June 20, 1939. D. S. McKITTRICK 2,162,963

PROCESS FOR DESULPHURIZING MINERAL OILS

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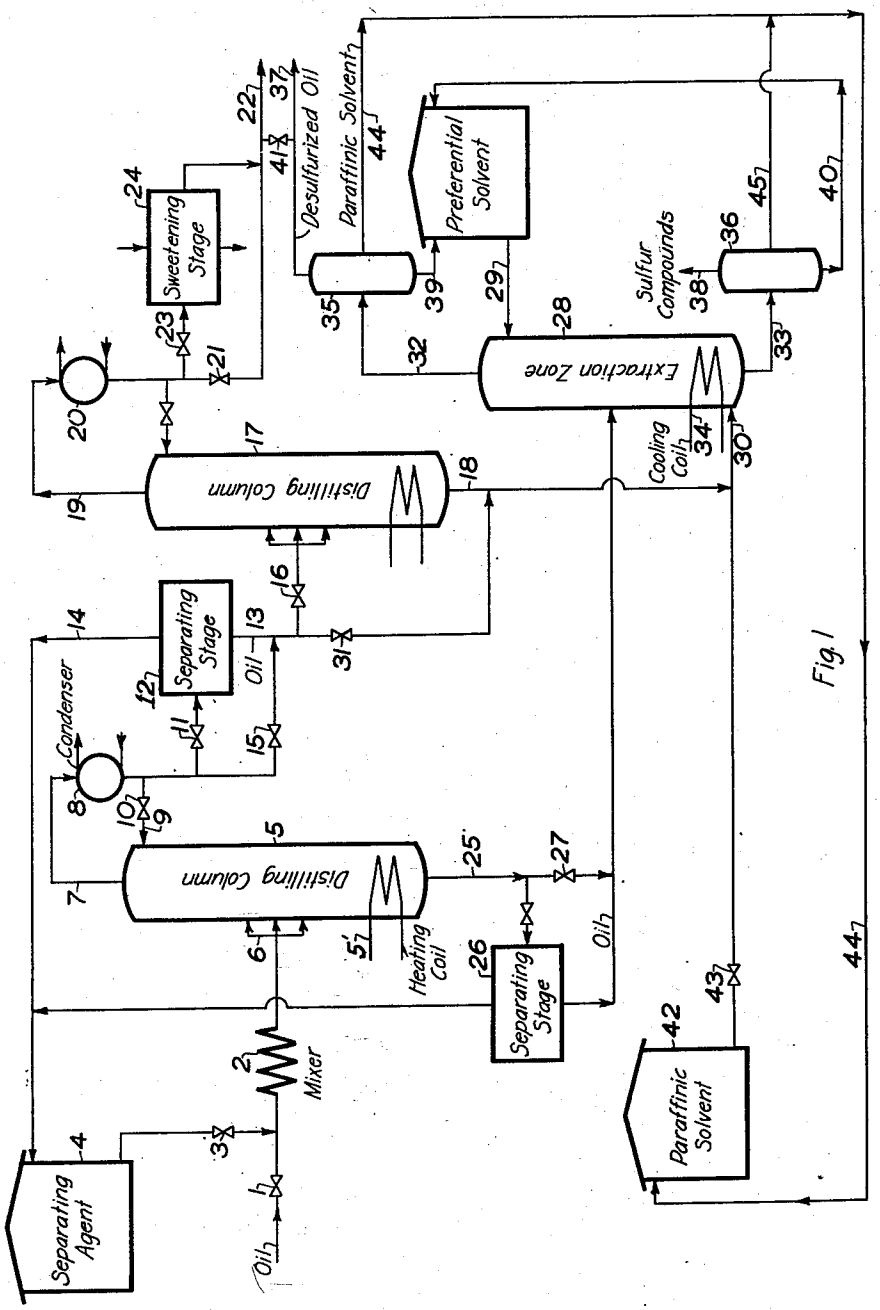


