# PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

# Improvements in or relating to the Separation of Hydrocarbons and Oxygenated Compounds from Mixtures.

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is directed to a method for treating hydrocarbon mixtures containing oxygenated organic compounds olefins, aromatic hydrocarbons, condensed ring and conjugated hydrocarbons resulting from the reaction of carbon monoxide and hydrogen over a catalyst. In its more specific aspects, the invention is directed to the removal of oxygenated compounds, aromatic hydrocarbons, condensed ring and conjugated hydrocarbons from such hydrocarbon mixtures to make the hydrocarbons suitable as a feed stock for lubricating oil synthesis.

Prior to the present invention, it has been customary to produce hydrocarbons and oxygenated organic compounds by the Fischer-Tropsch synthesis reaction wherein a mixture of carbon monoxide and hydrogen is contacted with a catalyst under conditions to form a product including hydrocarbons and oxygenated organic compounds. This material has been proposed as a feed stock for polymerization to produce polymers suitable for use as lubricating oils. Specifically, it has been found that alpha olefins in the product resulting from the contact of a mixture of carbon monoxide and hydrogen with a catalyst under suitable conditions are quite useful for synthesis to lubricating oil polymers. However, this product contains considerable amounts of oxygenated organic compounds which are usually deleterious in polymerization reactions. For example, Friedel-Crafts catalysts such as aluminium chloride, react with oxygenated organic compounds which results in degradation of catalyst and in poor yields and conversions.

We have also discovered that besides the contaminating oxygenated organic compounds, the naphtha produced by synthesis of carbon monoxide and hydrogen over a catalyst also contains a considerable amount of material having an aromatic or condensed ring structure. These hydrocarbon compounds have been found to be undesirable in the synthesis of the alpha olefins for lubricating oil fractions. The undesirability of these compounds is due to the fact that they compete with the olefins in the reaction and are alkylated to form material of lower boiling point than the desirable polymer. Furthermore, the presence of the ring structure in the lubricating oil polymer causes the polymer to be graded in quality for use as a lubricant. On the other hand, these ring structure hydrocarbons are very valuable compounds if they could be obtained free of the contaminating oxygenated compounds with which they are associated in the synthetic naphtha produced from carbon monoxide and hydrogen.

It has now been found that naphtha of the type mentioned before may be treated in a sequence of operations which will allow the removal of the deleterious compounds. In accordance with the present invention, the naphtha contaminated with oxygenated organic compounds which results from the Fischer-Tropsch reaction is subjected to a series of treatments which includes contacting the naphtha with a solvent which will selectively remove the oxygenated organic compounds, following which the solvent is removed from the naphtha which is then subjected to a treatment which will selectively remove the aromatic, condensed ring and conjugated hydrocarbons and allow its recovery for subsequent treatment for production of substantially pure aromatics. The naphtha which has been treated to remove both oxygenated organic compounds and aromatic, condensed ring and conjugated hydrocarbons is then polymerized to form a lubricating oil polymer.

It is, therefore, the main object of the present invention to provide a process whereby

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naphtha contaminated wih oxygenated organic compounds and aromatic, condensed ring structure and conjugated hydrocarbons is treated to remove the materials and then make the naphtha suitable as a feed stock for catalyic conversions.

Another object of the present invention is to provide a process for polymerizing olefinic hydrocarbons in the product resulting from the synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen whereby the deleterious effects of contaminating bodies is obviated.

A still further object of the present invention is to provide a process whereby pure aromatics are recovered from the product of a synthesis operation in which carbon monoxide and hydrogen are contacted with an iron-type catalyst to produce a product including aromatics, other hydrocarbons and oxygenated organic compounds.

Briefly, the present invention is based on the discovery that the product produced in the so-called Fischer-Tropsch synthesis contains, besides the usual oxygenated organic compounds such as ketones, esters, aldehydes, organic acids, olefins and paraffins, aromatic hydrocarbons, condensed ring hydrocarbons, and compounds having conjugated bonds such as acyclic dienes and styrene and its homologues. In accordance with the present invention, this product may first be subjected to a series of treatments, including distillation, to segregate a fraction containing the hydrocarbons of ring structure, which is then subjected to treatment with a solvent having the ability to remove selectively the oxygenated organic compounds of the type mentioned above, leaving a raffinate phase which is substantially free of the oxygenated organic compounds. This raffinate is then subjected to a second treatment with a solvent or adsorber having the ability to remove selectively the aromatic hydrocarbons, condensed ring hydrocarbons and conjugated hydrocarbons. The raffinate from this treatment is then subjected, after removal of solvent, to polymerization conditions in the presence of a Friedel-Crafts type catalyst to obtain a polymer having improved lubricating oil qualities while the extract in which the aromatic, condensed ring and conjugated hydrocarbons are present is treated for recovery of them.

