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SYNTHETIC LUBRICANTS

Thomas F. Rutledge, St. Louis, Mo., and Francis M. Seger, Pitman, Alexander N. Sachanen, Woodbury, and William E. Garwood, Haddonfield, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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This invention has to do with the preparation of synthetic lubricants from normal, alpha mono-olefins and, more particularly, has to do with the preparation of lubricants from certain complex mixtures containing such olefins.

As described in several related and copending applications, identified hereinafter, it has been found that normal, alpha mono-olefins of varied chain length can be converted to excellent synthetic lubricants. High viscosity indices, low pour points and/or superior stability characterize these lubricants. Not only have the individual normal, alpha mono-olefins proven of value in this regard, but mixtures of the same have been found to be satisfactory. In addition, complex mixtures containing substantial proportions of these olefins have been found to be suitable starting materials. A source for the complex mixtures containing these olefins is the Fischer-Tropsch process and related processes. As is well known in the art the Fischer-Tropsch process involves reaction of carbon monoxide and hydrogen in the presence of cobalt or chemically related catalysts, whereupon hydrocarbons, including olefins and paraffins, and oxygen-containing compounds are formed. When the carbon monoxide to hydrogen ratio is increased, larger quantities of oxygen-containing compounds are generally formed.

While the foregoing complex mixtures are converted to synthetic lubricants of low pour point and high viscosity index, as described in the applications referred to above, certain constituents therein are deleterious in reducing the yield and/or quality of the lubricants if present in excessive amount. Undesirable constituents include non-primary olefins, aromatics, naphthenes and paraffins; oxygen-containing compounds; suspended material, particularly metallic catalysts and their compounds. With regard to quality of the lubricants, it has been found that they are characterized by considerable color. This is a serious shortcoming inasmuch as these highly colored lubricants generally do not respond to conventional procedures, namely, filtration,

adsorption, etc., for removing color bodies. In addition, the carbon residue values of the lubricants are relatively high. A further shortcoming traceable to constituents of the complex olefinic charge stocks, is that the viscosity indices of the lubricants generally fall below those of the lubricants formed from individual normal, alpha mono-olefins. Still another undesirable feature is in the relatively low response of the lubricants to inhibitors, particularly oxidation inhibitors. This is well illustrated with an outstanding oxidation inhibitor comprising an oil-soluble, phosphorus- and sulfur-containing reaction product of pinene and phosphorus pentasulfide, which is described in detail in Patent No. 2,416,281.

It has now been found that synthetic lubricants having good color, low carbon residues and substantial inhibitor response, in addition to low pour points and high viscosity indices, can be obtained by treating the foregoing complex olefin charge with a solution of an alkali metal salt of a phenolic material, described in more detail hereinafter, whereby an olefinic raffinate is obtained, and converting the olefinic raffinate to a synthetic lubricant by the procedures described in the following applications.

In Patent No. 2,500,166, it has been shown that normal, alpha mono-olefins having six to about twelve carbon atoms per molecule form synthetic lubricants when heated at 500–750° F., in the absence of a catalyst. At temperatures of the order of 700–900° F., the use of a gas such as hydrogen, carbon monoxide and mixtures of such gases, with the aforesaid mono-olefins makes possible the formation of synthetic lubricants in substantial yield. This is described in Patent No. 2,500,159. The aforesaid mono-olefins are also converted to synthetic lubricants when contacted with lead tetra-acetate at elevated temperatures, particularly 400–700° F., as explained in Patent No. 2,500,161. Another related development involves condensation, at 500–750° F. of an olefin mixture comprising a short chain mono-olefin of two to six carbon atoms and a long chain normal, alpha mono-olefin of ten to thirty carbon atoms; the mean carbon chain length is maintained within the range of six to twelve carbon atoms by proper proportioning of the olefins. This is described in Patent No. 2,500,162.

