June 9, 1942. C. L. DUNN 2,285,696

PROCESS FOR DESULPHURIZING MINERAL OIL DISTILLATES

Filed Aug. 26, 1940 2 Sheets-Sheet 1

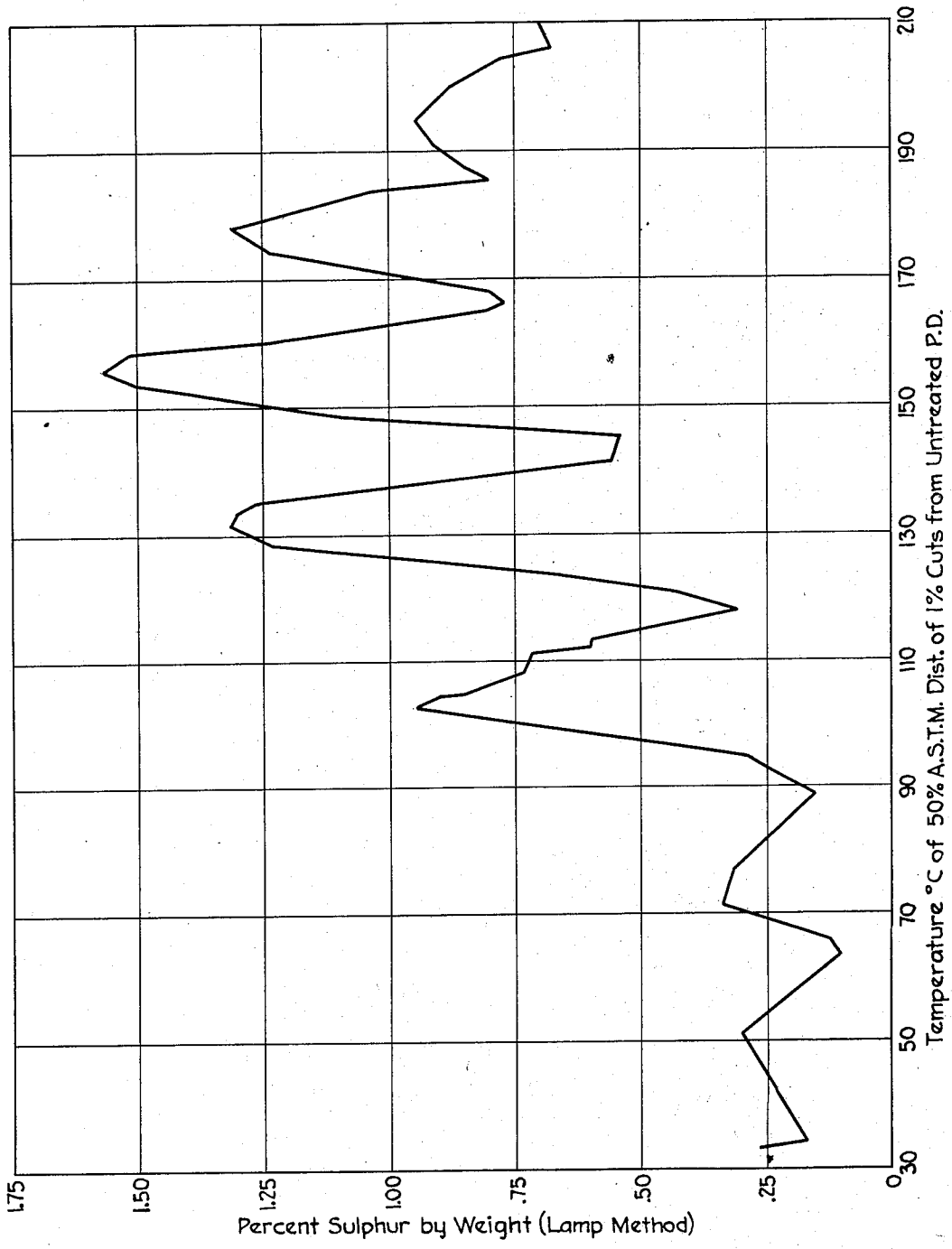


Fig. I

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By his Attorney: S. W. Dunn

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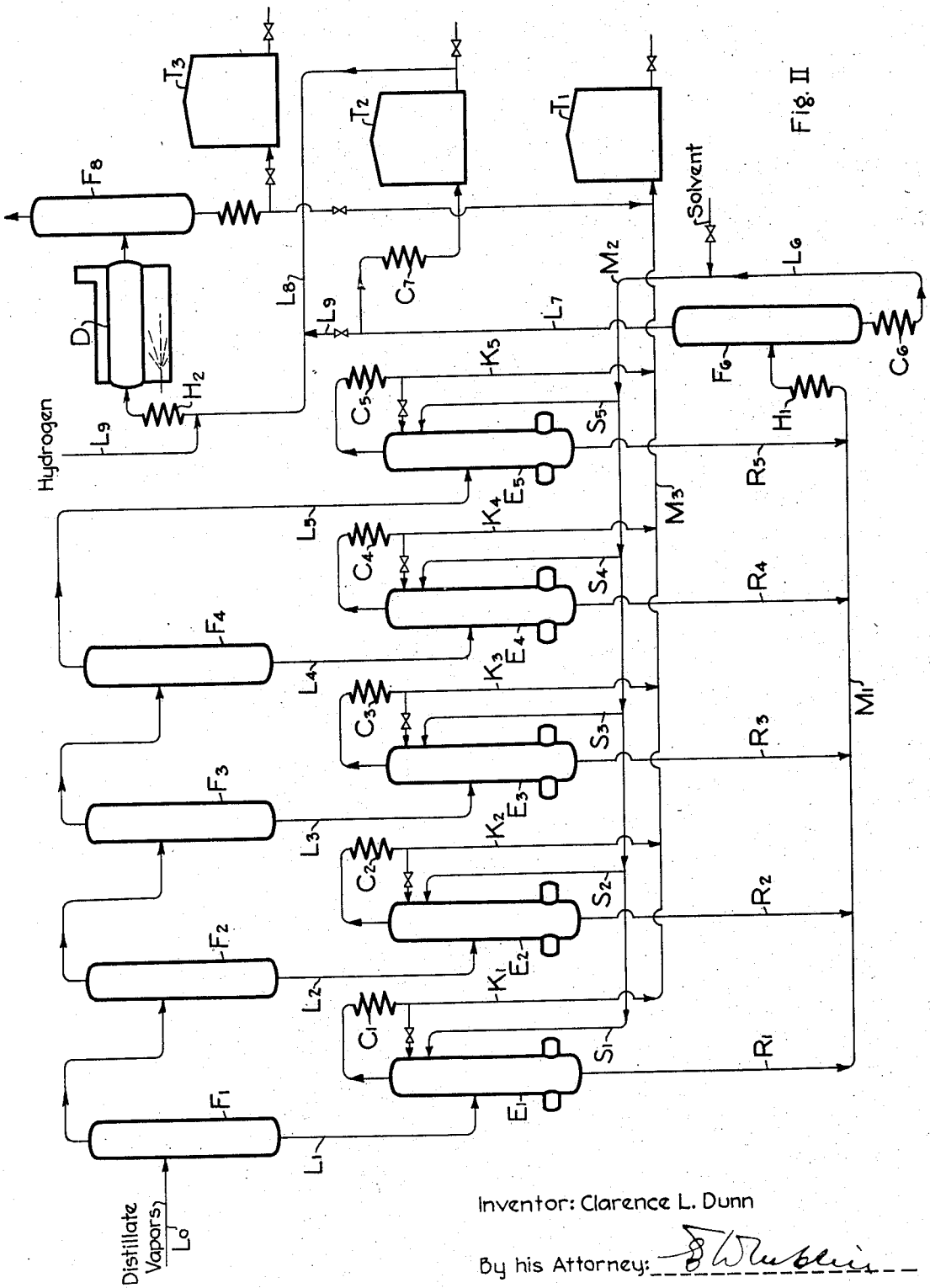


Fig. II

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By his Attorney: [signature]

Patented June 9, 1942 2,285,696

UNITED STATES PATENT OFFICE

2,285,696

PROCESS FOR DESULPHURIZING MINERAL OIL DISTILLATES

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Application August 26, 1940, Serial No. 354,188

15 Claims. (Cl. 196—13)

This invention pertains to the treatment of hydrocarbon oils for the removal of sulphur, and is particularly concerned with an improved process for desulphurizing cracked distillates, although similar distillates from other sources, such as straight-run distillates and polymerized oils, may also be desulphurized in accordance with the present invention.

More specifically, the present process is concerned with the removal of the more refractory sulphur compounds, such as thiophene and its homologues, particularly alkyl thiophenes, from lower boiling distillates, such as gasoline, kerosene, gas oil, and cracked naphtha, but it may be applied for the removal of other sulphur compounds, and may, moreover, be applied to the treatment of higher-boiling hydrocarbon fractions.

The low-boiling hydrocarbon fractions produced as a result of the application of heat to higher boiling hydrocarbon oils or shales contain objectionable sulphur compounds, such as hydrogen sulphide, mercaptans, aliphatic and cyclic thioethers and thiophenes. Certain of these sulphur compounds are readily removed or rendered innocuous by simple methods of treatment, such as extraction with solvents or conversion into disulphides. Other sulphur compounds, particularly thiophene and the alkyl thiophenes, are difficult to remove except by intensive methods which concurrently destroy or remove unsaturated hydrocarbons, including aromatics. Since cracked distillates contain large amounts of unsaturated hydrocarbons, such as aromatics, olefines and diolefines, these methods have heretofore been uneconomical, and have not been applied to the treatment of such distillates save when hydrogenation or a similar conversion of the unsaturated hydrocarbons was at the same time an object of the treatment. The sulphur compounds most difficult to remove from pressure distillate without adversely affecting the yield or knock rating of the gasoline are those occurring in the upper ends of the gasoline boiling above about 140° C., and appear to be polymethyl and higher derivatives of thiophene.