In one specific mode of practicing the present invention, the naphtha resulting from the contact of carbon monoxide and hydrogen with a catalyst under suitable conditions is subjected to treatment with an aqueous alkaline solution to remove acidic bodies. The naphtha is then subjected to a distillation operation to segregate a fraction boiling from about 100° to about 600°F. This fraction is extracted with a solvent such as aqueous methanol under conditions to cause formation of raffinate and extract phases. The raffinate phase is separated from the extract phase and solvent is removed therefrom. The raffinate is then subjected to treatment with a solvent, such as liquefied sulfur dioxide, to cause the formation of a second raffinate and second extract phase. The second raffinate phase is separated from the second extract phase and treated for the removal of sulphur dioxide and then subjected to contact with a Friedel-Crafts type catalyst to produce a lubricating oil having desirable characteristics.

In accordance with another mode of our invention, a product such as that described above is washed with an alkaline solution to remove organic acids. The product in this particular mode is then extracted with an aqueous solution of methanol to form a first raffinate and a first extract phase and the two are separated from each other. The first raffinate phase is then distilled to segregate fractions boiling up to 400°F. and between 400° and 600°F. The fraction boiling between 400° and 600°F. is subjected to a second extraction with a solvent or adsorbent having the ability to separate aromatic, condensed ring and conjugated hydrocarbons from the paraffinic and olefinic constituents in the fraction. The second extraction, such as, for example, with sulfur dioxide at a low temperature, causes the formation of a second raffinate and second extract phase which are separated from each other. The raffinate phase is then subjected to a distillation operation to remove solvent and the raffinate is admixed with the fraction boiling up to 400°F. In this particular mode of practicing our invention, advantage is taken of the discovery that the material boiling below 400°F. does not contain any appreciable quantities of hydrocarbons having condensed ring structure. Neither does the material boiling below 400° F. have appreciable quantities of hydrocarbons having aromatic structures. Thus, in accordance with this particular mode of our invention, only the fraction containing the deleterious compounds is subjected to the series of extractions. The combined fraction is suitable as a feed stock for the synthesis of lubricating oil polymer.

In accordance with a still further mode of our invention, a mixture of carbon monoxide and hydrogen which is controlled at a ratio in the range between 1.5:1 to 1.8:1 is subjected to conditions including contact with a catalyst such as an oxide or metal of the Group VIII, at a temperature in the range between 500°F. and 650°F. and a pressure of 300 to 500 pounds per square inch gauge. In this operation, it is desirable to provide a recycle ratio of unreacted material to feed mixture in the range from about 2:1 to 5:1. This synthesis produces a product including paraffinic, aromatic, and olefinic hydrocarbon and oxygenated organic compounds such as ketones, aldehydes, organic acid, esters, alcohols and the like. The presence of the oxygenated organic compounds makes the separation of the aromatic hydrocarbons from the other hydrocarbons of similar boiling points very difficult. Therefore, in accordance with this mode of our invention, the product is subjected to a distillation operation to obtain a fraction boiling between 100°F. and 600°F. This fraction is then subjected to treatment to remove the oxygenated organic compounds. The treatment may involve extraction with aqueous methanol or contacting with a treating reagent comprising an alkali metal hydroxide, oil-soluble alkali metal petroleum sulfonate, and a hydrocarbon boiling in the lube oil boiling range at a temperature of approximately 300°F. Such treatment, whether solvent extracting or contacting, effectively removes the oxygenated organic compounds from the hydrocarbon fraction. The naphtha now substantially free of oxygenated compounds is then subjected to solvent extraction for separation of the predominantly aromatic hydrocarbons, condensed ring and conjugated hydrocarbons from the predominantly paraffinic hydrocarbons. The raffinate may then be subjected to polymerization conditions in accordance with other modes of our invention while the extract may be treated for removal of olefins and separation of pure aromatic hydrocarbons.

It must be emphasized that in accordance with this mode of our invention, it is possible to obtain higher purity aromatics from synthesis naphthas than has been possible from products resulting from catalytic conversions of hydrocarbon fractions obtained from petroleum. This is due, primarily, to the ratio of olefins to paraffins in the non-aromatic portion of the aromatic fraction of synthesis naphtha which is appreciably higher than in the corresponding fractions from converted petroleum fractions. For example, the olefin to paraffin ratio in the synthesis naphtha extract is approximately 10:1 while the olefin to paraffin ratio in extracts from converted petroleum fraction is in the range of 1:1 to 1:10. Thus, when acid treating the former fraction the olefins are easily removed while in the latter case the olefins are in a minor amount and paraffins are present in major quantities and are unaffected by the acid.

