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SHALE OIL REFINING

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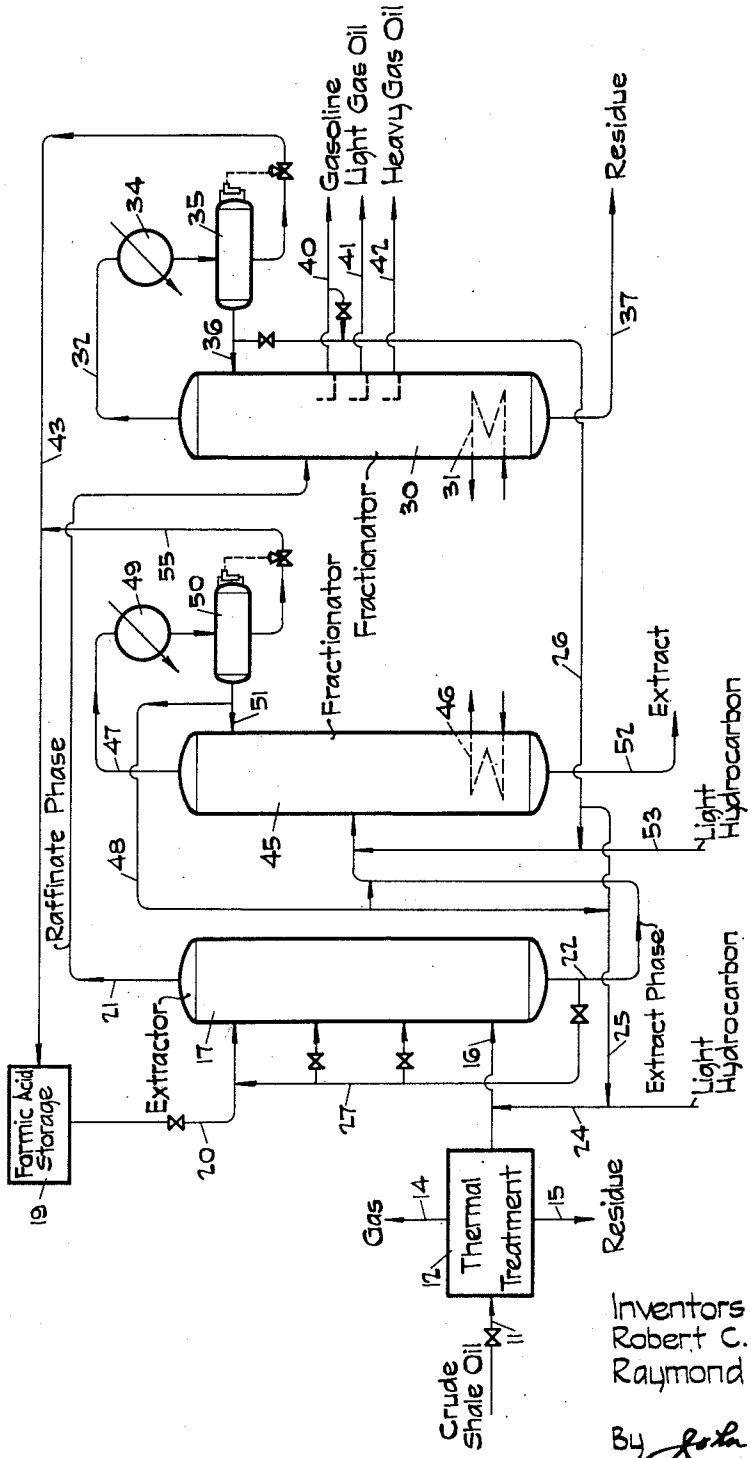

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SHALE OIL REFINING

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This invention relates to the refining of shale oil. More particularly, the invention relates to a method for improving the characteristics of charging stocks from shale oil for use in catalytic cracking processes while minimizing the loss of suitable cracking material.