Fig. 1

Inventor: Donald S. McKittrick

By his Attorney: _____

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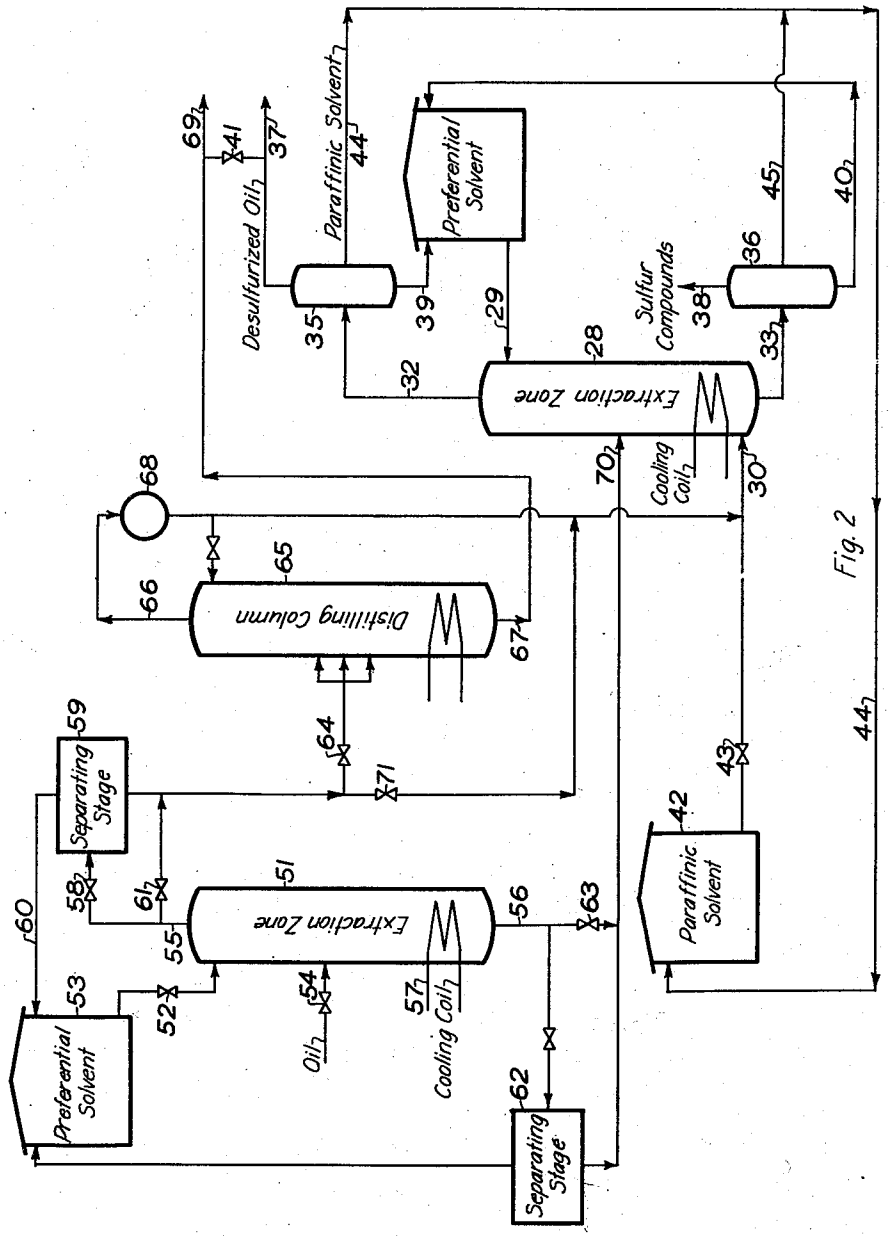


Fig. 2

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By his Attorney: [signature]

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UNITED STATES PATENT OFFICE

2,162,963

PROCESS FOR DESULPHURIZING MINERAL OILS

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20 Claims. (Cl. 196—13)

This invention relates to the treatment of hydrocarbon oils for the removal of sulphur, and is particularly concerned with the removal of sulphur from low boiling distillates, such as naphthas, gasoline, and cracked or straight-run distillates containing the same, although other distillates, such as kerosene, gas oil, and polymerized low boiling oils, as well as higher boiling mineral oil fractions may also be desulphurized in accordance with the present process.

More specifically, the present process is concerned with the removal of sulphur compounds, particularly the more refractory sulphur compounds, such as thiophene and its homologues, like alkyl thiophenes, from lower distillates, but may also be employed to remove the less refractory sulphur compounds, such as thioethers, mercaptans, and sulphides. The present invention is especially useful in the refining of distillates containing aromatic hydrocarbons, in which it is desired to retain the aromatic hydrocarbons in the desulphurized oil together with other hydrocarbons, such as gasoline, wherein the aromatic hydyrocarbons are desirable for improving the anti-knock properties of the fuel; but it may be applied to fractions containing little or no aromatics.

It has already been proposed to separate sulphur compounds from hydrocarbon oils by extracting the oil with a polar solvent which preferentially dissolves sulphur compounds and forms two liquid phases upon being mixed with the oil. (See U. S. Patent No. 2,024,117.) A disadvantage of such a process has been that an appreciable quantity of valuable hydrocarbons, and particularly of aromatic and unsaturated hydrocarbons, is lost together with the sulphur compounds. This is due to the fact that the preferential solvents are not totally immiscible with the hydrocarbons, under the conditions of the extraction, and a complete separation between sulphur compounds and hydrocarbons is not possible either in the usual batch or single countercurrent extractions.

It has now been found that the losses incident to such an extraction can be greatly reduced by preliminarily fractionating the sulphur-bearing oil to produce a first cut containing a concentrate of hyrdrocarbons of low carbon to hydrogen ratios, such as paraffinic hydrocarbons, and a second cut containing a concentrate of hydrocarbons of high carbon to hydrogen ratios, such as aromatic hydrocarbons, sulphur compounds being usually concentrated in the second cut; flowing the first cut through an extraction zone countercurrently to the preferential solvent for sulphur compounds; introducing the second cut into the extraction zone at a point intermediate to the points of introduction of the first cut and the solvent; and withdrawing raffinate and extract phases at spaced points in the extraction zone, The first cut may, optionally, be fractionally distilled to produce a modified cut containing the hydrocarbons of low carbon to hydrogen ratio in a more concentrated form, and this modified first cut employed in the extraction zone,