The invention will now be further illustrated by reference to the drawing, in which:

Fig. 1 is a flow diagram of one mode of practicing our invention;

Fig. 2 presents a flow diagram of a second mode of practicing the invention; and

Fig. 3 presents a flow diagram of a third mode of practicing the invention.

Referring now to the drawing and specifically to Fig. 1, numeral 11 designates a charge line through which a hydrocarbon fraction, which is the product obtained by synthesis of hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen over a catalyst, is introduced into the system. The product flows through line 11 and is admixed with an alkaline solution introduced thereto by line 12, as will be described further. The mixture of product and alkaline solution is intimately contacted in an incorporator 13 and the mixture discharged by way of line 14 into a settling vessel 15. Settling vessel 15 is of sufficient capacity to allow separation by gravity between the hydrocarbon fraction and the alkaline solution. The alkaline solution is removed from vessel 15 by line 16 and recycled in part by line 17 and pump 18 to line 12. A portion of the used alkaline solution may be discharged from the system by manipulation of valve 19 in line 16 and an equivalent amount of fresh alkaline solution to compensate for that withdrawn may be introduced into the system by opening valve 20 in line 12. The hydrocarbon fraction separated from the alkaline solution in vessel 15 is withdrawn by line 21 and discharged into a fractionation zone 22. Fractionation zone 22 is illustrated by a single distillation tower provided with a heating means illustrated by coil 23. It is to be understood, however, that fractionation zone 22 may be a series of fractional distillation towers, each equipped with suitable internal baffling equipment to provide internal contact between vapors and liquid.

The treatment with alkaline solution in incorporator 13 and vessel 15 serves to remove organic acids from the hydrocarbon naphtha which is then subsequently distilled in fractionation zone 22 to remove material having less than 5 carbon atoms which is withdrawn from the system by line 24. Heavier fractions boiling about 600°F. are withdrawn from fractionation zone 22 by line 25 while a fraction having 5 or more carbon atoms and boiling up to 600°F. is withdrawn by line 26. This fraction will contain the desirable alpha mono-olefins and is also contaminated with aromatic hydrocarbons and conjugated condensed ring structures. The fraction is also contaminated with oxygenated organic compounds, such as ketones, aldehydes, esters and organic acids, which may not have been removed in vessel 15 in the alkaline solution separated from the hydrocarbon. Consequently, it is necessary in accordance with the present invention to subject this fraction boiling up to 600°F. to a solvent extraction treatment with aqueous methanol or other suitable polar solvent having the ability to separate oxygenated organic compounds from hydrocarbons. Such solvents are, for example, aqueous acetone, aqueous acetic acid, mono- or di-ethylene glycols, and the like. In this particular instance aqueous methanol containing approximately 20% of water is introduced into an extraction tower 27 by line 28. The hydrocarbon fraction boiling up to

600°F. is introduced thereto by line 26 as has been described. The conditions in extraction tower 27 are adjusted to produce a raffinate phase and an extract phase. The raffinate phase will include substantially only hydrocarbons while the extract phase will include the solvent and the oxygenated organic compounds remaining in the naphtha after the treatment in vessel 15. The extract phase may be removed from extraction tower 27 by line 29 for further treatment and recovery of the solvent and oxygenated organic compounds contained therein. The raffinate phase discharged by line 30 from extraction tower 27 may be treated in a tower, not shown, for recovery of any dissolved solvent therein and then discharged into a second extraction tower 31 wherein the primary raffinate is subjected to extraction with a solvent, such as liquefied sulfur dioxide at a low temperature, to cause the formation of a second raffinate and a second extract phase. The solvent employed in the second extraction zone 31 should be a solvent which will selectively separate aromatic, condensed ring structure and conjugated hydrocarbons from other hydrocarbons, such as olefins and paraffins. Such solvents, besides sulfur dioxide, will include phenol, aniline, tri- or hexa-ethylene glycols, sulfolanes, sulfolenes and furfural. Solid selective adsorbents such as silica gel may also be used. In this particular instance, it will be assumed that sulfur dioxide is the solvent and that it is employed at a temperature of the order of −50°F. Sulfur dioxide will be introduced by line 32 into the top of extraction tower 31, the hydrocarbon raffinate from primary extraction zone 27 being introduced by line 30. Conditions are adjusted in extraction zone 31 to form a second raffinate and a second extract phase. The second extract phase will include substantially all of the solvent and the aromatic, condensed ring and conjugated hydrocarbons which may be removed by line 9 for recovery of the solvent and these hydrocarbons. The second raffinate phase will be withdrawn by line 33 into a solvent recovery stripping zone 34 for removal of solvent from the raffinate. Stripping zone 34 is equipped with a heating or temperature controlling means illustrated by coil 35 for removal of the solvent, in this particular instance, sulfur dioxide, from the raffinate. Sulfur dioxide is removed by line 36 for reuse in the process while the sulfur dioxide-free raffinate is discharged by line 37. The raffinate now substantially free of oxygenated organic compounds and aromatic, condensed ring and conjugated hydrocarbons may then be polymerized in polymerization zone 38. While polymerization zone 38 has been shown as a block, it will be understood to include all auxiliary equipment necessary to conduct such polymerizations. Line 39 is provided for the introduction of aluminum chloride into polymerization zone 38 and aluminum chloride sludge is discharged through line 40. The polymer, which will include unreacted hydrocarbons, may be recovered from polymerization zone 38 by line 41 and subjected to distillation or treatment for recovery of the desirable product having lubricating oil characteristics.