Shale oil as produced from oil shale contains only a minor proportion of materials which are suitable for use directly in motor fuels without prior chemical conversion thereof. It is essential, therefore, that the shale oil, for the most part, be subjected to conversion processes of the general character used for increasing the yield and quality of motor fuels derivable from heavy crude oils. However, a serious drawback to the use of shale oil for the production of motor fuels therefrom by catalytic processing is the large amount of coke formed when the oil is subjected to catalytic cracking.

Shale oil as produced from Colorado oil shale by the usual retorting processes, such as the so-called N–T–U retorting process, is a black heavy waxy oil with an API gravity of about 20° and a pour point of around 90° F., containing about 2% by weight nitrogen, 1% sulfur and 1% oxygen, and having a low naphtha content, usually less than 3%. Only 20–25% of the oil is aliphatic and perhaps alicyclic as well and probably at least 25% is aromatic in character; the remainder is accounted for by compounds containing nitrogen, sulfur, and oxygen. A representative sample of N–T–U shale oil produced at the Rifle, Colorado, demonstration plant of the U. S. Bureau of Mines had the following approximate analysis expressed as weight per cent: C—84.5, H—11.5, N—1.9, S—0.8, and O—1.3. From this analysis, it will be noted that the shale oil contains more nitrogen and oxygen than most petroleum and has an H:C atom ratio corresponding approximately to a California straight run long residue.

Many of the problems associated with the refining of shale oils, and various methods proposed and used, have been discussed in considerable detail in a report of the Bureau of Mines, Report of Investigations 4652, Synthetic Liquid Fuels, Part II—Oil from Oil Shale, February 1950. Thus, it is stated therein that gasoline of good octane rating can be made by catalytic cracking of shale-oil fractions, but coke formation on the catalyst causes a short catalyst life. Attributing the high coke formation to the presence of organic nitrogen compounds, and observing that the heavy gas-oil fraction from shale oil educted in an N–T–U retort was found to contain more than 40 percent nitrogen compounds, it was indicated that solution to the problem should be sought for in the development of catalysts which are more suitable for this application.

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It has already been pointed out that it is advantageous to subject the shale oil, because of its high viscosity, to a thermal treatment for reduction of pour point prior to any refining thereof. Thus far, large scale operations on refining of shale oil have been directed primarily to thermal processing, including visbreaking, thermal coking, and the like, separation of distillate fractions and removing tar acids from the distillate fractions by caustic extraction and removing tar bases from the caustic-treated distillate fractions by sulfuric acid extraction. It will be clear from the results of previous work on the refining of shale oil that many problems still exist and require solution before the most economical utilization of shale oil can be made.

Considerable work has been done in an attempt to separate undesirable from desirable components of shale oil by extraction with liquid solvents. However, in general, those which removed undesirable substances were not sufficiently selective and removed desirable substances, such as aromatics, as well. Thus, liquid sulfur dioxide, as well as the usual well known organic selective solvents, lacks the required selectivity. Liquefied ammonia had too low a solubility for the nitrogen compounds. Certain strong acids, for example, 96% wt. H_2SO_4 to the amount of 100 lbs. H_2SO_4/bbl. of shale gas oil yielded a raffinate containing only 0.1% wt. nitrogen. The yield of raffinate was about 54% wt. of the gas oil, but the extract could only be recovered by springing the nitrogen compounds with caustic. Weak acids such as sulfurous and carbonic acids have been found to be only slightly more effective than water. Anhydrous hydrofluoric acid, although a relatively weak acid, has been found to yield a raffinate containing only 0.13% nitrogen; however, other substances were also extracted to such an extent that the raffinate yield was low. Fur-

thermore, removal of all of the fluorine from the oil is difficult.

It is a principal object of this invention to provide an improved method for the production of improved products from shale oil.

Another object of the invention is to produce from shale oil, feed stocks of improved quality for conversion thereof into motor fuels.

Still another object is to produce from shale oil, feed stocks of improved quality for catalytic conversion thereof into motor fuels while minimizing the loss of suitable cracking material.

The foregoing objects will be better understood, and other objects will become apparent, from the description of the invention, which will be made with reference in part to the accompanying drawing, the sole figure of which is a process diagram representing a preferred method of carrying out the invention.

