

July 11, 1950

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METHOD FOR REMOVING SULFUR AND ITS COMPOUNDS
FROM NONAROMATIC HYDROCARBON FRACTIONS
Filed June 1, 1948

2,514,997

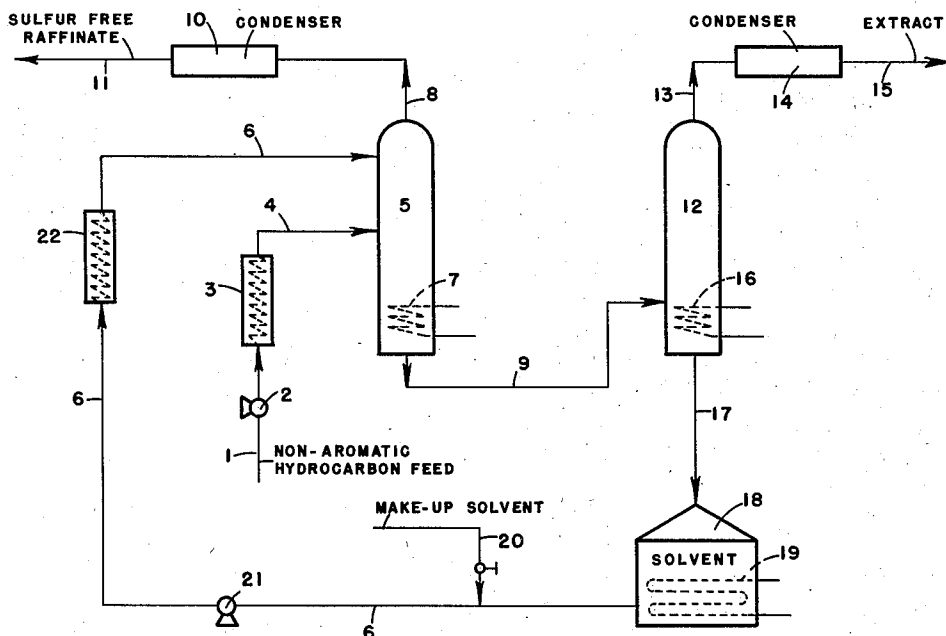
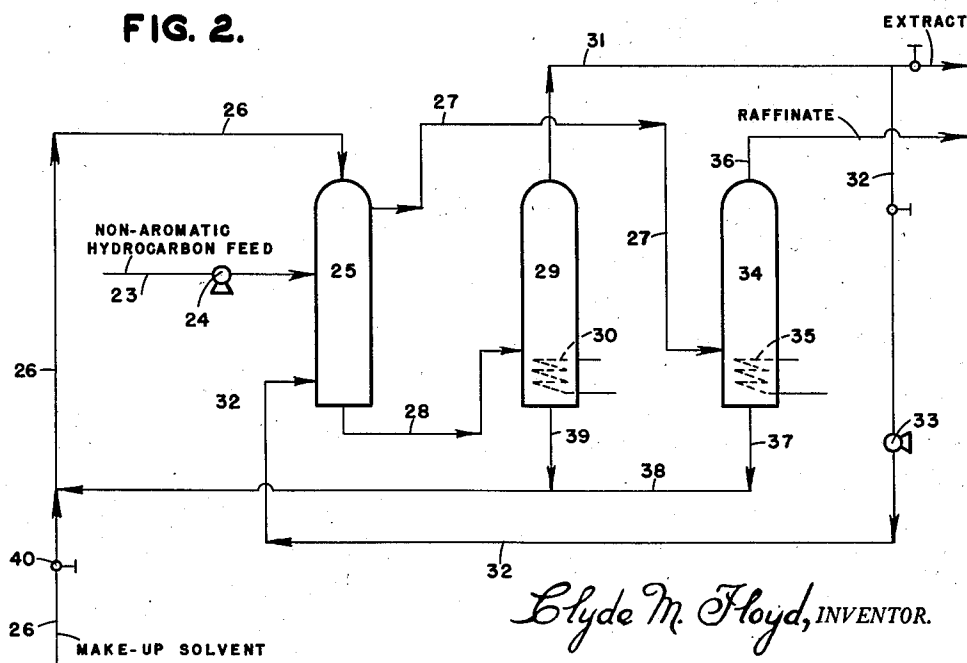


FIG. 1.

FIG. 2.