Polymerization of the aforesaid mono-olefins of six to fourteen carbon atoms per molecule, in the presence of a paraffin at temperatures in excess of 700° F., forms the subject matter of Patent No. 2,500,165. Monocyclic aromatics and/or naphthenes may be used in this polymerization, in place of the paraffin, as shown in Patent No. 2,500,244. Polymerization of said mono-olefins may also be accomplished at temperatures within the range of 550–750° F., using small amounts of sulfur, selenium and/or tellurium; this is described in Patent No. 2,500,164. Small amounts of sulfur, selenium and/or tellurium can be used also in converting polymeric materials of said mono-olefins, to excellent synthetic lubricants, following the procedure explained in copending application Serial No. 148,504, filed March 8, 1950. At temperatures of the order of 600–750° F., small amounts of phosphorus sulfides affect the polymerization of the aforesaid mono-olefins; this is described in Patent No. 2,500,163.

A catalytic conversion of normal, alpha mono-olefins having from six to eighteen carbon atoms, to synthetic lubricants is described in copending application Serial No. 776,428, filed September 26, 1947, now abandoned; the catalysts used are silica-alumina composites.

Styrene also reacts with the aforesaid mono-olefins, at temperatures from about 500° F. to about 700° F., with the formation of synthetic lubricants, as shown in Patent No. 2,500,161. Conjugated hydrocarbons and sulfur react with normal, alpha mono-olefins having from about five to about eighteen carbon atoms to form lubricants (Patent No. 2,500,167). A related development involves reaction of conjugated hydrocarbons, phosphorus sulfides and the corresponding mono-olefins of six to fourteen carbon atoms, as shown in Patent No. 2,500,247. Still another related development is that wherein lubricants are formed by reaction of vinyl-substituted aromatic compounds, thiols and normal, alpha mono-olefins, described in Patent No. 2,500,672.

In copending application Serial No. 673,892, filed June 1, 1946, now 2,551,638, it is shown that normal, alpha mono-olefins having from about seven to about twelve carbon atoms per molecule react with organic peroxides at 120–570° F. to form synthetic lubricants. With the corresponding mono-olefins of six to eighteen carbon chain length, organic peroxides and halogenated olefins are reacted at 120–570° F. with the formation of lubricants; Serial No. 776,427, filed September 26, 1947, now 2,551,640. As a related development, organic peroxides, conjugated hydrocarbons and the aforesaid mono-olefins of from five to eighteen carbon atoms are reacted at 120–570° F. to form lubricants; Serial No. 53,372, filed October 7, 1948, 2,551,641. Organic peroxides, aromatic hydrocarbons and said mono-olefins of five to eighteen carbons also react to form lubricants as described in copending application Serial No. 72,744, filed January 25, 1949, now 2,551,642. Certain heterocyclic compounds may be used in place of the aromatic hydrocarbons in the last-mentioned development; this is explained in copending application Serial No. 83,772, filed March 26, 1949. Lubricants of high viscosity are formed by reacting the aforesaid mono-olefins of five to eighteen carbon atoms with certain unsaturated esters and organic peroxides; copending application Serial No. 72,745, filed January 25, 1949, now 2,551,643.

Normal, alpha mono-olefins also react with olefinic mono-oxides and -sulfides at 500–700° F. to form lubricants, as explained in Patent No. 2,486,441.

It is to be understood, therefore, that the treated complex olefinic charge may be converted to synthetic lubricants by any of the foregoing conversion procedures shown in the above-identified applications and patents.

EXTRACTION TREAT

As indicated above, the complex olefinic charge stocks are extracted with certain solutions of alkali metal salts of phenolic materials prior to conversion to synthetic lubricants. The solutions selectively extract and separate the various constituents of the raw material. For example, oxygenated compounds and aromatic hydrocarbons are separated from normal, alpha mono-olefins present therein.

Solutions suitable for use herein are aqueous and/or alcoholic solutions of alkali metal salts of mono-hydroxy aromatics represented by the general formula:

$$R_n—A—OH$$

wherein A is an aromatic nucleus such as phenyl, naphthyl, anthryl, etc., and is preferably phenyl; R is an alkyl group having less than about six carbon atoms, and is preferably methyl; and n is an integer from zero to 3, and is preferably one. Alkyl groups (R), when present, preferably have a total number of carbon atoms of less than about six. Illustrative of such compounds are: phenol, m-cresol, o-cresol, p-cresol, and mixtures thereof such as "Selecto" mixtures, p-tertiary butyl phenol, 2-4-xylenol, 2-3-xylenol, m-isopropyl phenol, etc. Particularly preferred, however, in view of its excellence herein, is m-cresol.