Now, in accordance with the present invention, it has been found that shale oil, preferably after having been mildly thermally cracked to lower the viscosity and pour-point substantially, as by a mild visbreaking operation, is effectively separated by solvent extraction with formic acid under certain conditions, as will be discussed hereinafter, whereby substantially a minimum of the nitrogen-containing compounds, yet representing essentially all of the more undesirable coke-forming nitrogen-containing compounds, are separated in the extract and a maximum amount of good quality cracking stock is separated as raffinate.

In accordance with the invention, there is no attempt made to extract all, or even substantially all, of the nitrogen-containing compounds. To do so would unnecessarily greatly lower the quantity of material obtainable as feed stock for cracking operations for the production of motor fuel. Thus, the method of this invention effects a selective removal of the undesirable coke-forming materials.

In the removal of the deleterious and undesirable materials from the shale oil, including certain nitrogen-containing compounds, in the practice of the present invention, it is not known to what extent those compounds are removed simply by physical solution in the formic acid and to what extent they are removed by chemical reaction with formic acid and the dissolving of the resulting thermally unstable reaction product in the formic acid. Thus, it has been found that as the proportion of formic acid used is increased up to the amount corresponding to about two stoichiometric equivalents of formic acid for each atomic proportion of nitrogen in the oil (about 0.1 volume of 90% formic acid per volume of oil, i. e., about 10% by volume), the proportion of separated raffinate oil phase and the percentage of nitrogen remaining in said raffinate decrease together. But, as the amount of formic acid used for the extraction is increased further, the amount of raffinate oil remains essentially constant, whereas the nitrogen content of the raffinate oil continues to decrease and at the same time the quality of the raffinate oil as catalytic cracking feed stock is improved still further. It has been found further, however, that the quality of the raffinate oil as cracking feed stock is not improved still further to any appreciable extent by extracting with a still larger proportion of formic acid after the nitrogen content of the raffinate has been reduced to a value of about 0.4–0.5% by weight, which is obtainable by extraction of the visbroken shale oil with about an equal volume of 90% formic acid, The same reduction in nitrogen content can also be obtained by extraction with only one-half volume of 90% formic acid per volume of visbroken shale oil, corresponding to a ratio of stoichiometric equivalents of formic acid to nitrogen atoms in the oil of about 8 to 12. The reduction in the nitrogen content of the raffinate oil is illustrated by the results shown in Table I.

TABLE I

Extraction of thermally treated, filtered gas flow shale oil with 90% formic acid

Vol. Ratio: Acid/Oil	4/100	6/100	8/100	10/100	20/100	40/100
Percent N in Raffinate Layer	1.80	1.45	1.23	1.09	1.08	0.74
Raffinate Layer, percent v Oil	70	61	58	54	53	53

To determine the suitability of the raffinate as a catalytic cracking stock, a representative formic acid raffinate from thermally treated N–T–U oil, which had a nitrogen content of 0.74% by weight, was subjected to laboratory catalytic cracking at 540° C. at a liquid hourly space velocity of 0.74, over a commercial silica-alumina catalyst of 84 square meters per gram surface area, with the production of products in the following weight percentages, based on the weight of feed: gas—27%; gasoline—32%; gas oil—29%; coke—12.2%. For comparison, a raffinate was prepared from the same thermally treated N–T–U oil, having a nitrogen content of only 0.14% wt. When this raffinate is subjected to the same catalytic cracking conditions the results are essentially the same, with no advantage being gained for the additional expense of reducing the nitrogen content to the lower value.

The nitrogen content of the raffinate oil obtained in the extraction depends not only on the proportion of formic acid used, expressed as 100% formic acid, but also on the ratio of formic acid to water in the formic acid solution. Thus, whereas an equal volume of 90% formic acid extracts a visbroken shale oil to a raffinate having a nitrogen content of 0.4–0.5% by weight, extraction with an equal volume of 52% aqueous formic acid yields a raffinate oil having a nitrogen content of 0.8–0.9% by weight. Nevertheless, the raffinate oil having a nitrogen content of 0.8–0.9% is a suitable stock as feed to a catalytic cracking operation. Extraction with about six-tenths of a volume of 90% formic acid (same hydrogen formate proportion as in one volume of 52% formic acid) per volume of oil yields a raffinate oil having a nitrogen content of about 0.5–0.6% by weight.