In a second mode of practicing our invention, a product similar to that employed with respect to the example described in conjunction with Fig. 1 is introduced into the system by line 50 from a source not shown. Line 50 discharges the product into a caustic washing zone 51 which, for convenience, is illustrated as a rectangle. It will be understood of course that caustic washing zone 51 will include means for introducing, withdrawing and circulating caustic, which, for convenience, may include line 52, provided for introducing fresh caustic, and line 53 for discharge of the used caustic. The naphtha is separated from the caustic solution in zone 51 and is withdrawn therefrom by line 54 into a first extraction zone 55. Extraction zone 55 is similar to extraction zone 27 described with respect to Fig. 1 and is provided with a line 56 for introduction of a polar solvent, such as aqueous methanol, thereto. Similar to extraction zone 27, other polar solvents of the type mentioned may be used in extraction zone 55. These solvents should have the ability to remove selectively oxygenated organic compounds from hydrocarbons. Conditions are adjusted in extraction zone 55 for formation of a primary raffinate and a primary extract phase which are separated from each other. The extract phase will include the greater portion of the solvent and the oxygenated organic compounds and may be removed from extraction zone 55 by line 57 for recovery of the solvent for reuse and oxygenated organic compounds which are quite valuable in themselves.

The primary raffinate phase is removed from extraction zone 55 by line 58 and similar to the mode of Fig. 1 may also be treated by means not shown for recovery of the solvent. In this particular instance, it is assumed that such means, although not shown, are provided and the substantially solvent-free raffinate is introduced by line 58 into a distillation zone 59. Distillation zone 59, similar to distillation zone 22, may be a series of distillation towers but for convenience is shown as one tower. Distillation zone 59 is equipped with a heating means illustrated by coil 60 for adjusting temperature and pressure therein to cause removal by line 61 of a fraction having 5 or more carbon atoms boiling up to 400°F. and by line 62 a fraction boiling between 400° and 600°F. and by line 63 a fraction boiling above 600°F.

The fraction boiling between 400° and 600°F. in this particular instance contains a substantial amount of aromatics present in the orginal naphtha and also condensed ring and conjugated hydrocarbons. This fraction, therefore, is then subjected to treatment in a second extraction zone 64 with a solvent having the ability to remove selectively these types of hydrocarbons from the other hydrocarbons contained in the fraction introduced in zone 64 by line 62. Similar to the solvents employed in extraction zone 31, any solvent having the ability to remove selectively aromatic, condensed ring and conjugated hydrocarbons from other hydrocarbons may be employed. However, sulfur dioxide is the preferred solvent which may be used at a low temperature of approximately —50°F. This solvent may be introduced into extraction zone 64 by line 65 and conditions are adjusted in zone 64 to cause the formation of a second raffinate and a second extract phase. The second extract phase, which will include a substantial amount of the solvent and the aromatic condensed ring structure hydrocarbons may be withdrawn by line 66 for further treatment for recovery of the solvent and the hydrocarbons which have been removed. These hydrocarbons in themselves are valuable materials and may be recovered for further use. The raffinate is withdrawn from extraction zone 64 by line 67 and is discharged thereby into a solvent stripping zone 68. Solvent stripping zone 68 is provided with a temperature adjusting means which is illustrated by coil 69 for adjustment of temperature and pressure in zone 68 for recovery of solvent from the raffinate. This recovered solvent may be returned to extraction zone 64 by line 70 as will be described further. The substantially solvent-free raffinate is withdrawn from stripping zone 68 by line 71 and has admixed with it the fraction boiling up to 400°F. withdrawn from distillation zone 59 by line 61. The combined fractions boiling up to 600°F. substantially free of oxygenated organic compounds and objectionable aromatic, condensed ring and conjugated hydrocarbons may then be subjected to the catalytic conversion operation, such as polymerization, in the presence of a Friedel-Crafts type catalyst in zone 72. Similar to zone 38, polymerization zone 72 is provided with a line 73 for introduction of aluminum chloride and line 74 for withdrawal of aluminum chloride sludge. The product, including lubricating oil polymers, may be withdrawn by line 75.