The alkaline constituent of the extractant is preferably potassium. It can also be any other alkali metal of Group I of Mendelejeff's Periodic Table, namely, lithium, sodium, rubidium and cesium. The concentration of the alkali metal salt in the solvent is preferably at its upper limit of solubility. However, it can be as low as 50%.

Low molecular weight alcohols such as methyl, ethyl, n-propyl and i-propyl alcohols, are useful herein as solvents for the alkali metal salts. Liquid polyhydric alcohols, such as the glycols, are also advantageous. Suitable glycols include: ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol and the like. The alcohols and/or glycols can be used alone or mixed with water.

Extraction of the complex olefinic charge can be effected in any one of several ways. For example, the charge and extractant solution can be agitated in a suitable vessel; the resultant mixture can be allowed to settle, whereeupon two layers form; and the olefinic layer or raffinate can then be separated from the extract which contains the undesirable constituents of the complex charge. Another typical operation is that of continuous countercurrent extraction, in much the same manner as conventional solvent extraction procedures for preparing lubricating oils from oil stocks.

The ratio of charge stock to extractant solution can be varied considerably. Naturally, the quantity of extractant solution required for a desired degree of improvement is dependent upon the quantity of undesirable materials present in the complex olefinic charge. By way of illustration, with a charge comprising about 60 per cent (by volume) of normal, alpha mono-olefins and about 40 per cent of undesirable components, appreciable extraction is obtained with about 0.25 part of a concentrated extractant solution for each part of the charge, or a ratio of 0.25:1 in a single stage operation. It is preferred, however, that multiple stage operation be employed and that the over-all ratio be maintained from about 0.25:1 to about 4:1.

Temperatures and pressures employed during the extraction do not appear to be critical. As a rule, however, low temperatures—of the order of 25–75° C.—are preferred.

The extracted constituents of the charge stocks used herein are predominantly oxygenated materials and aromatic hydrocarbons, which are readily removed from the extract when the latter is diluted with water, or topped out by distillation at atmospheric or reduced pressure. A steam distillation of the oxygenated materials at moderate superheat is preferred. The recovered materials—particularly, the oxygenated compounds—are highly effective and valuable solvents and chemical intermediates.

The olefinic raffinate obtained in the extraction is thereafter converted to a synthetic lubricant by any of the procedures described in the aforementioned copending applications and patents. A raffinate boiling from about 100° F. to about 600° F. and boiling predominantly within the range 150–500° F., is suitable for conversion. It is to be understood, however, that fractions boiling over this range and those boiling within a portion of the range can be so converted. For example, fractions boiling from 200° F. to 300° F. and from 300° F. to 450° F. have proven excellent charge stocks for conversion. The raffinate fraction boiling from 300 to 450° F. contains a substantial proportion of normal, alpha mono-olefins of nine to twelve carbon atoms per molecule, and represents a preferred charge stock inasmuch as the synthetic lubricants obtained therefrom have particularly advantageous characteristics.

EXAMPLES

The following examples serve to illustrate, and not limit, the invention.

Example I

A complex olefinic charge stock obtained in a Fischer-Tropsch reaction with an iron catalyst and having the following properties, was selected:

Boiling range, °F. (ASTM)	280–574
Specific gravity	0.8137
Olefins and paraffins, per cent by volume	66
Aromatics, per cent by volume	20
Oxygenated compounds, per cent by volume	14
Bromine number	72.5

A quantity, 750 parts by weight, of the olefinic charge was agitated for about five minutes, at room temperature (20–25° C.) with about 250 parts by volume of a 62 per cent (saturated) aqueous solution of potassium salts of a mixture of phenol and cresols ("Selecto"). The resulting mixture was allowed to settle, whereupon two layers formed, a lower layer comprising the extract and an upper layer comprising the raffinate. The layers were separated.

