, aniline-naphtha, phenol-naphtha, naphtha, nitromethane-naphtha, methyl alcohol-phenol-naphtha, and perhaps pyridine-naphtha. The next part of the work was a detailed study of each of the above solvents.

DETAILED STUDY OF SOLVENTS

In the initial tests of solvents no attempt was made to study the oil after treatment. Also the procedures used in treating were not standardized. Therefore, to determine quantitatively the effect of a specific solvent, a standardized procedure of treating was established. The specific gravity referred to water at 60 F, nitrogen and sulphur contents, odor, cast under natural and ultraviolet light, recovery of treated oil, and in some cases the gross heating value were determined for the treated oils. Because of lack of equipment for continuous solvent extraction, the procedure was of necessity a batch process. The solvents

used were furfural, aniline, nitromethane, phenol, phenol-methanol, pyridine, sulphuric acid, and dilution naphtha.

Procedure

The procedure used in the detailed studies was arbitrary. As noted before, the oil contained a large amount of undesirable compounds. The usual procedure in lubricating oil manufacture is to use very large volumes of solvent compared to oil, sometimes as much as four or five times the amount of oil. Several qualitative tests were made on the oil contacted with varying amounts of solvent. It was found that the larger the amount of solvent per contact, the more oil was dissolved in the solvent on each contact. Therefore it was considered a somewhat better procedure to use a small amount of solvent a large number of times than a large amount of solvent only once or twice.

The procedure finally adopted was to deasphaltize 200 ml of oil and then treat the remaining oil with various solvents. Each 200 ml of crude shale oil was contacted five times with 100 ml of fresh solvent per contact. This ratio of 2:1 of original charge of shale oil to solvent per contact was maintained at all times. The use of five contacts enabled the maximum effect of each solvent to be shown. The method of contacting was to agitate a measured volume of oil and solvent in a separatory funnel, allow a separation to occur, and then contact the oil again with fresh solvent. The solvent left in the oil was removed by repeated warm water washes.

Tests Performed on Oil

The tests performed fall into two classes: quantitative and qualitative. The quantitative tests include nitrogen and sulphur determination, specific gravity, recovery, and gross heating value. The qualitative tests include odor and color or cast under natural and ultra-violet light.

Solvent Tests

From the preliminary work, several solvents showed promise. The solvents and their methods of application were:

- (1) Furfural used on shale oil deasphaltized with naphtha which had been removed by distillation.
- (2) Dilution naphtha used in a 3:1 ratio on crude shale oil.
- (3) Deasphaltizing with naphtha followed by dewaxing.
- (4) Furfural used on a mixture of naphtha and shale oil.
- (5) Furfural used on a mixture of naphtha and shale oil after the shale oil was first dewaxed.
- (6) Phenol plus 5% water used on a mixture of naphtha and shale oil.
- (7) Phenol plus 5% water used on a mixture of naphtha and shale oil after the shale oil was first dewaxed.
- (8) Nitromethane used on a mixture of naphtha and shale oil.
- (9) Nitromethane used on a mixture of naphtha and

shale oil after the shale oil was first dewaxed.

(10) Aniline used on a mixture of naphtha and shale oil.

(11) Pyridine plus 10% water used on a mixture of naphtha and shale oil.

(12) Sulphuric acid (10%) used on a mixture of naphtha and shale oil.

(13) Phenol-methanol solution (30%) used on a mixture of naphtha and shale oil.

Experimental Results

Furfural Used on Deasphaltized Shale Oil: The first solvent studied was furfural used on the deasphaltized shale oil. It may be remembered that this was the only solvent which appeared promising when used with the crude oil directly. In the preliminary work furfural was used on the crude shale oil directly. However, in the detailed studies it was used on shale oil which had first been deasphaltized. It was believed that a more representative picture of the effectiveness of the solvent could be obtained by first removing asphaltic material by dilution with naphtha, since all other solvents were used on deasphaltized oils. The oil used was diluted 3:1 with dilution naphtha, allowed to stand in order that the asphalt would precipitate, separated from the asphalt, and distilled to 250 F to remove the dilution naphtha. This oil was then treated five times with 100 cc of fresh furfural per contact.

Recovery: The recovery of treated oil was 23% of the original crude shale oil. This huge loss is not strange since, as was pointed out before, shale oil contains a large amount of aromatics and resins which are soluble in furfural. Also the large number of contacts and the batch method of contacting contributed to the loss.

Nitrogen and Sulphur Content: This oil, as would be expected from the large losses, was very much better than the original oil. The nitrogen content was reduced to 0.397% and the sulphur content was reduced to 0.603%. The bulk of the nitrogen and sulphur were probably in some difficultly removable forms such as pyrroles and thiophenes.

Color: The oil had a greenish cast in natural light and a light grey-green in ultraviolet light.

Odor: The odor was very good (see p. 63), tending to be more like that of a lubricating oil.