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2,514,997

METHOD FOR REMOVING SULFUR AND ITS COMPOUNDS FROM NONAROMATIC HYDROCARBON FRACTIONS

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Application June 1, 1948, Serial No. 30,236

6 Claims. (Cl. 196—24)

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The present invention is directed to a method for removing sulfur from hydrocarbon fractions containing them. More particularly, the invention is concerned with the selective removal of sulfur and its compounds from non-aromatic hydrocarbon fractions. The invention has particularly to do with the solvent extraction of non-aromatic hydrocarbons to remove sulfur compounds therefrom.

Heretofore, it has been known to remove sulfur and its compounds from hydrocarbon fractions containing them by contacting the sulfur-containing fraction with strong sulfuric acid. While the strong sulfuric acid effectively reduces the sulfur content of hydrocarbon fractions, it also converts desirable hydrocarbons to less desirable compounds such as sulfonated derivatives of sulfuric acid. The sulfuric acid may also polymerize low boiling hydrocarbons to less desirable high boiling hydrocarbons. In effect, while the sulfuric acid reduces the sulfur content of hydrocarbon fractions, it also causes a loss in yield of the hydrocarbons by conversion to less desirable products.

Another method of reducing sulfur contents of hydrocarbon fractions, such as petroleum distillates, is to treat the hydrocarbons with an alkaline solution of sodium plumbite. This treatment per se does not remove the sulfur compounds, but converts the sulfur compounds to a form where they do not cause detrimental results when the hydrocarbon fraction is employed as a motor fuel. However, conversion of the sulfur compounds by the so-called sodium plumbite treatment usually requires some after treatment, such as distillation and the like, to separate the converted sulfur compounds from the desirable hydrocarbons.

It is also well known in the art to treat petroleum oils with various solvents to segregate the relatively more paraffinic constituents from the relatively less saturated constituents. Conditions are selected in the process so that the mineral oil is contacted with the solvent at a temperature below that at which complete miscibility occurs. The solvent usually selected is from the class which has a preferential selectivity for the more aromatic compounds as compared with the more paraffinic compounds. Solvents of this class are, for example, phenol, furfural, sulfur dioxide, nitro-benzene, aniline, organic esters and the like. All of these solvents have the disadvantage that a separation between the aromatic constituents and the olefinic constituents is not obtained with any high degree of selectivity. It is

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possible to obtain a separation between the more or less unsaturated compounds which are represented by the aromatic and olefin hydrocarbons and the aliphatic compounds as represented by the paraffins but it has been impractical to segregate the aromatic hydrocarbons from the olefins when employing solvents of the class enumerated hereinabove.

The prior art workers have also taught that aromatic hydrocarbons may be separated from mixtures thereof with other hydrocarbons by selective solvent extraction with a poly-olefin glycol having a molecular weight above about 1,000. The poly-olefin glycol is quite effective in obtaining substantially pure aromatic hydrocarbons from mixtures thereof.

I have now discovered that sulfur and its derivatives may be removed from hydrocarbon fractions containing them by extracting the sulfur-containing hydrocarbon with a poly-olefin glycol having a molecular weight in the range from about 400 to 4,000.

In accordance with the present invention, hydrocarbon fractions such as those boiling below about 165° F. and those containing substantially no aromatic hydrocarbons and those from which the aromatic hydrocarbons have been removed boiling up to about 600° F. may be extracted with a poly-olefin glycol, such as polyethylene glycol, having a molecular weight in the range from about 400 to 4,000 so that a fraction comprising essentially non-aromatic hydrocarbons and substantially free of sulfur compounds is obtained.

In the present invention, mineral oil and other hydrocarbon fractions boiling below about 165° F. and high boiling hydrocarbon fractions from which aromatics have been removed are contacted with a poly-olefin glycol of high molecular weight so that the sulfur compounds are dissolved in the solvent and are thereby segregated and removed from the olefinic and paraffinic constituents.

In the present invention the solvent and the hydrocarbon being treated are contacted with each other at temperatures from about 120° F. up to the boiling point of the distillate being treated. In distinction to the conventional treating processes heretofore employed in the solvent extraction art, the present invention is conducted at temperatures substantially above atmospheric, whereas other solvents require low temperature operation which entails considerable refrigeration or high temperature operations which necessitate employing excessively high pressures and

special equipment. Even with the best solvents employed before, removal of sulfur from the hydrocarbon distillates was not obtained.

The present invention may be conducted with both the solvent and the hydrocarbon being treated in the liquid phase or it may be conducted with the solvent in the liquid phase and the hydrocarbon in the vapor phase.