The raffinate layer, comprising the olefinic portion of the complex charge stock, was then treated in a similar manner with seven successive portions of the aqueous potassium salt solution. The raffinate finally obtained was washed with a 5 per cent aqueous sodium hydroxide solution (600 parts by volume) to remove and recover phenol and cresols of the extractant. Following this, the raffinate was washed with water (2400 parts by volume) and filtered through paper. The raffinate, now neutral to litmus, comprised 704 parts by weight. The raffinate contained 72% olefins plus paraffins, about 26.5 per cent of aromatic hydrocarbons and about 1.5% oxygenated compounds.

The olefinic raffinate was charged to a bomb and the atmosphere therein was replaced with nitrogen. The bomb was then heated at about 652° F. for about ten hours, with additional time required to heat the bomb to this temperature and to cool the bomb. The bomb was discharged and the contents were vacuum distilled at a maximum vapor temperature of 356° F. at 3 mms. (Hg) pressure, to recover the more volatile materials. The remaining product was filtered. To distinguish the conversion product from the distillate product, the refined oil is defined as "residual oil." The latter term identifies the oil from which unreacted materials and products of intermediate boiling range have been separated. The residual oil comprised 207 parts by weight.

The tests and analyses to which the residual oil were subjected are well known standard tests. In this connection, it will be noted that the designation "N.N." refers to the neutralization number, which is a measure of the acidity of the oil; the carbon residue is determined by the Ramsbottom procedure; the abbreviation "V.I." represents viscosity index.

The oxidation tests used reveals the stability of oils toward catalytic oxidation. The test oil, 25 ccs., is placed in a 200 x 25 mms. test tube with 15.6 square inches of sand-blasted iron wire, 0.78 square inch of polished copper wire, 0.87 square inch of polished aluminum wire, and 0.167 square inch of polished lead plate. Dry air is passed through the sample of oil at a rate of 10 liters per hour. The test tube is heated at 260° F. for 40 hours in an aluminum block bath. The results reported at the end of the test are: neutralization number (N.N.); per cent viscosity increase at 210° F.; sludge and lacquer; lead weight loss (in milligrams); and appearance of copper, iron and lead. The oil is compared with a reference oil of similar viscosity and is rated on the basis of viscosity increase, N.N. increase, sludge and lead weight loss. A maximum of three demerits is assigned to each factor rated. The sum of the demerits for an oil is called the stability number and ranges from 0 to 12. The reference mineral oils, solvent-refined Pennsylvania oils, have a stability number of 6 to 7. An oil-soluble, phosphorus- and sulfur-containing reaction product of pinene and P_2S_5 prepared as described in Example III of U. S. Patent No. 2,455,668, was incorporated in the oil before test in order to demonstrate the "inhibitor response" and the stability of the oil.

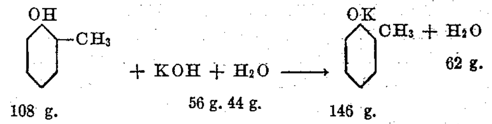
In the following tabulation, a residual oil obtained as described above is compared with a residual oil obtained by converting the untreated complex olefinic charge stock at 650° F. for 10 hours.

Residual Oil	Treated Charge	Untreated Charge
Yield, Wt. Per Cent	27.6	28.0
Specific Gravity	0.8713	0.8762
API Gravity	30.9	30.0
Pour Point, °F	+5	+5
K.V. at 100° F., Cs	26.20	37.79
K.V. at 210° F., Cs	4.85	6.01
Viscosity Index	120.3	113.5
Lovibond color	33	100
N.N	0.2	0.3
Carbon Residue (Ramsbottom)	0.2	0.2
Concentration of Oxidation Inhibitor, per cent	1	1
Analysis of oil after oxidation:		
N.N	0.5	12.0
K.V. at 210° F., Cs	4.89	12.39
Per Cent Viscosity Increase	0.8	104
Pb loss, mg	0.9	132.3
Sludge, Tube	Nil	Dark
Copper Coil	Black	Red, Black
Stability Number	0	5

It is apparent that the treated charge stock, when converted, yields a residual oil of higher viscosity index and better color than does the untreated charge. Notable, too, is the superior oxidation stability of the residual oil obtained from the treated charge.