In the present specification and claims, the word "thiophenes" is used to designate thiophene and its homologues.

It is an object of this invention to provide an effectve method for desulphurizing hydrocarbon distillates without causing material losses of valuable hydrocarbons. A further purpose is to decompose thiophenes in gasolines to hydrocarbons and H_2S without chemically altering hydrocarbons, such as olefines which normally are affected by treatments of a severity sufficient to break down thiophenes. Another purpose is to eliminate thiophenes from gasolines by a process capable of maintaining or raising the octane ratings and lead susceptibilities of the fuels. Another object is to carry out this desulphurization by a combination of steps, wherein the sulphur compounds are first concentrated in a portion of the distillate, and the resulting concentrate is subjected to a chemical process for desulphurizing, preferably one involving catalytic desulphurization.

It has already been suggested to fractionally distill gasoline distillates to segregate low and high sulphur fractions, subjecting the high sulphur fraction to a desulphurization treatment such as sulphuric acid treatment, and then combining the low sulphur fraction and desulphurized fraction to produce the finished gasoline (Morrell U. S. 1,827,537).

Further, it has been suggested to subject suitable high sulphur fractions to azeotropical distillation in the presence of a polar solvent having preferential solvent power for the sulphur compounds, to produce a high sulphur bottom product and a low sulphur azeotropic mixture. The bottom product is desulphurized, while the azeotrope is separated into a hydrocarbon liquid and solvent. The desulphurized bottom product and the overhead hydocarbon liquid are then combined (McKittrick U. S. 2,114,852).

Both the above processes, while quite effective in the matter of desulphurizing in a limited number of cases, possess certain disadvantages which so far have prevented their widespread adoption. For example, when merely fractionally distilling to produce sulphur concentrates which are desulphurized, one is still confronted with the alternative of drastically desulphurizing at the cost of high hydrocarbon losses, or instead, of mildly desulphurizing for the the sake of minimizing losses. This is due to the fact that simple fractional distillation only separates according to boiling temperature and not according to chemical composition, with the result that the sulphur concentrates normally are highly contaminated with unsaturates which are normally responsible for the losses sustained upon desulphurization, as by formation of high-boiling polymers.

Moreover, it is usually difficult or impractical to produce definite sulphur concentrates in commercial distillation units so that the benefits obtainable from the pre-fractionation are meager and normally do not pay for the cost of the special fractional distillation.

Azeotropical distillation presents a somewhat more favorable picture in that it enables separation by chemical classes, thus making possible the production of sulphur concentrates consisting predominantly of sulphur compounds and aromatic hydrocarbons. However, this method of distillation is not only expensive, in that it requires the vaporization of a large amount of selective solvent, but also is rather difficult to

control, inasmuch as the formation of the azeotropical mixture depends on a definite ratio of solvent to feed, which ratio changes with changes in the composition of the feed. Thus small fluctuations in the feed are liable to offset the balance between feed and solvent which must be maintained for proper operation, thereby causing sulphur compounds to go overhead, or unsaturates to go into the bottom product. Moreover, in order to make possible at all a bottom product substantially free of components other than sulphur compounds and aromatic hydrocarbons, it is essential to utilize in the azeotropical distillation fractions having narrow boiling ranges. These fractions must be produced in precision distillation columns requiring very high rates of reflux, and their production materially adds to the already high cost of the process.

Now I have discovered that equally good or better desulphurization can be achieved with a much greater freedom in the choice of operating condition and at a considerably less cost by the combination of the steps described below. In my process I subject a suitable gasoline distillate containing thiophenes and/or other sulphur compounds, and, if desired, aromatic hydrocarbons, to an extractive distillation or vapor phase extraction with a liquid polar solvent having preferential solvent power for the aromatic hydrocarbons, under conditions to cause the liquid solvent to flow down the distillation or extraction column and to dissolve thiophenes and aromatic hydrocarbons if the latter are present. While descending through the lower portion of the extraction tower, the resulting fat liquid is continually refluxed with a bottom reflux consisting of preferentially soluble vapors either by reboiling the fat solution or by introducing from the outside vapors recovered by stripping the fat solution in a separate stripper. In this manner, most absorbed gasoline distillate vapors other than aromatic hydrocarbons and sulphur compounds are expelled. The refluxed fat solution is then stripped to recover the absorbed portion of the distillate comprising most of the sulphur compounds originally contained in the feed but having a low percentage of olefines, and to produce a lean solvent, the latter being returned to the top of the extraction tower. Unabsorbed vapors are refluxed in the top portion of the distillation column leaving it overhead and are condensed. The sulphur content of the resulting condensate is greatly reduced in comparison with that of the feed.