Specific Gravity: The specific gravity of the oil was the lightest of all oils treated, being 0.8514 or 34.7 A.P.I.

Gross Heating Value: The heating value of the oil was not determined.

Dilution Naphtha: As was noted in the preliminary tests, the addition of dilution naphtha to crude shale oil precipitated asphalt from the oil. The ratio of dilution naphtha to crude oil used in this test and in all future tests was 3:1. It was found that the quantity of asphalt which was deposited varied from test to test, probably because of slight

variations in sampling or small changes in temperature. Almost all oil samples fell between 8 and 10% asphalt, with the bulk between 8 and 9%. Crude shale oil was diluted as stated, shaken well in a separatory funnel, and allowed to stand for 24 hours. After that time, the fluid solution of naphtha and oil was decanted, and the black, gummy asphalt was left in the funnel. This deasphalting procedure was followed in all subsequent tests so that results from various tests would be comparable. In this particular test, the naphtha was distilled off to a vapor temperature of 250 F after which the residual oil was tested as usual for nitrogen and sulphur contents and other properties.

Recovery: The recovery of treated oil was from 90 to 92%. The only loss was due to asphalt.

Nitrogen: The nitrogen content of the deasphaltized oil was 1.47%. This is almost identical with the nitrogen content of the crude, which was 1.45%. This gives another indication that the nitrogen cannot be separated in any one particular part of the oil.

Sulphur: The sulphur content was 0.98% compared to crude oil of 0.955%. As with nitrogen, no drastic change was evident.

Odor: The odor of the recovered oil was foul, having the typical shale-oil odor. This is not surprising, considering the high sulphur and nitrogen contents reported above.

Color: The color of the oil was black and no

improvement over that of the crude shale oil was evident. The color of the oil under ultraviolet light was dark brown.

Specific Gravity: The specific gravity of the oil was 0.9117 or 23.7 A.P.I. This is somewhat lighter than the crude, which tested 0.9176 or 22.7 A.P.I.

Gross Heating Value: The heating value of the oil was 18,262 Btu per lb. This value correlated with the specific gravity at 60 F gives a value of less than 10 for the characterization factor for this oil. The heating value determined for the crude oil was 18,260 Btu per lb. The crude also had a characterization factor of less than 10. These values indicate the high unsaturation of the material.

Pour Point: The pour point of the deasphaltized oil was 65 F as compared to 61 F for the crude oil. The rise is logical, since it is known that asphaltic materials act as pour-point depressants.

Analysis of Shale Oil Asphalt: To determine the general composition of the material precipitated from the oil by the addition of dilution naphtha, an analysis of the asphalt was made following a rapid laboratory bitumen analysis method developed in the Petroleum Refining Department of the Colorado School of Mines. The method assumes the presence in such materials as natural bitumen or petroleum residue of five general groups of hydrocarbons in addition to moisture, volatile matter, fixed carbon, and mineral or other inert material. These general hydrocarbon groups are classified as oil, resins, asphaltenes, carbenes, and carboids.

A weighed, pulverized sample is placed in a filter paper of known weight. The sample on the filter is washed five times with 50 cc of a low boiling paraffin distillate within the range of A.S.T.M. precipitation naphtha. The 50 cc of naphtha is used in all five washes. After the last wash, the sample is placed in a drying oven at 210 F for 15 minutes, and is then cooled and weighed. The difference in weight is oil content.

The residue in the filter paper is washed five times with the same 50 cc of a 50/50 mixture of dilution naphtha and isopropyl alcohol. The sample is dried and weighed as before. The loss in weight is oil-soluble resins.

The foregoing procedure is repeated with 50 cc of pure benzol, and the weight loss is recorded as asphaltenes or asphalt-soluble resins. Only three washes are necessary with the benzol and the solvents in the following steps.

The procedure is repeated, using 50 cc of carbon disulfide. The material dissolved is carbenes.

It was found in working with the asphalt and other gums and precipitates from shale oil that these materials always seem to contain some amount of material which is readily soluble in a polar solvent such as methyl alcohol. Therefore in the analysis of the shale oil asphalt, methyl alcohol was used as a solvent following the carbon disulfide. Alcohol is not a solvent used in the procedure as originally developed. The procedure used with the methyl alcohol was similar to the procedure with the other solvents. The residue which should

contain only fixed carbon, sand, or mineral matter was washed five times with one 50-cc portion of methyl alcohol. The material dissolved is thought to be a highly oxygenated group of compounds of unknown structure.

The remainder of the material is burned in an oxidizing blast flame in a tared crucible and recorded as mineral matter.

The oily constituents made up 3.79% of the asphalt. These materials were amber in color, were oily, and smelled like a heavy lubricating oil distillate.

Oil-soluble resins made up 18.05% of the asphalt. The resins were black, tacky, and viscous and smelled like coal tar.