The fractionation to produce the aforesaid first and second cuts may be effected either by distillation or by solvent extraction, When distillation is employed for the preliminary fractionation, the initial sulphur-bearing oil is distilled in the presence of a separating agent of the type of preferential solvent for aromatic hydrocarbons to separate therefrom a distillate containing a concentrate of hydrocarbons of low carbon to hydrogen ratios, and constituting the first cut; the distillation residue constitutes the second cut, This distillation may, for example, be carried out in the manner described in the U. S. patent to Roelfsema, 2,069,329, the distillation temperature and/or the pressure being, however, preferably regulated so as to produce a distillate containing substantially only the most saturated hydrocarbons, particularly paraffines, leaving the olefinic and aromatic hydrocarbons in the residue.

When solvent extraction is employed for the preliminary fractionation, the initial sulphur bearing oil is contacted with a solvent capable of causing the formation of immiscible liquid phases, one of which contains the most saturated hydrocarbons in a concentrated form, and the other the remaining portion of the hydrocarbons, these phases being employed as the first and second cuts, respectively, in the subsequent extraction step. The sulphur compounds are usually concentrated in the second cut, but this is not necessary. The solvent may, for example, be a preferential solvent for aromatic hydrocarbons.

The process will be more particularly described in connection with the accompanying drawings, in which Figures 1 and 2 are schematic flow diagrams illustrating the steps of two specific embodiments of my process, it being understood that the flow diagrams are only exemplary, and not for the purpose of limiting the scope of the invention.

Referring to Figure 1 of the drawings, which illustrates the preferred embodiment, a feed of

sulphur-bearing low boiling hydrocarbon oil, such as a cracked distillate boiling within gasoline range, which may, if desired, have been given a preliminary light treatment with sulphuric acid or with an alkaline to remove the less refractory sulphur compounds, is introduced through a valve 1 into a mixer 2, together with a polar separating agent the type of preferential solvent for aromatic hydrocarbons supplied through a valve 3 from a tank 4; the resulting mixture is fed into the fractional distilling column 5 through a conduit 6, which may be provided with a heating coil 5' and with the usual contact means, such as bubble trays, and dephlegmating means, etc., not shown. In the column 5 the feed mixture is distilled to produce a distillate, withdrawn through the line 7, containing at least a portion of the most saturated hydrocarbons of the feed mixture, and little or no sulphur. The expression "saturated hydrocarbons" is intended to include both open chain and cyclic hydrocarbons, i. e., paraffinic and saturated naphthenic hydrocarbons. The distillate may, in addition, contain olefinic hydrocarbons the quantity of which is, however, kept to a minimum by careful operation of the column. The separating agent is preferably selected with regard to its boiling temperature to be distilled over, whereby all or the major portion is recovered with the overhead distillate. I may, however, also employ higher boiling separating agents which are only partially vaporized or which remain in the liquid state.

The distillate is condensed in a condenser 8 and a portion of the condensate may, if desired, be returned to the column through a reflux line 9 and a valve 10; the remainder flows through valve 11 and is treated in the separating stage 12 to remove the separating agent, if any, by further distillation, in situations where the formation of azeotropes is not a hindrance, or, in any case, by chilling the distillate and separating the resulting chilled condensate into an oil phase and a separating agent phase in a settling tank or a centrifugal separator, if necessary, in the presence of an added essentially oil-immiscible solvent like water or aqueous alcohol which dissolves the separating agent. The oil is withdrawn at 13, and the separating agent, or its solution in a solvent, at 14. The removal of the separating agent from the distillate is more specifically described in the U. S. patent to Roelfsema, 2,069,329. When the distillate contains little or no separating agent, the unit 11 may be by-passed through the valve 15.

With the limitations noted below as to the sizes of the distillation products, the column 5 may be operated either intermittently on successive batches of oil, or continuously, in the manner described in the above mentioned Roelfsema patent, i. e., the valves 1 and 3 may be adjusted to produce a distillation bottom product, withdrawn at 25, which is substantially free from the separating agent; or the same end may be achieved by separating the distillate into two liquid phases by cooling, and controlling the reflux of one or both of these phases to the column. It is not, however, essential to remove all of the separating agent overhead, because a small quantity does not interfere with the operation of the subsequent extraction step, especially when the separating agent is the same as the preferential solvent used for the extraction, and since the separating agent can, moreover, be separated from the residue in a separating stage 26, similar to the stage 12.