The high sulphur distillate portion resulting from the stripping operation is now subjected to a chemical desulphurization treatment, i. e., a treatment which removes thiophenes from hydrocarbons if thiophenes are contained in the original distillate. Among the many methods which heretofore had been devised for desulphurizing hydrocarbon oils, only a few are capable of eliminating the thiophenes. Among them are treatment with a concentrated sulphuric acid; selective catalytic hydrogenation over alumina, bauxite, and similar catalysts; selective catalytic cracking over sulphur-immune hydrogenation catalysts, such as sulphides of nickel, molybdenum, etc.; reactions with CO in the presence of sulphur-immune hydrogenation catalysts, etc.

Sulphuric acid eliminates thiophenes by absorbing them, probably by way of forming sulphonic acids. In the catalytic methods, the thiophenes are broken down to H_2S and hydrocarbons, the H_2S being eliminated by conventional means, such as fractional distillation, absorption in an alkaline liquid, as aqueous solution of tripotassium phosphate, sodium phenolate, ethanolamine, diamino isopropanol.

In the course of the desulphurization by any of these methods, several undesirable side reactions are liable to, and usually do, take place. Thus in the treatment with sulphuric acid, olefines are polymerized and/or converted to sulphates, mercaptans are converted to disulphides, etc. As a result, acid consumption and losses of valuable hydrocarbons are high, octane rating of the gasoline is reduced, etc. Likewise in the catalytic treatments, progressive desulphurization normally causes increasing losses in yields of treated distillate or depreciation of octane rating or both. This depreciation of octane rating is especially large in processes of the types involving selective hydrogenation of sulphur compounds, which types of processes are, on the other hand, desirable because they make possible long life of the catalysts. Substantial losses in yields are usually experienced at higher temperatures, i. e., above about 400° C.

The components of distillates which are responsible for these various drawbacks are primarily olefines, and by eliminating them prior to the desulphurization treatment, the disadvantages can largely be overcome.

In the vapor phase extraction process hereinbefore described, a fairly efficient separation can be achieved between aromatic hydrocarbons and thiophenes on the one hand and remaining hydrocarbons on the other hand. Thus it is possible to obtain a bottom product high in sulphur having greatly reduced olefine content. This bottom product can now be drastically desulphurized without incurring to any great extent any of the above-enumerated disadvantages.

The benefits obtainable from the separation into a high sulphur-low olefine fraction and a low sulphur-high olefine fraction are the greater the more complete the separation is. The ideal condition is the one which leads to the formation of a sulphur concentrate containing all the thiophene and other sulphur compounds and no olefines, and an overhead fraction containing no sulphur and all the olefines. When this is achieved, desulphurization can be made substantially complete without sustenance of any of the disadvantages.

When subjecting a gasoline distillate to the vapor phase extraction, which distillate has a relatively broad boiling range, say of about 50°–100° C., a fair separation can be achieved. For example, a California cracked distillate boiling from 89°–150° C. (A. S. T. M.) and having a sulphur content of .77%, was subjected to an extractive distillation with three volumes of a 60/40 mixture of phenol and cresols in a 44 plate distillation column operated under a top reflux of 3:1. 81% of the feed was taken overhead, containing .33% sulphur; while 19% of the feed went into the bottom product which contained 2.1% sulphur. Better than 90% of the olefines were contained in the top product.

It is noteworthy that no such considerable separation can be achieved by azeotropical distillation of the same distillate having this relatively broad boiling range.

Still better separation can be achieved, however, if the gasolines to be desulphurized are fractionally distilled into somewhat narrower

boiling fractions according to a plan which will be explained hereinafter.

It has already been established that when gasoline distillates, such as cracked gasolines which contain thiophenes, are fractionally distilled in an analytical precision distillation column into a large number of very narrow fractions, and the sulphur content of each fraction is determined, it is found that some of the fractions have higher sulphur contents than others. When plotting, for example, the 50% A. S. T. M. distillation points of 1% fractions versus their sulphur contents, a curve is obtained such as the one shown in Fig. 1 of the drawings, which represents distribution of sulphur content in a cracked California gasoline containing a total of .87% sulphur. As will be noted, this curve has definite peaks at about 103°, 132°, 156°, 178° and 195° C. Likewise, points of minimum sulphur contents between the peaks are found at about 118°, 143°, 166°, 188° and 206° C. It may be stated at this point that most cracked gasolines containing thiophenes show similar sulphur peaks and valleys which normally lie within 5° C. and more often within 2° or 3° C. of the temperatures herein shown.