In operating with the solvent in the liquid phase and the hydrocarbon in the liquid phase, it is preferred to contact the hydrocarbon with the solvent in an extraction system in which a temperature gradient is maintained so that fresh solvent contacts the partially stripped oil at the highest temperature and the extract contacts the solvent at the lowest temperature. In general, a temperature gradient say in the range of about 40 to 80° F. may be employed. Usually the maximum temperature at which treating occurs will range to about 180° F. while the lowest temperature in the extraction system will be about 120° F.

In operating with the hydrocarbon in the vapor phase and the solvent in the liquid phase, the reverse is generally true. The vaporized hydrocarbons are initially contacted with the solvent at the boiling point temperature of the heaviest hydrocarbon in the fraction, whereas the temperature at which the extract finally leaves the extract system is somewhat higher, generally in the neighborhood of from 20 to 50° F. higher. Temperatures of about 30° F. higher than the boiling point of the heaviest constituents in the raffinate may be found suitable as a maximum temperature at which the extract finally contacts the solvent in the extraction tower.

The invention will be better understood by reference to the following drawings in which

Fig. 1 is a diagrammatic flow plan of one embodiment in which the liquid solvent is contacted with the vaporized hydrocarbon; and

Fig. 2 illustrates another embodiment of my invention in which both the hydrocarbon and the solvent are maintained in the liquid phase and the apparatus illustrated in the flow diagram is a front elevation of equipment found suitable for conducting the invention.

Referring now specifically to Fig. 1, a hydrocarbon feed containing sulfur compounds and having a boiling range below 165° F., for example between 80° and 150° F., is introduced, from a source not shown, into the system through line 1 and pump 2 and is thereby routed through heating coil 3 in which the temperature of the hydrocarbon fraction is raised to its boiling point so that when it is injected by means of line 4 into solvent extraction tower 5 it immediately vaporizes. Solvent extraction tower 5 may comprise any suitable extraction equipment but preferably it is a packed tower so that intimate contact between the vaporized hydrocarbon and the solvent introduced thereto by means of line 6 is effected. Solvent extraction tower 5 is equipped with heating means 7 for maintenance of a suitable temperature therein. As mentioned before, it is preferred to maintain the bottom of solvent extraction tower 5 at a temperature about 30° higher than that maintained in the top of said tower. The temperature in the top of the tower should be about the boiling point of the hydrocarbon introduced thereto.

Solvent extraction tower 5 is equipped with line 8 for withdrawal of raffinate consisting of hydrocarbons and line 9 for withdrawal of the sulfur compounds which are dissolved in the solvent. This latter mixture will hereinafter be

referred to as a wet extract. The raffinate leaving tower 8 in vapor form is passed through condenser 10 wherein the temperature of the hydrocarbons is lowered to below its dew point and a liquid stream which may comprise paraffins and naphthenes is withdrawn from the system through line 11 for further treatment. If olefins are present in the feed mixture they may be dissolved in the solvent with the sulfur compounds.

The wet extract discharged from tower 5 through line 9 is introduced thereby into extract stripper 12, in which conditions are so adjusted that the sulfur compounds are removed from the solvent, leave extract stripper 12 through line 13, condensed in line 14, and discharged from the system by way of line 15. This latter stream comprises substantially all of the sulfur compounds originally present in the fraction charged to the system. This material may be discarded or used as desired.

The solvent stripped free of sulfur constituents leaves extract stripper 12 by way of line 17 and accumulates in solvent storage tank 18. Solvent storage tank 18 is equipped with a heating means 19 to maintain the solvent in a fluid state since at ordinary temperature it is a solid. As mentioned hereinbefore solvent is introduced in the top of extraction tower 5 by way of line 6 which connects to tank 18 and line 20 in which make-up solvent is introduced as required. Line 6 is equipped with pump 21 and heater 22 for insuring the proper temperature of the solvent introduced into extract tower 5.

With respect to the embodiment represented in Fig. 2, a hydrocarbon feed containing sulfur compounds and having a boiling range between about 150° and 400° F., which has been freed of aromatic hydrocarbons, is introduced into the system by means of line 23 and pump 24, connecting to extraction tower 25. The extraction tower 25 may be any suitable contacting device to insure intimate contact between the liquid solvent and liquid hydrocarbon fraction. Preferably, extraction tower 25 is a baffled or packed tower. It may be equipped with bell cap plates, Raschig rings or any other suitable packing or contacting means. The hydrocarbon fraction is introduced into extraction tower 25 about midway thereof so that the tower is thereby divided into extraction and stripping stages, the portion of the tower above the feed inlet being the extracting stage and that below the feed inlet being the stripping stage.