The temperature and pressure in the column 5 are regulated to produce a distillate which contains a concentrate of the most saturated hydrocarbons. Under these conditions sulphur compounds are usually for the greater part excluded from the distillate, although it may contain certain amounts of low boiling mercaptans when these are present in the oil fed through the valve 1. If the initial oil contains aromatic hydrocarbons, as most low boiling distillates do, the distillate from the column 5 is less aromatic than the initial oil. It may, for example, contain between about 30 and 75% of the original hydrocarbons, but since it is necessary to employ very exact fractionating control to void the distillation of undesirable quantities of aromatic and other unsaturated hydrocarbons when a large distillate is produced, I prefer to take off a distillate containing only between about 30 and 65% of the hydrocarbons. When the distillate contains large quantities of olefines, it is often desirable to distil even smaller quantities, such as 30 to 50%, to produce a distillate consisting substantially of, i. e., containing over about 85% of paraffinic and/or naphthenic hydrocarbons. Under any of these conditions, the concentration of hydrocarbons of high carbon to hydrogen ratios, such as the aromatics, in the distillate will be substantially less than in the original oil. As a specific example, a cracked gasoline fraction boiling between 175 and 200° C., containing 13% aromatics and 1% sulphur, may be distilled in the presence of ethylene diamine as the separating agent to produce a distillate containing about 60% of the original hydrocarbons, of which about 58% are non-aromatics and 2% are aromatics. The sharpness of the separation effected in the column 5 may be improved by initially distilling the oil into a number of narrower boiling fractions having boiling ranges of about 25° C. to 80° C., and subjecting each narrow boiling fraction separately to the distillation in the column 5.

According to the preferred embodiment of the process, the distillate from the column 5, constituting the first cut of the oil, is flowed through a valve 16 into a second distilling column 17, which may be similar to the column 5, wherein the first cut is distilled, substantially or totally in the absence of a separating agent to produce a distillation bottom product, withdrawn at 18, containing the most saturated hydrocarbons in a more concentrated form, and constituting a modified first cut. The conditions in the column 17 are such as to produce distillate withdrawn at 19, containing usually from about 10 to 50% of the feed to this column, although the process is not restricted to this range, since even greater amounts of oil may be taken off overhead. In general, it is desirable to take off overhead only enough oil to cause a concentration of the saturated hydrocarbons in the distillation residue. The distillate may be condensed in the condenser 20, flowed through the valve 21, and withdrawn at 22 as a separate product. If mercaptans and/or similar sulphur compounds are present, the distillate may be flowed through the valve 23, and the sweetening stage 24, wherein the distillate is treated by known methods, such as a sodium plumbite or a caustic soda treatment, preferably one which will remove sulphur.

The distillation residue withdrawn at 25, which may be passed either through the unit 26 to remove the separating agent or through the by-

pass valve 27, is the second cut of the original oil, and is fed into an extraction zone 28 at an intermediate point thereof. A preferential solvent for sulphur compounds, which is capable of forming two liquid phases when contacted with the oil, is introduced at 29 near one end of the extraction zone, and the residue from the column 17, constituting the modified first cut of the original oil, at 30 near the other end. If desired, the distillation in the column 17 may be eliminated, the distillate from the column 5 may be introduced at 30, by by-passing the column 17 through the valve 31. The extraction zone is arranged for the countercurrent flow of the distillate and the preferential solvent through a plurality of stages, which may be virtual, as in the case of a packed tower, or real, as in the case of a series of mixers and settlers. In the extraction zone, raffinate and extract phases (consisting predominantly of hydrocarbons and of a solution of sulphur compounds in the solvent, respectively,) are formed and flow countercurrently to one another, and are withdrawn at spaced points 32 and 33, respectively. The section between the intermediate inlet for the second cut and the inlet 29 for the preferential solvent is designated as the rectifying section of the extraction zone, and the section between the inlets for the first and second cuts as the stripping section, it being understood that raffinate phase from the stripping section flows into the rectifying section, and extract phase from the rectifying section flows into the stripping section. The temperature is regulated so that a minimum quantity of hydrocarbons is removed in the ultimate extract phase withdrawn from the stripping section, this quantity of hydrocarbons being in most cases between about 0.5 and 4% of the initial oil. Temperature regulating means, such as a cooling coil 34 may be provided for this purpose.

The solvent may be recovered from the separated phases in the units 35 and 36 by any suitable means, such as distillation or washing with water, etc. The desulphurized oil is withdrawn at 37 and the sulphur compounds at 38; the recovered preferential solvent is withdrawn at 39 and 40 and may be reused. The desulphurized oil may be blended with the distillate from the column 17 by means of the valve 41.

Instead of feeding only the first cut, i. e., distillate from the column 5, or the residue from the column 17 into the extraction unit at 30, the feed at this point may be augmented by introducing a paraffinic solvent having a boiling temperature range well outside of the distillate being desulphurized from a source 42 through a valve 43, and may be recovered from the raffinate phase at 44. Only negligible quantities of this solvent are usually in the extract phase, so that its separation from the preferential solvent in the unit 36 is not necessary; it may, however, be separated therein and withdrawn at 45. This may consist predominantly of paraffinic or naphthenic hydrocarbons, or their mixtures, the former being preferred. Thus, paraffinic hydrocarbons like light naphtha, pentane, isopentane, iso-octane, and highly refined white oils may be employed.