The asphalt-soluble resins extracted with benzol made up 34.78 % of the asphalt. These materials were hard, brittle and shiny, and smelled similar to the oil-soluble resins.

Carbenes made up 18.77% of the asphalt and were shiny, black, and brittle.

Methyl alcohol extracted material of unknown structure, which amounted to 8.12% of the asphalt. These materials were powdery, black, and dull.

Residue and mineral matter amounted to 16.49% of the asphalt and was black, dull, and powdery.

The analysis shows the bulk of the asphalt to be made up of resins, carbenes, and mineral matter. An appreciable part of the asphalt was soluble in the methyl alcohol. No further work was done on this subject.

Deasphaltizing-Dewaxing: To study the effect of dewaxing the shale oil, a quantity of oil was deasphaltized as

described under the previous section, the dilution naphtha removed by distillation, and the shale oil diluted with three times its volume of acetone. The acetone-shale oil mixture was chilled to 30 F and the wax filtered off. The acetone was removed by distillation leaving the deasphaltized, dewaxed oil.

Recovery: The recovery of deasphaltized, dewaxed oil was 84%. The wax was brown, amorphous, and low-melting.

Nitrogen: The nitrogen content of the recovered oil was 1.64%. Since the wax would contain little nitrogen, its removal would concentrate the nitrogen in the remaining oil.

Sulphur: The sulphur content of the oil was 0.957% or almost identical with that of the crude shale oil.

Odor: The odor of the oil was good.

Color: The color of the oil was a very dark brown.

Specific Gravity: The specific gravity of the oil was 0.9206 or 22.2 A.P.I. This is slightly greater than the crude shale oil or the deasphaltized oil. Some decomposition or polymerization may have taken place during the two distillations which removed the naphtha and the acetone.

Gross Heating Value: The heat of combustion of the oil was 18,490 Btu per lb. This value is higher than that of the crude oil or that of the deasphaltized oil. The characterization factor of the recovered oil was 10.19.

Pour Point: The pour point of the oil was 50 F or 15 F lower than the pour point of the deasphaltized stock and

11 F lower than the pour point of the crude shale oil.

It may be concluded from these results that the process of dewaxing and deasphaltizing the oil results in an oil whose properties are very similar to those of the original oil. The oil is naturally somewhat more fluid, but almost no nitrogen or sulphur compounds are removed by this process. The wax obtained from the shale oil is of poor quality, has a low-melting point, and is contaminated with much resinous and colored material that can be removed only with great difficulty.

Furfural on Shale Oil-Naphtha: The next solvent studied was furfural used on a 3:1 mixture of dilution naphtha to shale oil. The precipitated asphalt was separated from the oil before solvent treatment. Two samples of oil were treated. The first sample was treated with only two contacts of furfural; the second sample was treated with the usual five contacts with furfural. Since furfural seemed to be effective as a solvent, the effect of only a few contacts was compared to the effect of a large number of contacts in the case of the second sample.

The properties of the twice-contacted oil will be given, followed by the properties of the oil contacted five times.

Recovery: The oil recovery after two contacts was 77%. The recovery after five contacts was 58%.

Nitrogen: The nitrogen contents were 0.856% and 0.555% respectively.

Sulphur: Sulphur contents were 0.871% and 0.818%.

Odor: The odors were fair and excellent.

Color: The first treatment had a dark green color. The second oil had a green color which was grey-green under ultra-violet light.

Specific Gravity: No gravity was determined on the twice-treated oil. The specific gravity of the heavily treated oil was 0.8654, or 32.0 A.P.I. This represents a considerable decrease in gravity from the crude oil.

Gross Heating Value: The gross heating value of the lightly treated oil was not determined. The heating value of the heavily treated oil was 18,779 Btu per lb. This value, as might be expected from consideration of the reduction in sulphur, nitrogen, and specific gravity, was considerably larger than previous values. The characterization factor of the oil was 10.42.

From a study of the results of the tests it may be concluded that as low as two contacts of furfural with shale gives a large reduction in nitrogen content. Sulphur content was reduced but not too greatly as compared to nitrogen. Five contacts with furfural give results comparable to the results from two contacts. The nitrogen is further reduced, although not proportionately to the first two treatments. Sulphur is reduced but still remains high. The greatest change in properties is in specific gravity, which rises to the value of a heavy crude oil. The heating value is also materially increased, with a resultant increase in the characterization factor.

The recovery of the heavily treated oil was not very good

but it must be remembered that the method of treatment was by batch contacts, which always give lower recovery than a continuous countercurrent process such as would be used in commercial operation.

Furfural on Deasphaltized-Dewaxed Oil: A portion of the oil from the dewaxing operation was diluted 3:1 with naphtha, and this oil treated five times with furfural. The object of this experiment was to determine any holding effect of the wax for undesirable constituents in the oil.