Now then, in my preferred procedure, I fractionally distill the thiophene-containing gasoline to produce sharp fractions whose boiling ranges have as little as possible overlap and are such that each includes at least one and preferably only one sulphur peak or maximum, and whose A. S. T. M. 90% distillation points are about midway between the temperatures of their respective highest boiling sulphur maximum and the next succeeding sulphur minimum, i. e., ±5° C. of 122°, 137°, 160°, 172° and 200°–210° C. These fractions, of which there are in general not more than 5 to cover the entire normal distillation range of motor gasolines, or fewer to cover a narrower range such as that of an aviation gasoline, are then separately subjected to the vapor phase extraction hereinbefore described, and the several sulphur concentrates which are obtained as a result are then desulphurized, either singly or in combination.

By producing the fractions having the above properties, I am able to effect in the subsequent vapor phase extraction a remarkably complete concentration of the refractory sulphur compounds in the bottom product, while retaining practically no olefines therein. No other known simple method affords a similar highly efficient degree of separation. Because of this high efficiency of separation, the yields of the bottom products are relatively small. This, of course, is desirable in that a minimum volume of distillate need be desulphurized, which enables saving of treating reagent or catalyst, as the case may be. Normally, the bottom products are less than 10% of the fractions from which they are produced, although the yields will vary with the content of sulphur compounds and aromatic hydrocarbons.

In Fig. 2 of the attached drawings, a flow diagram is shown illustrating a preferred form of our process. Vaporized gasoline distillate having an A. S. T. M. end boiling point of around 210° C. enters the system through line L_0 from a source not shown. The vapors are fractionally distilled in a battery of four fractionating towers F_1–F_4 to produce five fractions. The distillation is so controlled that the A. S. T. M. boiling ranges of the several fractions overlap but little, and that their 90% A. S. T. M. boiling points are ±5° C. of 122° C., 137° C., 160° C., 172° C. and 200°–210° C., respectively, these being the temperatures halfway between the sulphur maxima and next succeeding minima indicated in Fig. 1. Each of these five fractions is now fed into one of the extractive distillation towers E_1–E_5 through lines L_1–L_5, respectively, the points of entrance of the several streams being about halfway between top and bottom of each tower. A high boiling selective solvent for aromatic hydrocarbons is fed to the extraction towers at a point somewhere below the top of each tower through lines S_1–S_5. Each tower is equipped with a reboiler, and is so operated to effect a maximum concentration of sulphur compounds in the bottom product, while causing non-aromatic hydrocarbons to go overhead. From each tower emerges from the bottom a fat solvent rich in sulphur compounds and aromatic hydrocarbons, and a desulphurized overhead product. The several fat solvents are withdrawn through lines R_1–R_5, and are combined in manifold M_1. The combined fat solvent is heated in heater H_1 and is fractionally distilled in column F_6 to drive off absorbed sulphur compounds and aromatic hydrocarbons, and to produce a lean solvent. The latter passes through bottom line L_6, cooler C_6 and thence to manifold M_2, which feeds lines S_1–S_5. The overhead product from towers E_1–E_5 are condensed in condensers C_1–C_5, a portion of the condensates being returned to the respective towers for reflux, and the remainder being conducted through lines K_1–K_5 to be collected in manifold M_3 and tank T_1.

The overhead product from fractionator F_6 passes through vapor line L_7 and condenser C_7 to storage tank T_2. This product which contains most of the sulphur compounds of the original gasoline distillate is now conducted through line L_8 and heater H_2 to catalytic desulphurizer D. Alternately the vapors from line L_7 may go directly by way of lines L_9 and L_8 to desulphurizer D. A small amount of hydrogen is injected through line L_9 into the stream of distillate or distillate vapors in line L_8 at some point ahead of the desulphurizer.

Desulphurizer D contains a desulphurizing catalyst, such as alumina or bauxite, preferably containing about 5%–20% of an oxide of chromium, molybdenum, tungsten, etc. The content of hydrogen in the feed to the desulphurizer may conveniently vary from about .5%–4% by weight. Suitable temperatures of reaction range from about 350° C. to about 520° C. at pressures up to about 40 atmospheres, preferably about 10 to 20 atmospheres.

During passage over the catalyst, sulphur compounds are broken down to hydrocarbons and H_2S. Therefore, the resulting product is fractionally distilled in fractionating tower F_8 to remove H_2S, and the remaining hydrocarbons, freed from H_2S, emerge from the bottom of the fractionator F_8 and pass through cooler C_8 to run-down tank T_3, or, if desired, to tank T_1, to be blended with the low sulphur overhead products from the extractive distillation.

While the described flow diagram illustrates the essential points of our process, it does not indicate the positions of pumps, heat exchangers, many of the valves, coolers, heaters, etc. The placement of such auxiliary equipment is within the skill of the designers of such equipment.