Referring to Figure 2, 51 represents an extraction zone, which may comprise one or more stages, for the countercurrent flow of a preferential solvent for aromatic hydrocarbons, fed into the extraction zone near one end through a valve 52 from a tank 53, and the feed of sulphur-bearing oil, fed through a valve 54, either at the other end of the zone, when the zone comprises only a rectifying section, or at an intermediate point as shown, when the zone comprises both rectifying and stripping sections. The rates of flow and temperature are regulated to produce counterflowing raffinate and extract phases which are withdrawn at 55 and 56, and constitute the first and second cuts of the initial oil, respectively, a sufficient quantity of solvent, or a solvent of sufficient solvent power being used to dissolve the unsaturated olefinic and aromatic hydrocarbons produce a raffinate which contains the most saturated hydrocarbons in a highly concentrated form, and amounting to between about 30 and 75% and, preferably, between about 30 and 65% of the hydrocarbons; when treating oils rich in olefines, raffinates containing less than 50% of the feed are preferred, as described above in connection with the process according to Figure 1. When the initial oil contains sufficient open chain paraffinic hydrocarbons (including branched and straight chain), to produce a raffinate containing only or over 85% of such hydrocarbons, the raffinate amounting to over about 30% of the initial oil, I prefer to remove all or most of the naphthenic hydrocarbons (i. e., cyclic paraffines) in the second cut; the naphthenic hydrocarbons may, however, be present in the first cut. In the stripping section, i. e., between the point of introduction of the feed and 56, the point of withdrawal of the extract phase, the extract phase may, if desired, be cooled by means of a coil 57 or otherwise treated to strip out saturated hydrocarbons which flow upwards and are ultimately recovered with the raffinate phase, this being particularly desirable when treating initial oils which are rich in olefines.

The raffinate phase may be flowed through a valve 58 to separating unit 59 for the removal of the preferential solvent, which may be returned to the tank 53 via the line 60; if desired, the unit 59 may be by-passed through a valve 61, especially when the preferential solvent for sulphur compounds employed in the subsequent extraction in the zone 28 is the same as that employed in the extraction zone 51 and the distilling unit 65 is by-passed. The extract phase may be similarly treated in the separating unit 62 for the removal of the preferential solvent, or by-passed via the valve 63.

The most saturated hydrocarbons in the first cut may be concentrated by passing through valve 64 into a distilling column 65, which may be similar to the column 17 of Figure 1, wherein the raffinate phase or first cut is distilled preferably in the absence of a separating agent or preferential solvent to produce a distillate, withdrawn at 66, containing the most saturated hydrocarbons in a more concentrated form, and constituting a modified first cut. The conditions in the column 65 are such as to produce a distillation residue, withdrawn at 67, containing usually from about 10 to 50% of the feed to this column, although the process is not restricted to this range, since even greater amounts of residue may be produced. In general, it is desirable to produce the largest possible distillate; therefore, preferably only sufficient residue produced to increase the concentration of the most saturated hydrocarbons in the distillate. The distillate is condensed in the condenser 68, and introduced into one end of the extraction zone 28. The distillation residue may be withdrawn at 69 as a separate product, or may be blended with the raffinate from the extraction zone 28, by means of a valve

41, if desired, after a sweetening or other mild desulphurizing treatment.

The arrangement and operation of the extraction zone 28 are similar to those of the zone 28 already described in connection with Figure 1; the second cut of the original oil is introduced at an intermediate point 70, the modified first cut, or, if desired, the original first cut, by by-passing the column 65 through the valve 71 near one end at 30, and the preferential solvent for sulphur compounds near the other end at 29, reference numerals 28, 29, 30 and 32 to 45 designating the same elements as in Figure 1.

The process according to Figure 2 involves two extractions: In the zone 51 the conditions are such that all of the initial oil save the most paraffinic portion is dissolved in the solvent and is in the extract phase; in the zone 28 substantially no hydrocarbons, or only a minor amount, i. e., less than about 4% of the initial, are dissolved in the preferential solvent together with the sulphur compounds, the remaining hydrocarbons passing into the raffinate phase. While about 4% is the maximum quantity of hydrocarbons which is dissolved in the extract phase from the zone 28 under the preferred operating conditions, both in the process according to Figure 1 and according to Figure 2, my invention is not limited thereto, but is intended to include also operations wherein a lower yield of desulphurized oil is obtained, for example, operation wherein as much as 10% of the initial hydrocarbons are present in the extract phase from the zone 28. The extract phase may, particularly when it contains larger amounts of hydrocarbons, be subjected to an intensive desulphurization treatment, such as, sulphuric acid, hydrogenation, oxidation, treatment with carbon monoxide, etc., and the desulphurized hydrocarbons may then be blended with the raffinate.