Recovery: The recovery of treated oil was 41%. This is somewhat lower than was anticipated.

Nitrogen: Nitrogen content was 0.638%.

Sulphur: The sulphur content was 0.841%.

Odor: The odor of the oil was excellent.

Color: Color of the oil was green in natural light and brown-yellow in ultraviolet light.

Gravity: Specific gravity of the oil was 0.8794 or 29.4 A.P.I.

Gross Heating Value: None was determined.

Conclusions of the above tests are that dewaxing does not appreciably affect the selectivity of the furfural solvent. In fact, the recovery and other properties are lower than would be expected as indicated by the removal of 10% of the oil as wax. It is probably that the adverse effect of the removal of the wax can be attributed to the increase in the concentration of aromatic and resinous compounds in the oil, which would cause a greater amount of the oil to be dissolved

in the solvent. The wax, being predominantly paraffinic, would tend to remain in the oil phase and perhaps help hold some of the aromatic compounds in the oil also.

Phenol on Shale Oil-Naphtha: From preliminary studies, phenol plus 5% water seemed to be effective as a solvent when used on a 3:1 mixture of dilution naphtha and shale oil. Therefore after separation of asphalt, the oil mixture was treated five times in the usual manner with pure phenol plus 5% water. The phenol-water mixture was heated in an oven until it was fluid, and during separation of the solvent and oil the separatory funnel was placed in a constant-temperature oven.

It may be noted that the use of phenol-naphtha together is similar to the familiar Duo-Sol Process used in the petroleum industry.

Recovery: The recovery of treated oil was 47%. This is somewhat lower than when furfural was used.

Nitrogen: Nitrogen content of the treated oil was 0.626%, which represents a great decrease in the amount of nitrogen.

Sulphur: Sulphur content was 0.841%. The large amount of sulphur still present is unexpected, considering the findings of Laspe 12/ who reduced the sulphur content of

12/ Idem., p. 55.

shale gasoline to half the initial value by treatment with phenol. This again proves the fallacy of attempting to draw conclusions of solvent treatment of material such as crude

shale oil from results obtained from a special product such as gasoline.

Odor: The odor of the finished oil was excellent.

Color: Color of the oil was green in natural light and very light green-yellow in ultraviolet light.

Specific Gravity: The specific gravity of the oil was 0.8692 or 31.3 A.P.I.

Heating Value: None was determined.

From a study of the above tests it can be seen that the phenol acted effectively as a solvent, although not so well as furfural. The sulphur and nitrogen contents of the treated oil were somewhat higher than those of the furfural-treated oil and the recovery was 10% less.

Phenol on Deasphaltized-Dewaxed Oil: A portion of the oil from the dewaxing operation was diluted 3:1 with naphtha, and this oil treated five times with phenol plus 5% water in the preceding test. It was desired to evaluate the effect of solvent extraction after wax removal.

Recovery: The recovery of treated oil was 39%. The reduction in recovery from the previous tests is due to wax removal.

Nitrogen: Nitrogen content was 0.575%. This is lower than in the preceding test. For furfural the results were exactly reversed; that is, the results from dewaxed oil were much higher than from nondewaxed oil. In the case of phenol, it appears from the data that the wax may exhibit some holding effect for nitrogen compounds.

Sulphur: Sulphur content was 0.866%. This is somewhat higher than in the previous test and follows the trend observed in furfural treatment. Apparently the wax exerts no holding effect on sulphur compounds, and wax removal only tends to concentrate the sulphur compounds in the oil.

Odor: The odor of the oil was excellent.

Color: The color of the oil in natural light was green and was brownish yellow in ultraviolet light.

Specific Gravity: The specific gravity of the oil was 0.8844 or 28.5 A.P.I. This is somewhat lower than in the previous tests but follows the trend set by furfural.

These tests show that in general the effect of dewaxing is the same for phenol as for furfural. Nitrogen content seems to be slightly decreased from the nondewaxed test, but all other properties increase as they did for furfural.

Nitromethane on Shale Oil-Naphtha: The usual 3:1 mixture of naphtha and shale oil was treated in the usual manner by nitromethane.

Recovery: Recovered oil was 77% of the original crude shale oil.

Nitrogen: Nitrogen content of the treated oil was 1.03%.

Sulphur: The oil contained 0.832% sulphur.

Odor: Odor of the oil was good.

Color: Color of the oil in natural light was greenish-brown. Ultraviolet light showed a dark brown.

Specific Gravity: Specific gravity of the oil was 0.8927 or 27.0 A.P.I.

It is evident from the results above that nitromethane is not so effective a solvent as either phenol or furfural. This is especially evident when considering nitrogen removal. Even two treatments with furfural were more effective than five contacts with nitromethane. It is interesting that sulphur reduction was almost the same with this solvent as with the phenol and furfural. In this respect, nitromethane does not seem to offer promise as an effective solvent.