The solvent removed from stripping zone 68 by line 70 is recycled to extraction zone 64 along with a diluent which may be normal butane, normal pentane or the like introduced by line 76. The normal butane or normal pentane serves to cause substantially complete separation between the non-aromatic and aromatic constituents in the fraction introduced in extraction zone 64 by line 62.

Referring now to Fig. 3, numeral 90 designates a synthesis unit which is provided with means for contacting a feed gas with a suitable catalyst to produce hydrocarbons and oxygenated organic compounds from carbon monoxide and hydrogen. It will be understood that, for convenience, synthesis unit 90 is shown as a block and will include means for contacting the feed with the catalyst, separating products from the catalyst, and recycling unreacted material. Leading to synthesis unit 90 is line 91 by way of which a mixture of carbon monoxide and hydrogen is introduced into the system. Conditions are maintained in unit 90 to obtain a product containing hydrocarbons and oxygenated compounds. This product is removed from unit 90 by line 92 and discharges to a treating zone 93 in which it is treated with an alkaline solution such as sodium hydroxide introduced by line 94. The sodium hydroxide is removed from zone 93 by line 95 either for reuse or is discharged from the system. The treated product is then discharged by line 96 into distillation zone 97. It will be understood that distillation zone 97 may include a series of distillation towers, but for convenience it is shown as a single distillation tower with a heating means such as illustrated by coil 98 for adjustment of temperature and pressure therein. It will be understood that zone 97 will be equipped with suitable internal baffling equipment such as bell cap trays to insure intimate contact between vapors and liquid.

A fraction boiling below 100°F. is removed from zone 97 by line 99, while a heavy fraction boiling above 600°F. is removed by line 100; a fraction boiling in the range between 100°F. and 600°F. is withdrawn by line 101 and routed thereby to a treating zone 102 which may be either a solvent extraction operation or other treating operations in which oxygenated compounds are removed. For example, it may be a solvent extraction zone in which aqueous methanol is employed as a solvent or zone 102 may be a contacting zone in which the naphtha boiling in the range indicated is contacted at a temperature of approximately 300°F. with a treating agent comprising sodium hydroxide, sodium mahogany sulfonates and a lube oil fraction, such as a solvent extract of a lubricating oil fraction. A fraction substantially free of oxygenated compounds is discharged from zone 102 by line 103 into solvent extraction zone 104, wherein it is contacted with a solvent selective for removal of aromatic, condensed ring and conjugated hydrocarbons, such as sulfur dioxide which may be introduced by line 105.

Conditions are adjusted in zone 104 to form raffinate and extract phases which are separated from each other. The raffinate phase may be removed by line 106, freed of solvent and subjected to polymerization conditions as has been described with respect to Figs. 1 and 2. The extract phase is discharged from zone 104 by line 107 to a solvent stripping zone 108, for removal of sulfur dioxide by adjustment of temperature and pressure therein by a heating means illustrated by coil 109. The solvent is removed by line 110 for further use while the solvent-free extract is discharged by line 111 into a treating zone 112 in which the aromatic naphtha is subjected to contact with a treating reagent such as aluminum chloride, sulfuric acid, toluene sulfonic acid, and other treating reagents having the ability to react with olefins. In this particular instance it is assumed that aluminum chloride is employed, which is introduced into zone 112 by line 113 from a source not shown. Aluminum chloride reacts with the olefins and is removed as sludge by line 114. The aromatic extract may be discharged from zone 112 by line 115 into a distillation zone 116 which is provided with a heating means such as coil 117 which allows adjustment of temperatures and pressures for segregation of pure aromatics as will be described. Zone 116 is provided with internal baffling equipment such as bell cap trays and other packing material for intimate contact between vapors and liquids. While zone 116 is shown as a single tower, it is apparent that it may be a series of towers for separate recovery of different boiling aromatic fractions. Conditions are adjusted in zone 116 to allow removal by line 118 of a fraction consisting substantially of toluene; higher boiling fractions may be recovered by lines 119 and 120, respectively.

Thus, it will be seen, in accordance with this mode of our invention, it is possible to remove oxygenated organic compounds and aromatic and other ring structure compounds, to produce valuable lubricating oil, and also to obtain substantially pure aromatic compounds from naphtha produced by hydrogenation of carbon oxides. Heretofore, it has not been realized that aromatic and other ring structure hydrocarbons were present in synthesis naphthas. Nor has it been realized that these compounds deleteriously affected the quality of polymers produced from such naphthas; similarly, it has not been appreciated that synthesis naphthas are a rich source of valuable aromatic hydrocarbons.