The use of at least an amount of formic acid which corresponds to about 10% by volume of 90% formic acid, and which is essentially two stoichiometric proportions of formic acid per each nitrogen atomic proportion in the oil, representing a substantial excess of formic acid on the basis of nitrogen separated in the extract, has been found to be required in order that the extract phase will be sufficiently fluid for ready separation from the raffinate phase. With up to about 10% by volume of 90% formic acid, the extract phase is extremely viscous and difficultly separable from the raffinate phase, while it becomes relatively fluid and quite readily separable when a larger proportion of the acid solution is used, such as substantially more than 10%, preferably at least about 20%.

As has been indicated, the visbroken shale oil can be readily and effectively extracted by the

method of this invention. On the other hand, if it is desirable, the shale oil can be distilled to recover a gas oil therefrom, representing, for example, all but about the first 5% overhead and a residue amounting to about 20% of the shale oil, and containing at the same time gas oil constituents formed by any thermal decomposition of heavier materials in the shale oil during the distillation, and the separated gas oil distillate can be effectively extracted in accordance with this invention. Still further, if it is desired to treat the shale oil without any kind of heat treatment, other than that which results from the retorting of the oil shale in the production of the shale oil, the extraction with formic acid can be effected in the presence of a suitable diluent, such as a light aromatic or aliphatic hydrocarbon, e. g., benzene and the like. Thus, whereas about one-half volume of 90% formic acid per volume of visbroken shale oil yields a raffinate having a nitrogen content of about 0.5%, the extraction of one volume of a mixture of 80% untreated shale oil and 20% by volume benzene, with one-half volume of 90% formic acid yields a raffinate having a nitrogen content of about 0.6% by weight, based on the shale oil content thereof. The nitrogen contents of raffinates obtained by extraction of a mixture of representative N–T–U shale oil and benzene with different proportions of formic acid are shown in Table II.

TABLE II

Extraction of 80% N–T–U shale oil +20% benzene with 90% formic acid

Vol. Ratio: Acid/(Oil+Benzene)	Feed	4/100	8/100	20/100	40/100
Percent N in Raffinate Layer	1.70	1.28	0.94	0.73	0.63

It has been found that when the shale oil is subjected to a first extraction with formic acid, and the raffinate oil from this first extraction is treated with a further portion of formic acid, a very stable emulsion is formed in the second treating operation, which emulsion is extremely difficult to break. However, it has been found that the emulsion is readily broken by admixing therewith a small proportion of extract recovered in the first extraction; the formation of the emulsion is essentially eliminated by adding a small portion of the first extract to the raffinate oil to be treated or to the formic acid to be used as treating agent, or to both, prior to said treatment. It appears that there is present in the initial shale oil some material which is a very effective demulsifier for the oil-formic acid system, or some material which forms with formic acid such a demulsifier, and that said material is readily and rather completely removed by treatment of the shale oil with a relatively small proportion of formic acid. Therefore, when the shale oil is treated with formic acid in a plurality of stages, it is essential that each treating stage, after the first one in which the shale oil is first extracted with the formic acid, be carried out in the presence of an added portion of extract phase, or extracted material, from said first treating stage.

Economic application of the extraction operation of this invention depends on the recovery of the formic acid from both the raffinate and the extract phases. The raffinate phase contains only a relatively small proportion of formic acid, generally from about 0.5 to about 2% by weight, and the recovery of the formic acid therefrom is readily accomplished by distillation, after which the formic acid is returned for use in the extraction operation. On the other hand, the extract phase contains a relatively large proportion of formic acid, as uncombined formic acid and as combined formic acid, generally from about 40% to about 75% by weight of the extract phase, while at the same time containing extracted shale oil constituents comprising vaporizable constituents ranging in boiling points from relatively low values to relatively high values, such as from about 150° C. to about 525° C. Representative formic acid raffinates and extracts of a visbroken shale oil are characterized in Tables III and IV while the nitrogen and sulfur contents of liquid product fractions of visbroken shale oil are shown hereinafter in Table V.