Nitromethane on Deasphaltized-Dewaxed Oil: In order to study the effect of dewaxing on the solvent action of nitromethane and to confirm the trends shown by phenol and furfural, a portion of the oil from the dewaxing operation was diluted 3:1 with naphtha, and this oil treated as before with nitromethane.

Recovery: Recovery was 39%. This is a very large drop from the 77% of the previous test.

Nitrogen: The oil contained 1.47% nitrogen.

Sulphur: The oil contained 0.882% sulphur.

Odor: The odor of the oil was excellent.

Color: The color of the oil was brown in natural light and dark brown under ultraviolet light.

Specific Gravity: The oil had a specific gravity of 0.9297 or 20.7 A.P.I.

The properties of this oil increased, as was expected from the results with phenol and furfural. However, the

results of the tests were much higher than expected, especially nitrogen content and specific gravity. It is believed that the explanation for this radical change in properties lies in the fact that during the distillation to remove naphtha, the oil began to crack. This may account for the high specific gravity and nitrogen content, since some of the heavy compounds polymerized to form a much heavier oil. The vapor temperature of the distillation was 250 F and the distillation was carried out in a standard Hempel distillation flask. This is another evidence of the sensitiveness of shale oil to heat.

From the results of this test and the previous one, it may be concluded that nitromethane is not so effective a selective solvent as furfural and phenol.

Aniline on Shale Oil-Naphtha : Aniline seemed to be promising from the preliminary test. Since a straight-chain nitro-compound such as nitromethane was not effective, a ring compound such as aniline containing nitrogen might prove to be better as an extracting agent, especially for nitrogen compounds.

Recovery: The treated oil was 51% of the original oil.

Nitrogen: The nitrogen content of the oil was 0.733%. This is considerably higher than with either phenol or furfural.

Sulphur: The oil contained 0.877% sulphur, which was also higher than the corresponding values for phenol and

furfural.

Odor: Odor of the oil was very good.

Color: Color was green in natural light and brown-yellow under ultraviolet light.

Specific Gravity: Specific gravity of the oil was 0.8855 or 28.3 A.P.I.

The results above show that aniline is not so effective a solvent as furfural or phenol, but is better than nitromethane.

Pyridine on Shale Oil-Naphtha: The preliminary tests of pyridine showed some extraction taking place, but the solvent effect did not seem to be good, since the solvent layer was greenish. However, a study was made on pyridine to determine if any solvent action was exhibited. Ten per cent by volume of water was added to the pyridine to give a separation of solvent and oil.

Recovery: Recovery of treated oil was 82%.

Nitrogen: The treated oil contained 1.14% nitrogen.

Sulphur: The oil contained 0.957% sulphur.

Odor: The odor of the oil was fair.

Color: The color of the oil was black in natural light and dark brown in ultraviolet light.

Specific Gravity: The gravity of the oil was 0.9024 or 25.3 A.P.I.

The effect of pyridine as an extraction agent is negligible.

Sulphuric Acid on Shale Oil-Naphtha: A treatment was made

with 10% sulphuric acid used exactly as the solvents to study the effect of acid-treating on the oil. As expected, considerable sludge was formed especially in the first several contacts. After treatment, the oil was washed with 5% sodium hydroxide and with water.

Recovery: The oil recovered was 66% of the original shale oil.

Nitrogen: The oil contained 1.06% nitrogen.

Sulphur: The oil contained 0.988% sulphur.

Odor: The odor of the oil was good.

Color: The color of the oil was greenish-brown in natural light and medium brown in ultraviolet light.

Specific Gravity: The specific gravity of the oil was 0.9030 or 25.2 A.P.I.

Heating Value: The heating value of the oil was 18,429 Btu per lb which corresponds to a value of the characterization factor of 10.03.

The above results show that a treatment with sulphuric acid is not very effective in removing all types of nitrogen compounds present in shale oil. The sulphur content of the oil increased slightly, and it is likely that a portion of the oil was sulphonated and that this material, being oil-soluble, raised the sulphur content of the oil. The acid used was not very strong, but was sufficient to remove light nitrogen bases. The Bureau of Mines 13/ uses 20% acid to remove tar bases

13/ Ball, J.S., Dinneen, G.U., Smith, J.R., Bailey, C.W., and Van Meter, R., Composition of Colorado shale-oil naphtha: Ind. and Eng. Chemistry, vol. 41, no. 3, p. 581-587, Mar. 1949.

quantitatively from shale oil naphtha.

It is evident from the results of the previous experiments that the poorest of the solvents tested is superior to sulphuric acid in almost every way. This solvent is nitromethane. The recovery with nitromethane was 11% greater than with the acid, the sulphur content was lower, and the nitrogen content in both cases was almost the same.