By "preferential solvent for sulphur compounds" is meant a solvent possessing such characteristics that the distribution ratio between the solvent or extract phase and the oil or raffinate phase is greater for sulphur compounds than for most soluble hydrocarbons, when the solvent is contacted with the oil under conditions causing the formation of liquid phases. It is not necessary that all sulphur compounds be preferentially dissolved, but only those which it is desired to extract, such as thiophenes. In the usual case the most soluble hydrocarbons present in the oil are aromatics. Most polar selective solvents employed for the extraction of mineral oils to separate them into relatively more paraffinic and aromatic portions, respectively, fall within this class, since thiophenes are generally more polar and are therefore more readily dissolved in such solvents than even aromatic hydrocarbons. The selectivity of these selective solvents between aromatics and sulphur compounds is, however, not the same for all, so that some are more suitable than others. The following solvents were found to be very suitable for the removal of sulphur by extracting such distillates: Lower aliphatic sulphonic acids, particularly methyl-sulphonic acid, ethyl-sulphonic acids, and isopropyl-sulphonic acid, thiophene aldehyde, ethyl cyanide, ethyl cyanoacetate, nitroaniline, aniline, methyl cyanide, ethylene diamine, liquid sulphur dioxide, a mixture of equal parts of liquid sulphur dioxide and acetone, methoxy methyl cyanide, methyl carbitol, and their mixtures. Solvents which are too miscible with the oil may be diluted with water or with a highly polar oxygenated aliphatic compound like methyl alcohol, ethyl alcohol, acetone, or their aqueous solutions. My invention, which resides in the combination of steps defined in the claims is, however, not limited to the use of these enumerated preferential solvents for sulphur, but may be employed in connection with any solvent which is sufficiently selective for sulphur compounds to permit these to be extracted without an undesirably high loss of hydrocarbons.

By "preferential solvent for aromatic hydrocarbons", similarly, is meant a solvent possessing such characteristics that when it is commingled with a mixture of hydrocarbons containing either open chain or cyclic saturated hydrocarbons together with aromatic hydrocarbons, under conditions causing the formation of two liquid phases, the distribution ratio between the solvent phase and the oil phase is greater for the aromatics than for the saturated hydrocarbons, solvents of this type being well known in the art. These solvents may be employed either in the distilling unit 5 of Figure 1 or in the first extraction zone 51 of Figure 2. As explained above, nearly all of these solvents are also preferential solvents for sulphur compounds and the same solvents can be employed for both purposes; but since the effectiveness of these solvents for the specific functions of extracting sulphur compounds on the one hand, and aromatics, on the other, is not the same, some being more effective for one purpose, and some for the other, a distinction in terminology is made. Thus, a solvent like ethylene glycol, while operative to extract sulphur compounds, is only very slightly selective between aromatics and sulphur compounds, and is, for this reason, not preferred in that capacity; but it has a fair selectivity between paraffinic hydrocarbons on the one hand, and aromatic hydrocarbons on the other hand, and may, therefore, be employed in the distilling unit 5. However, other substances which do not form two layers when commingled with the oil, but which have a preferential solvent affinity for aromatic hydrocarbons, and therefore cause the hydrocarbons of lower carbon to hydrogen ratios to be distilled over at a lower temperature than aromatic hydrocarbons of the same normal boiling temperature may also be employed for the distilling step in the embodiment according to Figure 1. The designation "separating agent of the type of preferential solvent for aromatic hydrocarbons" is, in the present specification and claims, used to include both of these types of separating agents. While any separating agent of this type may be employed in the distilling unit 5, it is preferable, in order to obtain a substantial yield of a distillate containing a concentrate of paraffinic hydrocarbons without the distillation of unduly large quantities of the separating agent or of the necessitating a very long column, it is desirable to use a separating agent which boils within or near, i. e., not more than about 80° C. below or 25° C. above the boiling range of the oil being distilled, the preferred boiling point being within the range: 25° C. below the initial boiling point of the fraction to the mid-point of the boiling temperature range of the fraction.

Any polar liquid which has the above described boiling temperature characteristics, and which has a preferential solvent attraction for aromatic hydrocarbons as compared with the more saturated hydrocarbons may be employed as the separating agent, such liquids having been found to cause the concentration in the distillation residue not only of the aromatics, but of the sulphur

compounds as well; these same agents will also cause the more saturated paraffinic hydrocarbons to be distilled at a lower temperature than the less saturated aliphatic hydrocarbons, such as olefines. These agents may, for example, be the solvents commonly employed for the solvent extraction of mineral oils, such as organic compounds, either aliphatic, carbocyclic, or heterocyclic, containing one or more of the following groups: $-NO_2$, $-CN$, $-SCN$, $=CO$, $-CH_2OH$, $=CHOH$, $\equiv COH$, $\equiv C-Cl$, $-NH_2$, $=O$, $=CS$, $-COOH$, $-OR$, and $-COOR$, wherein R designates an alkyl or aryl radical. Examples of these separating agents are: Nitrobenzene, benzonitrile, monochloracetonitrile, phenyl thiocyanate, phenolthiocyanate, formate of pyridine, benzaldehyde, acetone, furfural, furfuryl alcohol, chlorisopropyl alcohol, diacetone alcohol, methyl alcohol, ethyl alcohol, aniline, methyl lactate, triacetin, diacetin, methyl nitrobenzoate, formic acid, acetic acid, ethylenchlorhydrin, glycol monoacetate, glycol diacetate, lactic acid nitrile, toluidine, chlor pyridine, BB' dichloroethyl ether, chlor aniline, sulphur doxide, quinoline, isoquinoline, pyridine, chlorophenol, etc. My invention is not, however, limited to the specific solvents enumerated, nor to solvents containing the enumerated chemical groups, but may be used with any separating agent having a preferential solvent attraction for aromatics.

I have, however, found that when refining sulphur-bearing hydrocarbon mixtures boiling within gasoline range, superior results con be obtained by employing the following substances as separating agents, and their use constitutes the preferred form of my invention: Furfural, methyl cyanide, ethylene diamine, nitromethane and acetic anhydride.