Moreover, it is understood that it is not essential that all five fractions be produced in the distillation batteries F_1–F_4. Different numbers

of fractions may be produced and not all of them need be subjected to the extractive distillation. It may be desirable to pick out one or two or more of these fractions, perhaps because they possess an unusually high sulphur content, or because the hydrocarbon content in a particular fraction is particularly valuable or for some other reason. For example, a fraction may contain a high proportion of toluene, and it may be the aim to isolate substantially pure toluene. In such a case, obviously, the bottom product resulting from the extractive distillation of this fraction would not be combined with similar bottom products of other fractions, and on the contrary, this particular bottom product would separately be processed, i. e., separated from the solvent by fractional distillation and then be desulphurized without being combined with other bottom products.

Should it be desirable, as indicated above, to isolate aromatic hydrocarbons such as toluene, then the principles described in my copending application Serial No. 348,046, filed July 27, 1940, may be incorporated in this process.

Solvents suitable for my purposes are those which have preferential solvent powers for aromatics over paraffinic hydrocarbons, are substantially stable and inert under the conditions of the process, and have boiling temperatures substantially higher than the A. S. T. M. end boiling points of the distillates or distillate fractions to be desulphurized. Thus suitable solvents may be phenol, cresylic acids, alkyl phenol mixtures, aniline, alkyl anilines, diphenylamine, ditolylamines; carbitols (diethylene glycol mono ethers) such as methyl, ethyl, propyl carbitols; chlorinated dialkyl ethers such as beta-beta-dichlorethyl ether; nitrobenzene, nitrotoluene, nitroxylenes; naphthols, alkyl naphthols, benzophenone, phenyl tolyl ketone, diphenylene ketone; alkyl phthalates, such as dimethyl phthalate; alkyl salicylates, such as methyl salicylate; benzyl alcohol, benz chlorides, i. e., benzyl, benzal, benzo chlorides; benzonitrile, diphenyl oxide, ditolyl oxide, hydroxy pyridine, nitropyridine, chlorinated pyridines, quinoline, isoquinoline, chlorinated quinoline, hydroxy quinolines, 5-nitro quinoline, tetra hydro furfuryl alcohol, furfuryl alcohol, furfural, the mono glycerol ethers such as 1-methoxy glycerol, 2-methoxy glycerol, 1-ethoxy glycerol, 2-ethoxy glycerol, 1-propoxy glycerol, 2-propoxy glycerol, 1-isopropoxy glycerol, 2-isopropoxy glycerol; the glycerol di-ethers, such as 1,2-dimethoxy glycerol, 1,3-di-methoxy glycerol, 1,2-di-ethoxy glycerol, 1,3-di-ethoxy glycerol, 1,2-dipropoxy glycerol, 1,3-di-propoxy glycerol, 1,2-diisopropoxy glycerol, and 1,3-di-isopropoxy glycerol; the mixed di-glycerol ether esters, such as 1-ethoxy, 2-methoxy glycerol, 1-methoxy, 3-propoxy glycerol, 1-ethoxy, 2-isopropoxy glycerol.

The amounts of solvent to be used may vary between very wide limits. Thus solvent:feed ratios (by weight) ranging from .5 to 10 may be used. In this freedom of solvent:feed ratio, the extractive distillation fundamentally differs from the azeotropical distillation mentioned earlier, the latter depending for successful operation on an exact ratio, which in turn varies with variations in the feed and thus is difficult to control.

The following example further illustrates my process:

A pressure distillate obtained by cracking a California gas oil in a Dubbs cracking unit was fractionally distilled in a packed column (equivalent to 44 theoretical plates) under a 3:1 top reflux to produce a fraction having the following properties:

A. S. T. M. boiling range:	°C.
I. B. P.	87
10%	94.5
90%	108
F. B. P.	111.2
Bromine number	55.5 (equivalent to about 50%–55% olefines)
Sulphur	.76% (of which .74 was thiophene sulphur)
Toluene content	10% (weight)

This fraction was extractively distilled in a 43 plate column with a 50–50 mixture of phenol-cresols, the solvent:feed ratio being 2.4:1 by weight. The solvent was introduced on the ninth plate from the top and a top reflux ratio of about 2:1 was maintained. 88.7% of the feed was taken overhead, the remainder being dissolved in the solvent. The latter was then stripped thoroughly and an amount of distillate (herein called bottom product) equal to 11.3% of the feed was recovered. The sulphur distribution in the overhead and bottom products were as follows:

	Per cent sulphur	Per cent toluene
Overhead	.08	1.1
Bottom product	6.42	79.8

Thus 98% of the total sulphur was concentrated in the bottom product. Moreover, the bottom product contained only about 1.0% olefines (equal to about .2% of the total olefine content of the original fraction), all the remaining olefines having been accumulated in the overhead product.

The bottom product was now desulphurized by passing it in admixture with 4 mols hydrogen over an alumina catalyst, at 500° C. under 20 atmosphere pressures, the contact time being 32 seconds. The resulting product was freed from H_2S and the recovered distillate, after being freed from 1.3% of heavy ends had a boiling range as determined by analytical distillation of 30.6° C. to 126° C. It contained 79% toluene, .6% heavier hydrocarbons, the remainder being principally pentanes produced in the destruction of the thiophenes. Its sulphur content was .01%, and its bromine number .2.