Phenol-Methanol on Shale Oil-Naphtha: Only one solvent mixture was used utilizing three solvents simultaneously. The three solvents used were phenol, methyl alcohol, and naphtha. The solution of methanol and phenol was used at a 30% concentration of phenol by weight. This selection was arbitrary, but sufficient phenol was present that its solvent power could be utilized. The methyl alcohol served two purposes: first, it produced a separation of two phases, and second, phenol is infinitely soluble in methanol and thus tended to stay in the alcohol phase to a greater extent than if water had been used.

Recovery: The recovered oil amounted to 80% of the original crude shale oil.

Nitrogen: The treated oil contained 0.896% nitrogen.

Sulphur: The sulphur content of the oil was 0.85%.

Color: The color of the oil was black.

No further tests were made on the oil. There was no unusual reduction in sulphur and nitrogen contents. The use of three solvents may be found effective, but it may be seen that the possibilities of various combinations as well as the

action of various solvents in the phases formed are almost infinite and would require a large amount of study.

Summary of Detailed Studies

In Tables VIII and IX summaries are given of the data obtained in this section. Table VIII lists the quantitative tests performed on the oil; Table IX lists qualitative tests performed on the oil. The numbers in Table IX refer to the relative order of the oils in their apparent degree of refining. The greenest or lightest colored oil is listed as 1, the next darker is 2, etc. Odor is graded on a relative scale of excellent, very good, good, fair, and poor.

Discussion of Results

Although only a very small part of the field of solvent extraction was covered in this report, several interesting trends and effects were noted.

The first point established was the impossibility of isolating a large amount of nitrogen and sulphur in any one particular fraction of the oil. This fact leads to two alternative procedures: treating of the entire crude oil by some process of which solvent extraction is one possibility, or treating of each of the products from the crude oil by some process, which might also be solvent extraction. In either procedure, it is believed that the information brought forth by this report would be of value.

The most important study of this report has been the action of shale oil to various solvents. That is, shale oil

TABLE VIII

Quantitative Tests on Refined Shale Oils

Test*	N %	S %	Recovery %	Sp. Gr. 60/60	Degrees A.P.I.	Btu per lb	K
1	0.733	0.877	51	0.8855	28.3	----	----
2	1.45	0.955	100	0.9176	22.7	18,260	below 10
3	1.47	0.980	90-92	0.9117	23.7	18,262	" "
4	1.64	0.957	84	0.9206	22.2	18,490	10.19
5	0.397	0.603	23	0.8514	34.7	----	----
6a	0.555	0.818	58	0.8654	32.0	18,779	10.42
6b	0.856	0.871	77	-----	----	----	----
7	0.638	0.841	41	0.8794	29.4	----	----
8	1.03	0.832	77	0.8927	27.0	----	----
9	1.47	0.882	38	0.9297	20.7	----	----
10	0.626	0.841	47	0.8692	31.3	----	----
11	0.575	0.866	39	0.8844	28.5	----	----
12	1.14	0.957	82	0.9024	25.3	----	----
13	1.06	0.988	66	0.9030	25.2	----	----
14	0.896	0.85	80	-----	----	----	----

*Test

- 1 Aniline on shale oil-naphtha.
- 2 Crude shale oil.
- 3 Deasphaltized crude shale oil.
- 4 Deasphaltized-Dewaxed shale oil.
- 5 Furfural on undiluted deasphaltized oil.
- 6a Furfural on shale oil-naphtha five times.
- 6b Furfural on shale oil-naphtha two times.
- 7 Furfural on deasphaltized-dewaxed oil.
- 8 Nitromethane on shale oil-naphtha.
- 9 Nitromethane on deasphaltized-dewaxed oil.
- 10 Phenol on shale oil-naphtha.
- 11 Phenol on deasphaltized-dewaxed oil.
- 12 Pyridine plus 10% water on shale oil-naphtha.
- 13 Sulphuric acid (10%).
- 14 Phenol-Methanol on shale oil-naphtha.

TABLE IX

Qualitative Tests on Refined Shale Oils

Test *	Odor	Color Natural Light	Color Ultraviolet Light
1	Very good	Green 3	Brown-yellow 4
2	Poor	Black	Yellow-brown 6
3	"	"	Dark-brown 8
4	"	Very dark brown	Dark-brown 8
5	Excellent	Green 4	Gray-green 3
6	"	" 4	Brown-yellow 4
7	Very good	" 4	Light gray-green 3
8	Good	Green-brown 6	Dark brown 6
9	Excellent	Brown 7	Dark-brown 7
10	"	Green 1	Very light green-yellow 1
11	"	" 2	Green-yellow 2
12	Fair	Black	Dark-brown 7
13	Good	Greenish-brown 5	Brown 5
14	----	Black	----- -

* Test

- 1 Aniline on shale oil-naphtha.
- 2 Crude shale oil.
- 3 Deasphaltized crude shale oil.
- 4 Deasphaltized-Dewaxed shale oil.
- 5 Furfural on shale oil-naphtha five times.
- 6 Furfural on deasphaltized-dewaxed oil.
- 7 Furfural on undiluted deasphaltized oil.
- 8 Nitromethane on shale oil-naphtha.
- 9 Nitromethane on deasphaltized-dewaxed oil.
- 10 Phenol on shale oil-naphtha.
- 11 Phenol on deasphaltized-dewaxed oil.
- 12 Pyridine plus 10% water on shale oil-naphtha.
- 13 Sulphuric acid (10%)
- 14 Phenol-Methanol on shale oil-naphtha.