TABLE III

Extraction of thermally treated N–T–U shale oil

Feeds: 90% wt. HCOOH; filtered liquid product from thermally treated N–T–U oil.

Conditions: about 5 minutes contacting—20–60 minutes settling; room temperature.

Number of Stages	1	1	[1] 5
Oil Charged, parts by vol.	50	50	50
Acid Charged, parts by vol.	25	50	25
Composition of Raffinate Phase, parts by weight:			
Oil	28.3	27.3	26.7
Acid	0.7	0.7	0.6
Water	<0.05	<0.05	<0.05
Total	29	28	27.3
Composition of Extract Phase, parts by weight:			
Oil	17.7	18.7	18.4
Acid	26.3	53.3	26.7
Water	3.0	6.0	3.0
Total	47	78	48.1
Raffinate:			
Percent wt. of oil charged	61.5	59.3	60
Nitrogen content, percent wt.	0.53	0.50	0.47
Gravity, °API			32.8

[1] Countercurrent.

TABLE IV

Analyses of typical products from extraction of thermally treated N–T–U shale oil

	Raffinate	Extract
Nitrogen Content, percent wt.	0.4	4.5
Sulfur Content, percent wt.	0.7	0.4
Oxygen Content, percent wt.	0.5	1.6
Formate, as percent wt. HCOOH	0.05	0.3
Gravity, °API	33	6.7
Saybolt Furol Viscosity, sec. at 122° F.		206
Distillation Analysis, percent wt.:		
Gasoline, to 205° C.	20.2	ca. 0.5
Light Gas Oil, 205–345° C.	34.2	25.1
Heavy Gas Oil, 345–525° C.	36.8	41.8
Residue, >525° C.	8.8	32.6
N Content of Cuts, percent wt.:		
Gasoline	0.05	4.57
Light Gas Oil, 205–345° C.	0.15	
Heavy Gas Oil, 345–525° C.	0.52	4.60
Residue	1.59	4.50
S Content of Cuts, percent wt.:		
Gasoline	0.88	0.50
Light Gas Oil, 205–345° C.	0.70	
Heavy Gas Oil, 345–525° C.	0.64	0.44
Residue	0.64	0.74

It will be seen from the data in Table IV that oxygen, as well as nitrogen content, is lower in the raffinate than in unextracted shale oil, while sulfur is higher. Thus, formic acid selectively extracts both oxygen and nitrogen compounds, but not sulfur compounds. The API gravity of the raffinate was higher, and that of the extract was lower than that of the feed. This appears to be due to the gasoline fraction of the feed con-

taining relatively few oxygen and nitrogen compounds, thus being recovered almost exclusively in the raffinate, and to the aromatic character of the extracted material; that is, a high proportion of the nitrogen in shale oil exists as pyridine and pyrrole derivatives. The nitrogen content increases with boiling point in the raffinate, but is essentially independent of boiling point in the extract.

In order to recover the formic acid from the extract phase by distillation, it is necessary to heat the mixture sufficiently to decompose any addition or reaction products of the formic acid with shale oil components of the extract. However, it has been found that when the extract phase is heated alone to a temperature sufficiently high to remove all of the formic acid from the shale oil constituents, there is a substantial loss of formic acid in the process, presumably attributable to thermal decomposition of formic acid content of some of the formates present at the high temperatures required for removal of the formic acid from the extract. It will be seen from Table IV that the extract contains only a negligible proportion of low boiling constituents up to 205° C. It has been found that the loss of the formic acid is essentially eliminated and that the formic acid is recoverable substantially free from shale oil extract components by distilling the extract phase in the presence of an added amount of a light hydrocarbon, preferably a low boiling hydrocarbon fraction obtained from the raffinate produced in the extraction, and particularly a light hydrocarbon fraction which is predominantly non-aromatic in character. The distillation of the extract phase in the presence of the light hydrocarbon is carried out so that the maximum temperature to which any appreciable amount of the formic acid or formate is subjected is about 165° C. The use of a portion of the low boiling fraction recoverable from the raffinate phase or from the initial thermal treatment or the retorting step by fractional distillation has the advantage that it can be returned to the extraction zone, together with the formic acid recovered from the extract phase by its aid, with its concomitant viscosity-reducing effect on the shale oil. On the other hand, the relative immiscibility of the formic acid and said light hydrocarbon makes it a simple matter to separate the two materials by condensation and stratification.