I claim as my invention:

1. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of separating said fraction into a first cut containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and a second cut containing the remainder of the fraction, flowing said first cut through an extraction zone countercurrently to a preferential solvent for sulphur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the second cut into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the first cut washes hydrocarbons from the extract phase to produce a washed extract phase containing the solvent sulphur compounds and not more than a minor amount of the hydrocarbons contained in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone at spaced points.

2. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of separating said fraction into a first cut containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and comprising between about 30 and 75% of the hydrocarbons of the initial fraction and a second cut containing the remainder of the fraction, flowing said first cut through an extraction zone countercurrently to a preferential solvent for sulphur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the second cut into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the first cut washes hydrocarbons from the extract phase to produce a washed extract phase containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing the raffinate phase and the washed extract phase from said extraction zone at spaced points.

3. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of separating said fraction into a first cut containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and a second cut containing the remainder of the fraction, distilling said first cut to separate it into a first distillation product containing the hydrocarbons of low ratios of carbon to hydrogen in a more concentrated form than said first cut, and a second distillation product, flowing said first distillation product through an extraction zone countercurrently to a preferential solvent for sulfur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the second cut into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the distillation product washes hydrocarbons from the extract phase to produce a washed extract phase containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone at spaced points.

4. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises distilling said initial fraction together with a polar separating agent of the type of preferential solvent for aromatic hydrocarbons in a distillation zone, maintaining conditions of temperature and pressure in said zone to distil over a top product containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and forming a distillation bottom product in which the sulphur compounds and hydrocarbons of relatively high ratios of carbon to hydrogen are concentrated, flowing hydrocarbons from said top product through an extraction zone countercurrently to a preferential solvent for sulfur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the concentrate of sulfur compounds and hydrocarbons from said bottom product into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the hydrocarbons from said top product wash hydrocarbons from the extract phase to produce a washed extract phase containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons containing in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone at spaced points.

5. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises distilling said initial fraction together with a polar separating agent of the type of preferential solvent for aromatic hydrocarbons in a distillation zone, maintaining

conditions of temperature and pressure in said zone to distil over a first top product containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and forming a first distillation bottom product in which the sulfur compounds and hydrocarbons of relatively high ratios of carbon to hydrogen are concentrated, distilling the first top product substantially in the absence of a polar separating agent to produce a second top product and a second distillation bottom product, flowing hydrocarbons from said second bottom product through an extraction zone countercurrently to a preferential solvent for sulphur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the concentrate of sulphur compounds and hydrocarbons from said first bottom product into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the hydrocarbons from said second bottom product wash hydrocarbons from the extract phase to produce a washed extract phase and containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone at spaced points.

6. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises distilling said initial fraction together with a polar separating agent of the type of preferential solvent for aromatic hydrocarbons in a distillation zone, maintaining conditions of temperature and pressure in said zone to distil over a first top product containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and forming a first distillation bottom product in which the sulphur compounds and hydrocarbons of relatively high ratios of carbon to hydrogen are concentrated, distilling the first top product substantially in the absence of a polar separating agent to produce a second top product and a second distillation bottom product, flowing hydrocarbons from said second bottom product through an extraction zone countercurrently to a preferential solvent for sulphur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the concentrate of sulphur compounds and hydrocarbons from said first bottom product into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the hydrocarbons from said second bottom product wash hydrocarbons from the extract phase to produce a washed extract phase and containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction, withdrawing raffinate and washed extract phases from said extraction zone at spaced points, subjecting said second top product to a sweetening treatment, and blending the sweetened top product with oil contained in said raffinate phase.

7. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises distilling said initial fraction together with a polar separating agent of the type of preferential solvent for aromatic hydrocarbons boiling not lower than about 80° C. below the initial boiling point nor higher than about 25° C. above the end point of said initial fraction, in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distil at least a substantial portion of the separating agent together with hydrocarbons of relatively low ratios of carbon to hydrogen, thereby forming a rectified top product derived from the combined mixture containing a concentrate of hydrocarbons of low ratios to carbon to hydrogen and a distillation bottom product in which the sulphur compounds are concentrated and containing a concentrate of hydrocarbons of relatively high ratios of carbon to hydrogen, flowing hydrocarbons from said top product through an extraction zone countercurrently to preferential solvent for sulphur compounds under conditions causing the formation of counterflowing raffinate and extract phases, introducing the concentrate of sulphur compounds and hydrocarbons from said bottom product into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the hydrocarbons from said top product wash hydrocarbons from the extract phase to produce a washed extract phase containing the solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone at spaced points.

8. The process according to claim 7 in which the separating agent has a boiling point falling within the range: 25° C. below the initial boiling point of the initial fraction to the midpoint of the boiling temperature range of the initial fraction.

9. The process according to claim 7 in which a paraffinic solvent which is substantially immiscible with the preferential solvent for sulphur compounds is flowed through at least a portion of the extraction zone concurrently with the hydrocarbons from the top product.

10. The process according to claim 7 in which the separating agent is separated from the top product, and only the hydrocarbons thereof are introduced into the extraction zone.