From this distillate, substantially pure toluene could easily be recovered by distillation.

When combining this distillate with the low sulphur overhead product obtained earlier, a blend was obtained which was doctor sweet and contained about .07% sulphur. Its octane rating and lead susceptibility were better than those of the original high sulphur fraction.

I claim as my invention:

1. In the process of desulphurizing a hydrocarbon distillate containing organic sulphur compounds and olefines, the improvement comprising subjecting said distillate to a vapor phase extraction with a liquid selective solvent having preferential solvent powers for aromatic hydrocarbons under conditions to produce a fat solvent containing absorbed portions of the distillate preferentially soluble in said solvent including sulphur compounds, and an overhead residual vapor of low sulphur content containing the major portion of said olefines, said residual vapor being substantially free from said solvent

refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the distillate and subjecting the resulting recovered portion to a desulphurization treatment of sufficient intensity to remove the dissolved sulphur compounds, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said distillate, and being chemically inert under the conditions of said extraction.

2. The process of claim 1 wherein said distillate has an A. S. T. M. boiling range not broader than about 100° C.

3. The process of claim 1 wherein the extraction is an extractive distillation.

4. The process of claim 1 wherein said desulphurization treatment of the recovered portion comprises treatment with a concentrated sulphuric acid under conditions to absorb sulphur compounds in the acid.

5. The process of claim 1 wherein said solvent consists essentially of phenols.

6. In the process of desulphurizing a hydrocarbon distillate containing thiophenes and olefines, the improvement comprising subjecting said distillate to a vapor phase extraction with a liquid selective solvent having preferential solvent powers for aromatic hydrocarbons under conditions to produce a fat solvent containing absorbed portions of the distillate preferentially soluble in said solvent including thiophenes, and an overhead residual vapor of low sulphur content containing the major portion of said olefines, said residual vapor being substantially free from said solvent refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the distillate and subjecting the resulting recovered portion to a desulphurization treatment of sufficient intensity to remove thiophenes, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said distillate, and being chemically inert under the conditions of said extraction.

7. The process of claim 6 wherein the desulphurization treatment of said recovered portion comprises passing said portion over a sulphur-immune hydrogenation catalyst at a temperature between 350°–520° C.

8. The process of claim 6 where the desulphurization treatment of said recovered portion comprises passing said portion admixed with .5%–4% hydrogen over an oxide of alumina at a temperature between 350°–520° C. under a superatmospheric pressure below 40 atm.

9. In the process of desulphurizing a hydrocarbon distillate containing organic sulphur compounds and olefines, the improvement comprising subjecting said distillate to a vapor phase extraction with a liquid selective solvent having preferential solvent powers for aromatic hydrocarbons under conditions to produce a fat solvent containing absorbed portions of the distillate preferentially soluble in said solvent including sulphur compounds and an overhead residual vapor of low sulphur content containing the major portion of said olefines, said residual vapor being substantially free from said solvent refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the distillate, subjecting the resulting recovered portion to a desulphurization treatment of sufficient intensity to remove the dissolved sulphur compounds, and combining the resultant desulphurized portion with the condensate obtained from condensing said refluxed vapors, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said distillate and being chemically inert under the conditions of said extraction.

10. In the process of desulphurizing a hydrocarbon distillate containing organic sulphur compounds and olefines, which distillate upon analytical fractional distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said distillate to produce at least one sharp fraction including a sulphur maximum, the 90% A. S. T. M. boiling point of which fraction is ±5° C. of the temperature half-way between the temperature at which this maximum and the next succeeding minimum occurs, subjecting said fraction to a vapor phase extraction with a liquid selective solvent having preferential solvent power for aromatic hydrocarbons under conditions to produce a fat solvent containing absorbed portions of said fraction preferentially soluble in said solvent including sulphur compounds, and an overhead residual vapor of low sulphur content containing a major portion of the olefines contained in said fraction, said residual vapor being substantially free from said solvent refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the fraction and subjecting the recovered portion to a desulphurization treatment of sufficient intensity to remove the dissolved sulphur compounds, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said fraction and being chemically inert under the conditions of said extraction.

11. In the process of desulphurizing a hydrocarbon distillate containing organic sulphur compounds and olefines, which distillate upon analytical fractional distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said distillate to produce at least one sharp fraction including one and only one sulphur maximum, the 90% A. S. T. M. boiling point of said fraction being ±5° C. of the temperature halfway between the temperatures at which the maximum and the next succeeding minimum occurs, subjecting said fraction to a vapor phase extraction with a liquid selective solvent having preferential solvent power for aromatic hydrocarbons under conditions to produce a fat solvent containing absorbed portions of said fraction preferentially soluble in said solvent including sulphur compounds, and an overhead residual vapor of low sulphur content containing a major portion of the olefines contained in said fraction, said residual vapor being substantially free from said solvent refluxing both the fat solvent and residual vapors, the former with vapors obtained

by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the fraction and subjecting the recovered portion to a desulphurization treatment of sufficient intensity to remove the dissolved sulphur compounds, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said fraction and being chemically inert under the conditions of said extraction.