Example II

Evaluation of the extractant solutions, and of related material which proved of little value, was based upon miscibility studies. The extractants were made by first dissolving the alkaline agent in a solvent and then adding the phenolic compound in equimolar proportion. In cases where complete solution was not attained at room temperature (25° C.), additional solvent was added until the resulting solution became clear. The calculated concentration of the salt takes into account the water of formation from the neutralization. For example, Run 4 shown in Table I below, can be represented as follows:



The concentration of the salt is therefore 70% in water.

Extractions were conducted by adding 10 parts by volume of petroleum ether, benzene, decanol, n-decene-1 or a Fischer-Tropsch product, as indicated in Table I, to 10 parts by volume of the extractant in a vessel having a capacity of 25 parts by volume and calibrated to 0.2 part. The vessel was then closed and the contents agitated for about thirty seconds. The vessel was set at rest at room temperature (unless otherwise indicated) until equilibrium was reached, usually less than thirty minutes. The change in volume of the two layers in the vessel was then noted. Since the vessel is calibrated to 0.2 part, the results are accurate to about one per cent.

The Fischer-Tropsch product used in this investigation was one having the following properties:

Boiling range:	
ASTM, °F	280–574
50% point, °F	416
Specific gravity	0.8137
Bromine number	72.5
Oxygenated compounds (Adsorption analysis), percent	14
Aromatics, percent	20
Olefins and paraffins, percent	66

As indicated, the 50% point in the ASTM distillation was 416° F., which corresponds to a boiling point of 419° F. for n-dodecene-1. Therefore, n-decene-1 and decanol are representative of some of the olefins and oxygenated compounds which are present in this complex olefinic charge, while petroleum ether and benzene are representative of the general class of paraffins and aromatics.

The results of these extractions are shown below in Table I.

TABLE I

Preparation of extractant and extractions on petroleum ether, benzene, decanol, decene-[1] and Fischer-Tropsch charge

Number	Page Reference	Extractant							
		Acidic Component			Alkali			Solvent	
		Name	Parts by Wt.	Moles	Name	Parts by Wt.	Moles	Name	Parts by Wt.
1	389, 911	H_2SO_4, 96%							
2	375, 378	H_3PO_4, 85%							
3	389, 924	Sodium xylene sulfonate	50					Water	55
4	375, 353	meta-Cresol	108	1	KOH	56	1	do	44
5	389, 911	do			None				
6	389, 911	None			KOH	56	1	Water	44
7	375, 372	meta-Cresol	108	1	KOH	56	1	do	140
8	375, 379	do	108	1	NaOH	40	1	do	155
9	375, 354	do	108	1	KOH	56	1	Triethylene glycol	128
10	375, 354	ortho-Cresol	108	1	KOH	56	1	Water	44
11	375, 370	para-Cresol	108	1	KOH	56	1	do	57
12	375, 366	do	108	1	KOH	56	1	Water Methanol	44 34
13	375, 371	do	108	1	KOH	56	1	Methanol	84
14	389, 927	None			None			do	
15	375, 370	para-tertiary-Butyl phenol	150	1	KOH	56	1	Water	102
16	375, 358	Phenol	94	1	KOH	56	1	do	39
17	375, 359	"Selecto" [3]	101	1	KOH	56	1	do	68
18	375, 379	do	101	1	KOH	56	1	Methanol	60
19	375, 396	2,4-Xylenol	122	1	KOH	56	1	Water	50
20	389, 911	Resorcinol	110	1	KOH	56	1	do	44
21	389, 911	do	110	1	KOH	112	2	do	44
22	375, 396	K_2HPO_4	81					do	49
23	389, 905	Propionic acid	74	1	KOH	56	1	do	30
24	389, 905	Lactic acid	90	1	KOH	56	1	do	37

[1] Composite of ASTM boiling range 280–574° F., cf. p. 375, 346.

[3] 50% phenol, 50% cresylic acid.