Having discussed in detail various factors which affect the process of the present invention, the application of the process and the method whereby those factors are taken into consideration to effect the desired refinement of shale oil, will be better understood from a description of the process which is made with specific reference to the process scheme shown in the drawing.

A crude shale oil, such as an N–T–U retorted shale oil as produced at the Rifle, Colorado, demonstration plant of the U. S. Bureau of Mines, is fed by means of line 11 to a pour-point and viscosity reducing operation such as is frequently applied to heavy crude or residual petroleum oils, as represented by thermal treatment in 12, wherein the crude shale oil is subjected to an elevated temperature appropriate to the operation, such as about 460° C., and in general, under superatmospheric pressure, for example, about 500 pounds per square inch, for sufficient time to effect a suitable reduction in the viscosity of the shale oil. A small proportion of gaseous product, for example of the order of about 5%, is separated by means of line 14 and a small proportion (0.5–3%) of residue is removed as indicated by line 15. It will be understood here that the remainder of the visbroken shale oil may be separated by distillation into various fractions, such as a gasoline fraction, a light gas oil fraction, a heavy gas oil fraction and a residuum fraction, such as indicated in the aforementioned Bureau of Mines Report, and the separate fractions may be treated separately by the process of this invention. However, it has been found that the total visbroken oil, after separation of the gaseous product and the small proportion of residual material, is effectively treated by the process of the invention, and for purposes of illustration the description made with reference to the drawing is made in connection with such total visbroken oil. Typical data pertinent to the thermal treatment and the resulting products of N–T–U oil and gas-flow retorted oil are shown in Table V.

TABLE V

Thermal treatment of shale oil to reduce pour point

	(1)	(2)
Feed		
Temperature, °C	460	460
Pressure, p. s. i. g	510±50	510±50
WHSV (Wt. Hourly space Vel.):		
preheat	18	19
reaction	3.6	3.6
Products, percent wt. feed:		
Gas	5.0	5.4
Liquid	94.0	92.5
Insoluble Residue	0.4	2.7
Unaccounted for	0.6	−0.6
Properties of Liquid Product:		
Percent wt. N	2.10	2.61
Percent wt. S	0.66	0.57
Percent wt. O	1.03	1.24
Solids, g./100 ml. (centrifuge)	0.9	2.8
Gravity, °API	24.0	19.3
Pour Point, °F	0	10
Liquid Product Composition, percent wt. Feed:		
Water	0.4	0.5
Gasoline, to 205° C	13.9	12.0
Light Gas Oil, 205–345° C	29.7	27.2
Heavy Gas Oil, 345–525° C	35.1	33.7
Residue, >525° C	14.9	19.1
Total	94.0	92.5

Nitrogen and Sulfur Contents of Liquid Product Fractions, percent wt.:	N	S	N	S
Gasoline	0.57	0.70	0.69	0.67
Light Gas Oil	1.6	0.64	2.0	0.61
Heavy Gas Oil	2.4	0.52	2.8	0.51
Residue	3.4	0.55	3.8	0.50

[1] N–T–U Oil.
[2] Gas Flow Oil.