11. The process for refining an initial hydrocarbon fraction including components boiling within gasoline range and containing sulphur compounds and aromatic and non-aromatic hydrocarbons, which comprises distilling said initial fraction together with a polar separating agent of the type of preferential solvent for aromatic hydrocarbons in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distil at least a substantial portion of the separating agent together with non-aromatic hydrocarbons, thereby forming a rectified top product derived from the combined mixture containing a concentrate of non-aromatic hydrocarbons and a distillation bottom product containing a concentrate of sulphur compounds and aromatic hydrocarbons, flowing hydrocarbons from said top product through an extraction zone countercurrently to a preferential solvent for sulphur compounds under conditions causing the formation of counter-flowing raffinate and extract phases, introducing the concentrate of sulphur compounds and aromatic hydrocarbons from said bottom product into the extraction zone at an intermediate point thereof, the conditions within the extraction zone being such that the hydrocarbons from said top product wash hydrocarbons from the extract phase to produce a washed extract phase containing the solvent, sulphur compounds, and less than

about 10% of the hydrocarbons contained in the initial fraction and withdrawing raffinate and washed extract phases from said extraction zone as spaced points.

12. The process according to claim 11 in which the hydrocarbons in the top product contain over about 85% of saturated hydrocarbons.

13. The process according to claim 11 in which the initial fraction is a fraction containing saturated, olefinic, and aromatic hydrocarbons, and the top product contains between about 30 and 75% of said hydrocarbons.

14. The process according to claim 11 in which the initial fraction is a fraction containing saturated, olefinic, and aromatic hydrocarbons, the top product contains between about 30 and 50% of said hydrocarbons, and the hydrocarbons in said top product contain over about 85% of saturated hydrocarbons.

15. The process according to claim 11 in which the conditions within the extraction zone are such that the extract phase contains less than about 4% of the hydrocarbons contained in the initial fraction.

16. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of extracting said fraction in a first extraction zone with a selective solvent, which, when contacted therewith, is capable of forming two liquid phases containing concentrates of hydrocarbons of different ratios of carbon to hydrogen, under conditions causing the formation of a first cut containing a concentrate of hydrocarbons of relatively low ratios of carbon to hydrogen and a second cut containing the remainder of the fraction, said first cut containing over about 85% of saturated hydrocarbons, flowing said first cut through a second extraction zone countercurrently to a preferential solvent for sulphur compounds, under conditions causing the formation of counterflowing raffinate and extract phases, introducing the second cut into the second extraction zone at an intermediate point thereof, the conditions within said second extraction zone being such that the first cut washes hydrocarbons from the extract to produce a washed extract phase containing the preferential solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing the raffinate phase and the washed extract phase from said second extraction zone at spaced points.

17. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of extracting said fraction in a first extraction zone with a selective solvent for aromatic hydrocarbons which, when contacted therewith, is capable of forming an extract phase containing a concentrate of hydrocarbons of relatively high carbon to hydrogen ratios, and a first raffinate phase containing a concentrate of relatively low carbon to hydrogen ratios, under conditions to produce a raffinate containing between about 30 and 75% of the hydrocarbons of the initial fraction, and a first extract containing the remainder of the fraction, flowing said first raffinate through a second extraction zone countercurrently to a preferential solvent for sulphur compounds, under conditions causing the formation of counterflowing second raffinate and extract phases, introducing said first extract into the second extraction zone at an intermediate point thereof, the conditions within said second extraction zone being such that the first raffinate washes hydrocarbons from the second extract to produce a washed second extract phase containing the preferential solvent, sulphur compounds, and less than about 10% of the hydrocarbons contained in the initial fraction and withdrawing the second raffinate phase and the washed extract phase from said second extraction zone at spaced points.

18. The process according to claim 17 in which the first raffinate contains over about 85% of saturated hydrocarbons.

19. The process according to claim 17 in which the second extract phase contains less than 4% of the hydrocarbons contained in the initial fraction.

20. The process for refining an initial hydrocarbon fraction containing sulphur compounds and hydrocarbons of different ratios of carbon to hydrogen, which comprises the steps of extracting said fraction in a first extraction zone with a selective solvent for aromatic hydrocarbons which, when contacted therewith, is capable of forming an extract phase containing a concentrate of hydrocarbons of relatively high carbon to hydrogen ratios, and a first raffinate phase containing a concentrate of relatively low carbon to hydrogen ratios, under conditions to produce a raffinate containing between about 30 and 75% of the hydrocarbons of the initial fraction, and a first extract containing the remainder of the fraction, distilling said first raffinate to produce a distillate and a distillation residue, flowing said distillate through a second extraction zone countercurrently to a preferential solvent for sulphur compounds, under conditions causing the formation of counterflowing second raffinate and extract phases, introducing said first extract into the second extraction zone at an intermediate point thereof, the conditions within said second extraction zone being such that the distillate washes hydrocarbons from the second extract phase to produce a washed second extract phase containing the preferential solvent, sulphur compounds, and less than about 10% of the hydrycarbons contained in the initial fraction and withdrawing the second raffinate phase and the washed extract phase from the second extraction zone at spaced points.

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