TABLE I—*Continued*

Preparation of extractant and extractions on petroleum ether, benzene, decanol, decene[1] and Fischer-Tropsch charge

Number	Page Reference	Extractant		Extractions (1:1 Volume Ratio); Volume Per Cent Extracted From—				
		Calculated Concn. of the Salt, Per Cent	Saturated at 25° C.	Petroleum Ether	Benzene	Decanol	Decene-1[1]	Fischer-Tropsch Charge
1	389, 911	--------	--------	0	0	Gel	100	50
2	375, 378	--------	--------	0	0	Gel	0	4
3	389, 924	47.6	Yes	0	2	Gel	0	0
4	375, 353	70	No	0	0	100	0	13
5	389, 911	--------	--------	100	100	100	100	100
6	389, 911	--------	Yes	0	0	Gel	0	1
7	375, 372	48	No	0	0	Gel	0	4
8	375, 379	43	Yes	0	0	Gel	0	4
9	375, 354	[2] 50	No	--------	100	100	0	12
10	375, 354	70	No	0	0	100	0	3
11	375, 370	66	Yes	0	20	Gel	0	20
12	375, 366	60.4	Yes	10	40	100	6	20
13	375, 371	59	Yes	17	100	100	10	30
14	389, 927	--------	--------	100	100	100	22	40
15	375, 370	61	Yes	10	20	Gel	4	20
16	375, 358	62.5	Yes	0	0	Emulsion	0	4
17	375, 359	62	Yes	0	0	Gel	0	4
18	375, 379	64	Yes	8	80	100	4	25
19	375, 396	70	No	0	10	100	0	15
20	389, 911	(Monosalt) 70	No	0	0	0	0	0
21	389, 911	(Di salt) 70	No [4]	0	0	0	--------	0
22	375, 396	62	Yes	0	0	0	0	0
23	389, 905	70	No	0	0	0	0	0
24	389, 905	70	No	0	0	0	0	0

[1] Composite of ASTM boiling range 280–574° F., cf. p. 375, 346.

[2] Very viscous solution heated to 65° C. for extractions.

[4] Solidified on standing.

From the results in Table I, several observations can be drawn. As would be expected, cold concentrated sulfuric acid (No. 1) had no effect upon petroleum ether and benzene, but reacted vigorously with decanol, n-decene-1 and the complex olefin charge, as indicated by darkening and heat evolution. Upon standing, 50% of the complex olefinic charge separated.

Ortho phosphoric acid, 85% (No. 2), appears to be selective for oxygenated compounds. However, considerable darkening occurred in the complex olefinic charge. This is an undesirable feature since it indicates that at least some constituents have reacted and therefor are not directly recoverable.

Sodium xylene sulfanate (No. 3) failed to extract any material from the complex olefinic charge. Its solubility in water at 25° C. is only 47.6% however. It extracts only a small amount (2%) from benzene and gelled with decanol (indicating some solubility).

The 70% solution of potassium m-cresylate in water (No. 4) was the most effective of the several extractants, and is preferred herein. It is selective for decanol and extracted 13% of the complex olefinic charge. m-Cresol alone (No. 5) had no selectivity under the operating conditions, that is, it had no selectivity for compounds of such relatively low molecular weight. A 56% solution of potassium hydroxide in water (No. 6) had practically no extracting power. A 48% solution of potassium m-cresylate in water (No. 7) exhibited slight extracting power (4% of the complex olefinic charge), indicating that the more concentrated solutions are more advantageous. The sodium salt of m-cresylate (No. 8) is soluble in water only to the extent of 48%, thus limiting its effectiveness.

In No. 9, triethylene glycol was used as the solvent with potassium m-cresylate. The potassium salt was soluble when present in the amount of 70%; however, the solution was quite viscous. Dilution to a 50% concentration decreased the viscosity somewhat but it was still necessary to heat the extraction mixture to 65° C. to obtain intimate mixing. The extractant was then selective for benezene and decanol and extracted 12% of the complex olefinic charge. The glycol type solvent, therefore, increases the solubility of aromatic hydrocarbons in the extractant.

A 70% solution of potassium o-cresylate in water—No. 10—was selective for decanol, and extracted 3% of material from the complex olefinic charge. It is, therefore, less effective than the corresponding m-cresylate. Potassium p-cresylate (No. 11) was somewhat less soluble in water (66%), but partially dissolved both benzene and decanol and extracted 20% of the complex olefinic charge. The latter extractant is therfore advantageous for extracting both aromatic and oxygenated compounds. By using methyl alcohol, along with or in place of water, as the solvent, the solubility of benzene is increased further (Nos. 12 and 13, respectively). The solubilities of petroleum ether and n-decene-1 also increase, although to a lesser extent. Methyl alcohol used alone as an extractant exhibits little selectivity (No. 14).