Note: Colors are numbered according to the relative lightness of the oil; that is, the lightest colored oil is 1, the next darkest is 2, etc.

cannot be refined satisfactorily by one solvent alone, at least by none of the solvents studied in this report. There are two reasons for this: first, the solvent and oil are slow to separate, because of small difference in specific gravity; and second, a large part of the oil is soluble in the solvent, and thus produces unnecessarily large losses. In contrast to the use of one solvent, a mixture of two solvents of different types such as naphtha and furfural seems to work much more satisfactorily. Extraction of sulphur and nitrogen is not so good as that with a single solvent, but recovery is over twice as great. With regard to recovery, it must be remembered that all treating done in this report was batch, whereas any commercial process would utilize a continuous extraction with resulting better recovery.

The most effective solvent tested was furfural. The second most effective solvent was phenol. These two solvents seem to be similar in their action.

It is of interest to study the effect of solvents of various structures on the quality of the oil. The four most effective solvents were phenol, furfural, nitromethane, and aniline. Of these, one is a straight-chain compound containing a nitro-group, two contain six-membered rings, and one contains a five-membered ring.

The most effective solvent, furfural, is a heterocyclic five-membered-ring compound containing one atom of oxygen in the ring and one CHO group attached to the ring. It is believed that the bulk of the sulphur in shale oil occurs as

thiophenes and the difficulty-removed nitrogen as pyrroles. Both thiophene and pyrrole are five-membered-ring compounds closely related to furfural. It may well be that the effectiveness of furfural as a solvent extraction agent is due to the similarity in structure of the solvent to the material whose removal is desired. Furfural has been used in the petroleum industry for the desulphurization of gas oil. 14/

14/ Kemp, L.C., Hamilton, G.E., and Gross, H.H., Furfural as a selective solvent in petroleum refining: Ind. and Eng. Chemistry, vol. 40, no. 2, Feb. 1948. pp. 220-227.

After only two or three contacts of furfural on gas oil, the sulphur content was greatly reduced. The effect of furfural on sulphur content of shale oil was small. Even with a loss of 75% of the oil to the solvent phase, the sulphur content of the oil was reduced only by about 30%. This is another illustration of the difficulty of sulphur removal from shale oil as compared with petroleum.

The second most effective solvent was phenol, an aromatic ring with an attached OH group. The effect of phenol was very similar to that of furfural except that loss was greater. This greater loss could be expected from two facts: one, that shale oil has a high aromatic content; and two, that phenol could not be separated from shale oil except by the use of water and naphtha. Laspe 15/ found that phenol was an ex-

15/ Op. cit., p. 60.

cellent sulphur removal medium for shale gasoline whereas the effect of furfural was negligible. This suggests the

possibility that phenol removes one type of sulphur compounds, whereas furfural removes another. Perhaps a larger reduction in sulphur could be obtained by the use of both solvents either concurrently or consecutively.

Aniline is an example of the heterocyclic six-membered-aromatic-ring compound. Aniline was less effective than either furfural or phenol in nitrogen reduction, and losses to the solvent layer were greater. This is again an example of the solvent effect of the benzene ring as shown by phenol. Perhaps the most interesting fact about aniline is that the nitrogen removal was less than that with either of the other two solvents, despite the presence of the nitrogen in this solvent. This tends to substantiate the theory that the major portion of the nitrogen does not occur in or attached to six-membered rings.

Despite the presence of a nitro group, nitromethane was ineffective as a solvent, probably because of its straight-chain paraffinic type of structure. This result again strengthens the belief that structure of the solvent is much more important than the groups present.

It has already been noted that the major part of the sulphur was very difficult to remove, not such is apparently the case with nitrogen. Even relatively poor solvents such as nitromethane reduced the nitrogen content by at least 25%. Furfural and phenol used in the presence of dilution naphtha removed as much as 60% of the nitrogen. A certain amount of both the sulphur and nitrogen is fairly easily removed, after

which further removal is very difficult. This is shown by the fact that two furfural contacts removed 40% of the nitrogen, whereas five contacts removed only 60% of the nitrogen originally present in the oil. Most of the nitrogen is in the dark compounds of the oil, for nitrogen content is inversely proportional to the color of the oil.

Dewaxing does not seem to have significant effect on the efficiency of solvent extraction.