12. In the process of desulphurizing a hydrocarbon distillate containing thiophenes and olefines, which distillate upon analytical fractional distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said distillate to produce at least one sharp fraction including one and only one sulphur maximum, the 90% A. S. T. M. boiling point of said fraction being ±5° C. of the temperature halfway between the temperatures at which the maximum and the next succeeding minimum occurs, subjecting said fraction to a vapor phase extraction with a liquid selective solvent having preferential solvent power for aromatic hydrocarbons under conditions to produce a fat solvent substantially free from olefines and containing absorbed a portion of said fraction which is preferentially soluble in said solvent, and an overhead residual vapor substantially free from thiophenes and said solvent, refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the fraction and subjecting the recovered portion to a desulphurization treatment of sufficient intensity to remove thiophenes, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said fraction and being chemically inert under the conditions of said extraction.

13. In the process of desulphurizing a hydrocarbon distillate containing thiophenes and olefines, which distillate upon analytical fractional distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said distillate to produce at least one sharp fraction including one and only one sulphur maximum, the 90% A. S. T. M. boiling point of said fraction being ±5° C. of one of the following temperatures: 122° C., 137° C., 160° C., 172° C., 200°–210° C., subjecting said fraction to a vapor phase extraction with a liquid selective solvent having preferential solvent power for aromatic hydrocarbons under conditions to produce a fat solvent substantially free from olefines and containing absorbed a portion of said fraction which is preferentially soluble in said solvent, and an overhead residual vapor substantially free from thiophenes and said solvent, refluxing both the fat solvent and residual vapors, the former with vapors obtained by boiling the fat solvent, condensing the refluxed unabsorbed vapors, stripping the refluxed fat solvent to recover the absorbed portion of the fraction and subjecting the recovered portion to a desulphurization treatment of sufficient intensity to remove thiophenes, said solvent having a boiling temperature substantially higher than the A. S. T. M. end boiling point of said fraction and being chemically inert under the conditions of said extraction.

14. In the process of desulphurizing a normal boiling-range motor gasoline containing thiophenes and olefines, which gasoline upon analytical distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said gasoline to produce five sharp fractions whose 90% A. S. T. M. boiling points are ±5° C. of 122° C., 137° C., 160° C., 172° C. and 200°–210° C., respectively, individually subjecting said fraction to vapor phase extraction with a selective solvent having preferential solvent powers for aromatic hydrocarbons under conditions to produce as many fat solvents substantially free from olefines containing absorbed portions of said fractions which are preferentially soluble in said solvent, and overhead residual vapors substantially free from thiophenes and said solvent, refluxing said fat solutions and residual vapors, the former with vapors obtained by boiling the fat solvents, condensing and combining the refluxed unabsorbed vapors, combining the refluxed fat solutions, stripping the combined solution to recover the absorbed portions of said fractions, and subjecting the resulting recovered liquid to desulphurization treatment of sufficient intensity to remove thiophenes, said solvent having a boiling temperature substantially higher than the end boiling point of said gasoline and being chemically inert under the conditions of said extraction.

15. In the process of desulphurizing a normal boiling range motor gasoline containing thiophenes and olefines, which gasoline upon analytical distillation into a great number of narrow fractions shows a sulphur content versus boiling temperature curve having definite maxima and minima, the improvement comprising fractionally distilling said gasoline to produce five sharp fractions whose 90% A. S. T. M. boiling points are ±5° C. of 122° C., 137° C., 160° C., 172° C. and 200°–210° C., respectively, individually subjecting said fraction to vapor phase extraction with a selective solvent having preferential solvent powers for aromatic hydrocarbons under conditions to produce as many fat solvents substantially free from olefines containing absorbed portions of said fractions which are preferentially soluble in said solvent, and overhead residual vapors substantially free from thiophenes and said solvent, refluxing said fat solutions and residual vapors, the latter with vapors obtained by boiling the fat solution, condensing and combining the refluxed unabsorbed vapors, combining the refluxed fat solutions, stripping the combined solution to recover the absorbed portions of said fractions, passing the resulting recovered liquid over a sulphur-immune hydrogenation catalyst in the presence of .5%–4% by weight of hydrogen at a temperature of 350°–520° C., whereby thiophenes are converted to hydrocarbons and hydrogen sulphide, separating the hydrogen sulphide from the hydrocarbons obtained in the catalytic treatment and combining the resulting hydrocarbon liquid with a condensate of said residual vapors, said solvent having a boiling temperature substantially higher than the end boiling point of said gasoline and being chemically inert under the conditions of said extraction.

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