The potassium salt of p-tertiary butyl phenol (No. 15) is slightly less soluble in water than is the potassium salt of p-cresol. Its extracting power is also somewhat different, for it partially dissolves petroleum ether and n-decene-1 in addition to benzene and decanol. However, it extracts 20% of the complex olefinic charge, thus indicating its extracting capacity.

A saturated aqueous solution of potassium phenate (No. 16) shows some capacity to dissolve decanol and extracts 4% of the complex olefinic charge. A saturated aqueous solution of the potassium salts of a mixture of phenol and cresols (No. 17), known in the art as "Selecto" and currently used in the Duo-Sol process, provides similar results. By using methyl alcohol as the solvent (No. 18), the solubility of each of the constituents is increased.

The potassium salt of 2,4-xylenol (No. 19) is quite soluble in water. It is selective for both decanol and benzene, and extracts 15% of the complex olefinic charge.

The succeeding examples failed to exhibit extracting power, as did No. 3 (sodium xylene sulfonate) and No. 6 (potassium hydroxide), referred to above. The mono- and di-potassium salts of resorcinol (Nos. 20 and 21, respectively) are soluble in water, but extract nothing from petroleum ether, benzene, decanol, n-decene-1 or the complex charge. Catechol, hydroquinone and pyrogallol would not form clear potassium salt solutions because of their tendency to oxidize, as evidenced by the rapid darkening of color and precipitation of oxidation product.

Saturated aqueous solutions of K_2HPO_4 (No. 22), a 70% solution of potassium propionate (No. 23) and a 70% solution of potassium lactate (No. 24), also failed to extract any material from petroleum ether, benzene, decanol, n-decene-1 and the complex charge.

Six of the foregoing extractants which exhibit varying degrees of effectiveness were used to extract the complex olefinic charge. A 2:1 (total) volume ratio of extractant solution to charge was used, following the procedure described in Example I above. The raffinate in each instance was finally water washed, filtered through paper and percolated through silica gel (as described in copending application Serial No. 144,912, filed February 18, 1950). Results of these extractions are provided in Table II following.

TABLE II

No. in Table I	Extracting Solution	Adsorption Analysis of Raffinate, Vol. Per Cent		
		Olefins and Paraffins	Aromatic Compounds	Oxygenated Compounds
	None	66	20	14
4	70% K m-Cresylate, H_2O.	78	22	0
4A	70% K m-Cresylate in H_2O.[1]	76	24	0
9	50% K m-Cresylate: 44% Triethylene: Glycol 6% H_2O.[2]	80	20	0
10	70% K o-Cresylate in H_2O.	76	22.4	1.6
16	62.5% K phenate in H_2O.	71	24	5
17	62% K salt of "Selecto" in H_2O.	72	26.5	1.5
18	64% K salt of "Selecto", 28% CH_3OH and 8% H_2O.	85	15	0

[1] Extraction made at 45–50° C.
[2] Extraction made at 65–75° C.

It will be noted that all of the examples shown in Table II demonstrate a selective extraction capacity of the several solutions therein. In all cases, oxygenated compounds are extracted from the complex olefinic charge. A 70% solution of potassium m-cresylate in water (Nos. 4 and 4*a*) is again shown to be outstanding.

Although the invention has been described above with emphasis upon certain complex olefinic charge stocks, the extraction procedure contemplated herein is also advantageous for beneficiating other complex mixtures containing oxygenated compounds having a molecular weight between about 30 and 300. The separation of naphthenic acids from hydrocarbon fractions containing the same, the fractionation of oxidized paraffin wax, etc. provide additional illustrations.

One unusual facet of the present invention is in the improved "inhibitor response" of the illustrative synthetic oils shown above. In contrast, when a complex olefinic stock from a Fischer-Tropsch reaction is treated with an acid to remove some undesirable materials and the acid-treated stock is converted to a lubricant, the latter either fails to exhibit "response" or has but a very minor "response." This also obtains when the stock is treated with an alkaline material, either in solution or in solid form. The oils obtained following an acid, or alkaline treat, however, are characterized by desirable properties, namely, low pour point, high viscosity index, good color and low carbon residue.