It will be seen from the foregoing description that our invention accomplishes both of these ends.

Thus, our invention is directed to a process for increased utilization of naphtha produced by catalytic hydrogenation of carbon oxides, wherein said naphtha is employed for the production of synthetic lubricating oils and chemical raw materials. By the use of our process, better conversion (selectivity) of olefins to lubricating oil is obtained and lubricating oil of better quality is obtained than is otherwise possible. In addition, by the use of our process aromatic concentrates of high purity suitable for the manufacture of solvents and chemicals are recovered. In this operation, the total synthesis naphtha is fed to a caustic wash operation for the removal of carboxylic acids and low molecular weight oxygenated compounds. Removal of carboxylic acids prior to distillation results in the elimination of the formation of additional quantities of high molecular weight esters in the distillaion step, said esters which if present in the feed to solvent extraction for oxygenated compound removal would be difficult to remove and lowered extraction efficiency would result. The caustic washed naphtha distillate of the desired boiling range ($C_5$-600°F. is shown in the example) is fed to a unit for removal of oxygenated compounds. The solvent employed for this purpose may be aqueous methanol or some other polar solvent of similar characteristics for oxygenated compound removal. The raffinate from the extraction of oxygenated compounds is then fed to another unit wherein aromatic condensed ring and conjugated hydrocarbons are extracted and a raffinate suitable for use as a charge stock to lube synthesis is prepared. The agent employed for extraction of the aromatic, condensed ring and conjugated hydrocarbons may be a selective solvent such as liquid sulfur dioxide, or a selective adsorbent such as silica gel, or some other agent of similar characteristics for aromatic removal and recovery of high purity aromatic extracts. In either case, conditions of operation are adjusted in a manner well-known to the art for the recovery of material of high aromatic content. It is necessary for efficient recovery and efficient removal of the aromatics from the naphtha that the oxygenated compounds be removed from the naphtha before the sulfur dioxide extraction step in order than high selectivity in extraction of aromatics may be obtained. The aromatic extract from the sulfur dioxide or silica gel extraction step may then be processed in a number of ways familiar to the art for the recovery of aromatic material of the desired boiling range and other characteristics. For example, the extract will contain small quantities of olefins, which may be undesirable. These olefins may be eliminated by treatment of the aromatic extract with sulfuric acid of 83 to 90 per cent purity, and then redistilled for the production of aromatics having desirable characteristics with regard to color, odor, and stability.

The removal of aromatics from the deoxygenated naphtha prior to the polymerization step results in increased selectivity of conversion of olefins to lube oil. For example, when a synthesis naphtha deoxygenated by use of a polar solvent but not freed of aromatics is employed as feed stock conversions of olefins to materials boiling outside (heavier than) the feed range is 90 to 95 per cent, but conversion to lubricating oil is only 65 to 85 per cent. On the other hand, if the aromatics are removed prior to polymerization, conversions and selectivity of the olefins to lubricating oil of over 90 per cent may be realized. It has been shown that if aromatics are present in the feed to lube synthesis that considerabel alkylation of the aromatics with olefins occurs, with net lowered conversion of olefins to synthetic lube oil, and production of sub-lube aromatic materials of higher boiling range than the feed, and unfit for use as lubricating oils.

In order to illustrate the invention further, two portions of a naphtha, resulting from contact of carbon monoxide and hydrogen with an iron-type catalyst, such as promoted iron oxide, under suitable conditions to form a product of hydrocarbons and oxygenated organic compounds, were treated. The total product was distilled to obtain a fraction boiling between 160° and 400°F. This fraction was distilled over a mixture of sodium mahogany sulfonates, a phenolyic extract of a lubricating oil fraction, and sodium hydroxide with an amount of sodium hydroxide in the mixture of approximately 41.5% by weight. During this distillation, substantially all the organic acids were removed. This fraction was divided into two portions. One was treated with two 80% treats of a solvent comprised of 20% water and 80% methanol. The raffinate was separated from the solvent and subjected to inspection. This fraction was then polymerized at 150°F. employing aluminum chloride as a catalyst. The aluminum chloride was added slowly over a period of about one hour and the reaction continued for another five hours.

In the second instance, the fraction boiling between 160° and 400°F. which had been distilled over the mixture of sodium sulfonates, lubricating oil phenol extract and sodium hydroxide was subjected to treatment in accordance with the present invention in which it was extracted with two 100% treats of 80% aqueous methanol. Following this treat, the raffinate was freed of methanol solvent and then extracted with five 100% treats of liquefied sulfur dioxide at —50°F. Normal butane was employed in the solvent extraction with sulfur dioxide to facilitate separation. The fraction, which was subjected to the series of treats as described, was then polymerized at 150°F. employing aluminum chloride as the catalyst, with the aluminum chloride being added slowly over a period of about one hour and the reaction continued for another five hours.