The visbroken oil produced by the thermal treatment in 12 is transferred by means of line 16 to the lower section of extractor 17, while formic acid is delivered to the upper end of extractor 17, from suitable storage 19, by means of line 20. As shown, extractor 17 is an upright elongated vessel which may suitably provided internally with any of the well-known means adapted to provide intimate contacting of counterflowing streams of at least partially immiscible liquid substances, such as a suitable packing material, perforated plates, and the like. Instead of a single extractor as shown, the extractor may comprise a plurality of mixer-settler combinations arranged for countercurrent contacting of immiscible liquids in known manner. Also, it has been found that a single mixer-settler combination is effective to an unexpectedly great extent for the present purpose as will be seen from the results shown already in Table I. The shale oil is effectively treated in extractor 17 with

from about one-half to one volume of formic acid solution of from about 40% to higher strength, preferably about 60% to 90% strength in aqueous solution, for each volume of the oil. The temperature of the extraction is about ambient atmospheric temperature, although lower or higher temperatures may be utilized, just so that the temperature is not so low as to cause the viscosity of the materials to become too great for effective contacting and handling and the temperature is not so high as to exceed the decomposition temperature of the formate salts; a temperature of about 50° C. has been found to be entirely satisfactory. The raffinate phase containing a small proportion of dissolved formic acid (see Table III) is removed from extractor 17, by means of line 21 and the extract phase is removed from the bottom of the extractor through line 22. As has been indicated before, the shale oil may be admixed with a suitable diluent to reduce the viscosity of the system. Such a diluent, for example, a light hydrocarbon, is suitably introduced by means of line 24 into line 16 carrying the shale oil. A particularly suitable diluent for this purpose is a portion of the light hydrocarbon fraction separated from the raffinate produced in the process, which is suitably delivered to line 24 by means of lines 25 and 26. As has also been indicated before, when effecting the extraction in a plural stage operation, because of emulsion difficulties, it is desirable to make certain that at least a portion of material which is first extracted from the shale oil in its first contacting with formic acid is present throughout the extracting zone. This is readily accomplished by withdrawing a portion of the extract phase from line 22 and delivering it, as by line 27, to formic acid feed line 20. Alternatively, a portion of the extract phase can be withdrawn directly from the bottom of the extractor and returned to the top of the extractor; portions can be injected at different levels as indicated. Instead of utilizing a portion of the extract phase, which represents a preferred method, a portion of the recovered extract may be used instead with satisfactory results.

The raffinate phase in line 21 is delivered thereby to a fractionator 30 for the recovery of the formic acid content thereof and of the oil constituents in one or more product fractions. Fractionator 30 is of conventional design and construction, provided with suitable heating means, such as a heating coil 31, overhead vapor line 32, condenser 34, overhead condensate collector 35, reflux line 36, bottoms drawoff line 37, and one or more side drawoff trays or collectors 39 and connecting drawoff lines 40, 41 and 42. The recovered formic acid is separated from the hydrocarbon by stratification in collector 35 and returned by means of line 43 from collector 35 to formic acid storage 19. It will be understood that all of the oil constituents of the raffinate phase can be recovered as a single bottoms product fraction from fractionator 30, and, if desired, the total oil product can be fractionated into various desired fractions in a separate fractional distillation operation.

The extract phase in line 22 is delivered by means thereof to a distilling fractionator 45, also of conventional design and construction, provided with suitable heating means, such as a heating coil 46, overhead vapor line 47 with vapor condenser 49, overhead condensate collector 50 and reflux line 51, and a bottoms drawoff line 52. A light hydrocarbon, preferably having an end boiling point not higher than about 150° C. and preferably only about 100° C. in order to avoid loss of formic acid by decomposition, and preferably being a portion of light hydrocarbons recovered from the raffinate phase, such as separated from the overhead condensate in 35 and/or withdrawn by line 40 from fractionator 30, is delivered to fractionator 45, as by means of line 53 or lines 53 and 26. By distilling the extract phase in column 45, in the presence of the light hydrocarbon, the distillation may be carried out while maintaining the temperature at any point therein where formates are present at a temperature below about 165° C. and the formic acid recovered in substantially 100% recovery in the overhead from the distillation. The lower the end boiling point of the light hydrocarbon the larger is the proportion thereof which is required for the recovery of the formic acid; on the other hand, the light hydrocarbon must have sufficient relative volatility to be readily distillable from the extract shale oil constituents. It is to be understood, of course, that the nature and the amount of light hydrocarbon which is used for this purpose is selected so as to minimize any unnecessary retreating and handling of materials. It is a feature of the embodiment of the invention as shown in the drawing that the light hydrocarbon which is utilized in the recovery of the formic acid from the extract phase can be returned to the extractor, by means of lines 48, 25 and 24, said light hydrocarbon removed from the extractor in the raffinate phase and then recovered in fractionator 30 for re-use in fractionator 45.