Treatment of crude shale oil with sulphuric acid seems to be the poorest procedure of all tested. Losses to sludge are high, and removal of nitrogen and sulphur is low.

CONCLUSIONS

The use of a selective solvent in the presence of a diluent--for example furfural with dilution naphtha-- is the best of the methods studied for solvent refining of shale oil. Furfural and phenol offer the most promise as selective solvents. The use of a diluent, such as dilution naphtha, reduces the viscosity of the oil, exhibits a holding effect for part of the oil, and permits better and more rapid separations of oil and solvent to take place.

Nitrogen reduction of 60% may be readily accomplished. Most of the nitrogen appears in dark compounds, possibly of high molecular weight and of ring structure.

Sulphur removal is very difficult and may prove a greater problem than nitrogen removal.

From the results of the work in this report, solvent refining seems to be a feasible process for the refining of crude shale oil.

FUTURE WORK

It must be emphasized that the work reported here represents but the barest introduction to solvent extraction of shale oil. An enormous amount of future work must be done to completely investigate this huge field of refining.

Future investigations might well be made on:

- (1) A lighter solvent such as propane a) used alone to de-asphaltize the oil and b) used together with furfural and phenol for extraction.
- (2) Continuous extraction of the oil in a column similar to that developed by Scheibel 16/.

16/ Scheibel, E.G., Fractional liquid extraction: Chem. Eng. Progress, vol. 44, no. 9-10, pp. 681-690 and 771-782, Sept. and Oct. 1948.

- (3) The types of compounds removed by various solvents studies by precise distillation and spectroscopy.
- (4) The effect of the sulfolanes as selective solvents. These compounds were developed during the last war by the Shell Development Co., but the writer was unable to obtain a quantity of them for evaluation. However, from their properties and structure (five-membered rings containing SO₂) as reported by Staaterman 17/ they appear very promising.

17/ Staaterman, H.G., Morris, R.C., Stager, R.M., Pierotti, G.J., Manufacture of sulfolanes and use as selective solvents; Chem. Eng. Progress, vol. 43, no. 4, pp. 148-151, April 1947.

- (5) A large class of solvents such as the copper or sodium salts of sulfonic acids and silver phenolsulfonate, 18/ which

18/ Souders, M. Jr., and French, F.A., U.S. Patent 2,449,793

has been used as a selective solvent or is known to exhibit selective properties for unsaturated compounds.

(6) The quality of products derived from solvent-refined shale oil as compared to products from crude shale oil.

(7) The effect of variation of temperature and pressure on the efficiency of various solvents.

(8) The effect of two selective solvents used simultaneously in the presence of a diluent such as propane or naphtha.

BIBLIOGRAPHY

- Ball, J.S., Dinneen, G.U., Smith, J.R., Bailey, C.W., and Van Meter, R., Composition of Colorado shale-oil naphtha: Ind. and Eng. Chemistry, vol. 41, no. 3, pp. 581-587, March 1949.
- Blanding, F.H., and Roetheli, B.E., Retorting oil shale by the fluidized solids technique: Oil and Gas Jour., vol. 45, no. 41, pp. 86-88, Feb. 15, 1947.
- Kemp, L.C., Hamilton, G.B., and Gross, H.H., Furfural as a selective solvent in petroleum refining: Ind. and Eng. Chemistry, vol. 40, no. 2, pp. 220-227, Feb. 1948.
- Laspe, W.E., The use of solid adsorbents and selective solvents in refining shale gasoline: Colorado School of Mines Thesis, p. 31, p. 55, p. 60, 1948.
- Oyle from a kind of stone: Ind. and Eng. Chemistry, vol. 40, no. 12, p. 16A, Dec. 1948.
- Parry, V.F., Goodman, J.B., Wagner, E.O., Lammers, G.C., and Cook, V.A., Processing Colorado mahogany oil shale in the Parry Retort: U.S. Bur. Mines Special Report C-3-69, Feb. 12, 1946.
- Reed, Homer, and Berg, Clyde, Shale and air counter-flow in new continuous retort: Petroleum Processing, vol. 3, no. 12, p. 1188, Dec. 1948.
- Sachanen, A.N., The chemical constituents of petroleum, p. 376, New York, Reinhold Publ. Co., 1945.
- Scheibel, E.G., Fractional liquid extraction: Chem. Eng. Progress, vol. 44, no. 9-10, pp. 681-690 and 771-782, Sept. and Oct. 1948.

Souders, M. Jr., and French, F.A., U.S. Patent 2,449,793.

Staaterman, H.G., Morris, R.C., Stager, R.M., Pierotti, G.J.,
Manufacture of sulfolanes and use as selective solvents:
Chem. Eng. Progress, vol. 43, no. 4, pp. 148-151, April
1947.

Synthetic liquid fuels, Part II, Oil from shale: U.S. Bur.
Mines Rept. Inv. 4457, p. 55, Jan. 1949.