It is to be understood that the foregoing specific treating conditions and examples serve to illustrate the invention, for it will be apparent to those skilled in the art that modifications and variations thereof may be used. It is to be understood, therefore, that such modifications and variations fall within the scope of the appended claims, and that the invention is to be construed broadly in the light of the language of the appended claims.

We claim:

1. A process for preparing a synthetic lubricant from an olefinic charge stock obtained by a Fischer-Tropsch reaction and having a substantial portion boiling within the range of about 150° F. to about 600° F., said lubricant having good color, low carbon residue and having inhibitor response with an oil-soluble, phosphorus- and sulfur-containing reaction product of pinene and P_2S_5, which comprises: contacting said charge stock with a substantially saturated solution of an alkali metal salt of a mono-hydroxy aromatic compound represented by the general formula R_n—A—OH wherein A is an aromatic nucleus, R is an alkyl group having less than about 6 carbon atoms, and *n* is an integer from 0 to 3, whereupon an extract layer and a raffinate layer are formed; separating said extract and raffinate layers; and converting said raffinate layer into said synthetic lubricant.

2. The process of claim 1 wherein the charge stock is one boiling predominantly within the range of about 200° F. to about 300° F.

3. The process of claim 1 wherein the charge stock is one boiling predominantly within the range of about 300° F. to about 450° F.

4. The process of claim 1 wherein the ratio of said charge stock to said solution is between about 0.25 and about 4.

5. The process of claim 1 wherein the solution is a substantially saturated aqueous solution.

6. The process of claim 1 wherein the solution is a substantially saturated, aqueous alcoholic solution.

7. The process of claim 1 wherein the alkali metal salt is potassium.

8. The process of claim 1 wherein the mono-hydroxy compound contains a phenyl group.

9. The process of claim 1 wherein the mono-hydroxy compound is m-cresol.

10. The process of claim 1 wherein the solution is a substantially saturated solution of potassium m-cresylate.

11. The process for separating oxygenated organic compounds and olefins from an olefinic mixture obtained by a Fischer-Tropsch reaction and having a substantial portion boiling within the range of about 150° F. to about 600° F., which comprises: contacting said mixture with a substantially saturated solution of an alkali metal salt of a mono-hydroxy aromatic compound represented by the general formula R_n—A—OH wherein A is an aromatic nucleus, R is an alkyl group having less than about 6 carbon atoms, and *n* is an integer from 0 to 3, whereupon an

extract layer and a raffinate layer are formed; separating said extract and raffinate layers, said extract layer being richer in said oxygenated compounds than the original olefinic mixture, and said raffinate layer being richer in olefin content than said original olefinic mixture.

12. The process of claim 11 wherein the olefinic mixture is one boiling predominantly within the range of about 300° F. to about 450° F.

13. The process of claim 11 wherein the solution is a substantially saturated aqueous solution.

14. The process of claim 11 wherein the solution is a substantially saturated, aqueous alcoholic solution.

15. The process of claim 11 wherein the alkali metal salt is potassium.

16. The process of claim 11 wherein the monohydroxy compound contains a phenyl group.

17. The process of claim 11 wherein the monohydroxy compound is m-cresol.

18. The process of claim 11 wherein the solution is a substantially saturated solution of potassium m-cresylate.

19. The process for separating an oxygenated organic compound and an olefin of similar boiling point and having a molecular weight from about 30 to about 300, from a mixture containing the same, which comprises: contacting said mixture with a substantially saturated solution of an alkali metal salt of a monohydroxy aromatic compound represented by the general formula R_n—A—OH wherein A is an aromatic nucleus, R is an alkyl group having less than about 6 carbon atoms, and n is an integer from 0 to 3, whereupon an extract layer and a raffinate layer are formed; separating said extract and raffinate layers, said extract layer being richer in said oxygenated compounds than the original olefinic mixture, and said raffinate layer being richer in olefin content than said original olefinic mixture.

THOMAS F. RUTLEDGE.
FRANCIS M. SEGER.
ALEXANDER N. SACHANEN.
WILLIAM E. GARWOOD.

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