Instead of recycling the formic acid and light hydrocarbon as recovered in accumulator 50, to the extractor 17, the mixture may be stratified into formic acid and hydrocarbon phases, by the addition of water if necessary, to cause separation and stratification, the hydrocarbon returned directly to the fractionator 45, as by means of line 51 and/or line 48 and the formic acid recovered from separated aqueous formic acid, if a more concentrated formic acid solution is desired, as by well known distillation methods.

The drawing, for simplicity, does not necessarily show all of the auxiliary equipment such as pumps, pipes, valves, outlets, inlets, tanks, heating lines, cooling lines, heat exchangers, temperature recording and control means, liquid level control means, and the like, which may be found to be desirable for the most effective operation of the process as applied to a given case under a selected set of operating conditions. The proper selection and placement of such equipment will be evident to one skilled in the art in view of the description of the invention as made hereinbefore.

We claim as our invention:

1. The method for the production of a shale oil product having improved catalytic cracking properties from shale oil, which method comprises: (1) intimately contacting the shale oil with from about two to about ten stoichiometrical proportions of formic acid for each atomic proportion of nitrogen present in said shale oil to reduce the nitrogen content of resulting raffinate oil phase to a value of from about 0.4% to about 0.9% by weight; (2) separating resulting extract and raffinate phases; (3) recovering dissolved formic acid from the separated raffinate phase and returning it for further extraction use; and (4) recovering formic acid from the separated extract phase by distillation in the presence of a light essentially non-aromatic hydrocarbon

under conditions to maintain formic acid and formates in the distilling zone at a temperature below about 165° C. and returning the recovered formic acid for further extraction use.

2. The method for the production of a shale oil product having improved catalytic cracking properties from shale oil, which method comprises: (1) subjecting crude shale oil to a mild thermal treatment to effect a substantial reduction in viscosity thereof with a minimum of thermal conversion; (2) intimately contacting the liquid product separable from the thermally treated shale oil with formic acid in excess of one stoichiometrical proportion thereof for each atomic proportion of nitrogen in the liquid product; (3) separating resulting raffinate and extract phases; (4) separating formic acid and a light essentially non-aromatic hydrocarbon fraction from the raffinate phase; (5) recovering formic acid from the extract phase by distillation in the presence of a portion of the light hydrocarbon fraction separated from the raffinate phase; and (6) recycling formic acid recovered from the extract phase, and at least a portion of the light hydrocarbon fraction separated therewith, to extraction utility in step (2).

3. The method for the production of a shale oil product having improved catalytic cracking properties from shale oil, which method comprises: (1) intimately contacting the shale oil having a nitrogen content substantially greater than 1% by weight with formic acid in substantial excess of one stoichiometrical proportion thereof for each atomic proportion of nitrogen in the shale oil in the presence of a light hydrocarbon fraction as defined hereinafter; (2) separating resulting raffinate and extract phases; (3) recovering dissolved formic acid from the separated raffinate phase and returning it for further extraction use; (4) recovering a light essentially non-aromatic hydrocarbon fraction from the raffinate oil and using a portion of it in extraction step (1) as defined hereinbefore; (5) recovering formic acid from the extract phase by distillation in the presence of another portion of said light hydrocarbon fraction separated from the raffinate oil; and (6) recycling formic acid recovered from the extract phase, and at least a portion of the light hydrocarbon fraction separated therewith, to the extraction step (1).

4. The process according to claim 1, wherein the contacting of shale oil and formic acid in step (1) thereof is carried out in a multistage countercurrent contacting zone and effective demulsification conditions are maintained throughout the contacting zone by introducing a small portion of separated extract phase obtained in subsequent step (3) to the contacting zone near the point of withdrawal of the raffinate phase therefrom.

ROBERT C. CASTNER.
RAYMOND C. ARCHIBALD.

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