The following table presents the results of the inspections of the product subjected to treatment in accordance with the foregoing description. In the first column, the feed inspections and the polymerization data on the material which have been extracted with aqueous methanol are given. In the second column, inspection and polymerization data are given for the fraction which had been treated in accordance with the present invention.

TABLE I.

| | | |
|---|---|---|
| Feed Inspections: | | |
| Bromine Number | 95.3 | 100.3 |
| % Alpha Olefins (of Total Olefins) | 88.2 | 87.8 |
| Oxygen Compound, Wt. % of Total Functional Groups | 0.05 | 0 |
| Specific Gravity at 60°F. | 0.7279 | 0.7420 |
| Ultraviolet Absorption coefficient, K at 232 Millimicrons | 1.733 | 0.749 |
| 235 Millimicrons | 1.709 | 0.578 |
| 258 Millimicrons | 0.858 | 0.189 |
| Infrared Coefficient at 14.3 micron | 0.246 | 0 |
| Polymerization Data: | | |
| Catalyst Added (grams $AlCl_3$ per 100 ml charge) | 1.5 | 1.5 |
| Lube Yield, Vol. % of Feed | 52.5 | 50 |
| Lube Inspections: | | |
| Viscosity at 210°F., S.S.U. | 75.4 | 67.8 |
| Viscosity Index | 97 | 105 |
| Gravity, ° API | 32.7 | 33.3 |

It will be seen from the foregoing data that the material treated in accordance with the present invention gives improved results as indicated by the quality of the lubricating oil polymer. It will be noted that the bromine number of the product treated in accordance with the present invention is substantially the same, if not greater than the material treated only with the methanol. It will also be noted that the alpha olefin content is substantially the same for the two materials while the oxygen content of the materials treated in accordance with the present invention has been reduced to zero. The higher specific gravity of the material treated in accordance with the present invention indicates removal of aromatic, condensed ring and conjugated hydrocarbon compounds. This is also indicated by the ultraviolet absorption coefficient K at 232, 285, and 258 millimicrons wave lengths. It has been established that high absorption coefficients at these wave lengths indicate the presence of certain aromatic and condensed ring structure hydrocarbons. Similarly, the infrared coefficient at 14.3 microns of the product treated in accordance with the present invention is substantially less than that in which aqueous methanol was used. Again this is an indication of substantially complete removal of aromatic constituents. The polymerization data further indicates the advantages of the present invention. While the lubricating oil yield was substantially the same for the two runs, it will be noted that the quality of the product treated in accordance with the present invention is substantially greater as indicated by the viscosity index than that treated in the conventional manner.

While not shewn by the data, runs were made on the same stocks in which smaller quantities of catalyst were added. In the product treated in accordance with the present invention by the same amount of catalyst, substantially greater yields of polymer of higher quality were also obtained.

The catalyst employed for the polymerisation process is one of the well known Friedel-Crafts type of catalyst such as illustrated by aluminum chloride, boron trifluoride, ferric chloride, titanium tetrachloride, zinc chloride, and many others too numerous to mention here.

The iron-type catalyst employed in the synthesis step may be iron, cobalt, or nickel or an oxide thereof. Preferably the synthesis catalyst is $Fe_2O_3$ or $Fe_3O_4$, with the former in the gamma form.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the separation of olefins from the mixture of hydrocarbons and oxygenated organic compounds produced in the Fischer-Tropsch synthesis process comprising treating the mixture with a solvent having the ability to remove selectively the oxygenated organic compounds to form an extract phase containing the oxygenated organic compounds and a raffinate phase, separating this raffinate phase, and treating it with a solvent or adsorbent which will remove selectively the aromatic hydrocarbons, condensed ring hydrocarbons and conjugated hydrocarbons to leave a second raffinate phase from which olefins suitable for polymerization to produce lubricating oil stocks may be separated.

2. A process as claimed in Claim 1 wherein the selective solvent for the oxygenated organic compounds is a polar solvent such as aqueous methanol, aqueous acetone, aqueous acetic acid or mono- or di-ethylene glycol.

3. A process as claimed in either of Claims 1 or 2 wherein a selective solvent is used for the removal of the aromatic, condensed ring and conjugated hydrocarbons such as sulfur dioxide, phenol, aniline, tri- or hexa-ethylene glycols, a sulpholane, a sulpholene or furfural.

4. A process as claimed in Claim 3 wherein the treatment with the selective solvent for the extraction of the aromatic, condensed ring and conjugated hydrocarbons comprises treatment with liquid sulfur dioxide at a temperature of about —50°F.

5. A process as claimed in any of Claims 1 to 4 wherein the first raffinate phase is freed from the solvent for the oxygenated compounds before treatment with the solvent for the aromatic, condensed ring and conjugated hydrocarbons.

6. A process as claimed in any of Claims 1 to 5 wherein the mixture is subjected to a preliminary treatment with an aqueous alkali solvent to remove acidic bodies before treatment with the solvent for the oxygenated compounds.

7. A process as claimed in any of Claims 1 to 6 wherein the mixture is fractionally distilled prior to the treatment and only the fraction boiling up to 600°F., and preferably the fraction boiling from 100-600°F., is subjected to the solvent treatment.

8. A process as claimed in any of Claims 1 to 7 wherein the raffinate fraction, after the extraction with the solvent for oxygenated compounds, is distilled to yield a fraction boiling up to 400°F. and a fraction boiling from 400-600°F., and a fraction boiling above 600°F., and the fraction boiling between 400 and 600°F. is subjected to the treatment with the selective solvent for the aromatic and conjugated and condensed ring hydrocarbons.

9. A process as claimed in Claim 8 wherein the fraction boiling below 400°F. is combined with the raffinate phase after the extraction of the fraction boiling between 400 and 600°F. with the solvent for the aromatic and conjugated and condensed ring hydrocarbons.

10. A process as claimed in any of the preceding claims wherein the raffinate phase obtained after treatment with the selective solvent for the aromatic and conjugated and condensed ring hydrocarbons is distilled to remove any entrained solvent, and is then polymerized to produce hydrocarbons boiling in the lubricating oil range.

11. A process as claimed in Claim 10

wherein the polymerization is effected by contacting with a Friedel-Crafts type catalyst.

12. A process as claimed in any of the preceding claims wherein the extract phase from the treatment with the solvent for the aromatic, condensed ring and conjugated hydrocarbons is treated to recover the aromatic, condensed ring and conjugated hydrocarbons.

13. The process for recovering olefins from mixtures of hydrocarbons containing them together with aromatic, condensed ring and conjugated hydrocarbons, and oxygenated compounds as hereinbefore described with reference to the accompanying drawings.

14. A method for the preparation of lubricating stocks as hereinbefore described.

Dated this 14th day of March, 1949.

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FIG. 1.

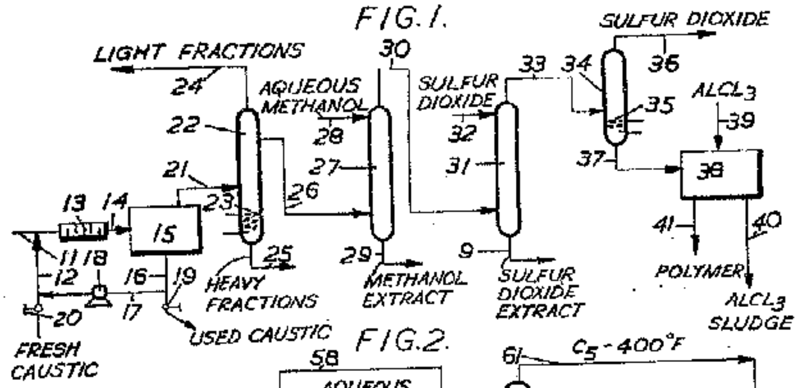

FIG. 2.

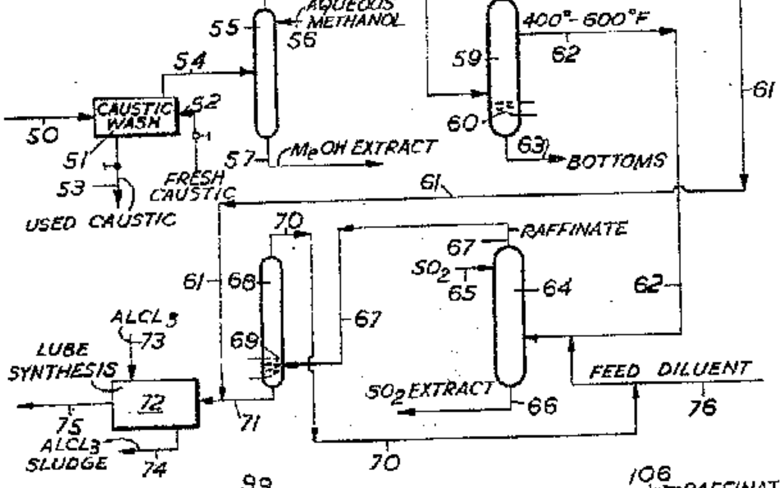

FIG. 3.