Polyethylene glycol in the liquid state is introduced into the top of extraction tower 25 by means of line 26 and countercurrently contact the hydrocarbon ascending therein. The raffinate fraction may comprise paraffins and naphthenes and is withdrawn from the top of extraction tower 25 through line 27 for further treatment as will be described hereinafter while the wet extract fraction is removed from the bottom of extract tower 25 by way of line 28 and is injected thereby into extract stripper 29. Any olefins which may be present in the feed will also be dissolved in the solvent. The wet extract discharged into extract stripper 29 is separated therein into a solvent phase and an extract phase free of solvent which comprises sulfur compounds. This is accomplished by adjusting temperatures in extract stripper 29 by means of heating means 30. The extract is distilled from the top of extract stripper 29, and is discharged therefrom through line 31, and is condensed in condensing means not shown and a portion of the

condensed fraction is withdrawn from the system. As mentioned before, only a portion of the extract is withdrawn from the system while a second portion is recycled by way of line 32 and pump 33 to extraction tower 25 for maintenance of reflux therein.

It is understood that extraction tower 25 is operated so that the highest temperatures are obtained in the top of the tower and the lowest in the bottom of the tower. In general a temperature of about 180° F. is maintained in the top of extraction tower 25 and a temperature of about 120° F. in the bottom thereof.

The raffinate leaving extraction tower 25 discharges by way of line 27 into raffinate stripper 34 which is equipped with heating means 35 so that the temperature in raffinate stripper 34 may be adjusted for distillation of raffinate from the solvent. The raffinate distilling overhead from stripper 34 leaves through line 36 and is condensed by means not shown and may be utilized or further treated in any manner desired. This raffinate is substantially free of sulfur and its compounds. Solvent is withdrawn from the bottom of raffinate stripper 34 by means of line 37 and combined in line 38 with the solvent discharged from the bottom of extract stripper 29 by means of line 39. The combined stream of solvent in line 38 then recycles to extraction tower 25 through line 26. Make-up solvent can be introduced into line 26 by opening valve 40 located therein.

In practicing the present invention it will be obvious to those skilled in the art that the ratio of solvent to liquid will vary with the concentration of sulfur and/or its compounds in the fraction being extracted. In general, good results may be obtained while operating with liquid to liquid extraction with ratios of solvent to liquid of 4:1 to 20:1, while in vapor-liquid extraction, the ratio of solvent to liquid will be somewhat higher of the order of about 10:1 to 50:1. The reflux ratios employed will likewise vary with the concentration of sulfur compounds in the feed stock but good results may be obtained in both liquid-liquid and vapor-liquid extraction with reflux ratios of the order of about 1:1 to about 10:1.

A preferred solvent specified for use in the present invention has been described as a polyethylene glycol having a molecular weight in the range of about 400 to 4,000. Solvents of this nature having molecular weights in excess of about 800 are solids at ordinary temperature. They are advantageously employed at elevated temperatures at which they are in a liquid state.

A typical solvent employed in the present invention has the following characteristics:

Table

Density (grams/cc. at 20° C.)	1.15
Melting point, °C	30-40
Viscosity, Saybolt Universal at 210° F.	60-90
Mol. wt. (Cryoscopic method)	1200 (approx.)

In general, glycols in the higher portion of the range from about 1,000 to 4,000 molecular weight will be employed. These glycols usually have a specific gravity slightly above that of water and melt in the neighborhood of about 100° to 130° F. The higher molecular weight poly-olefin glycols are usually solids, but like the lower molecular weight poly-olefin glycols, have a melting point in the range given. For example,

a poly-olefin glycol having a molecular weight of 4,000 has a melting point of about 125° F.

In order to illustrate the practice of the present invention further, a kerosene fraction which had been substantially freed of aromatic constituents by extraction with liquid sulfur dioxide and having a sulfur content of 0.25% by weight was extracted with polyethylene glycol at a temperature of 135° F. to obtain a raffinate and an extract phase. The raffinate was tested and found to contain 0.125% by weight of sulfur.

A light naphtha boiling below about 165° F. and substantially free of aromatic hydrocarbons was contacted at about 225° F. with polyethylene glycol having a molecular weight of approximately 1,200. A raffinate phase and an extract phase was obtained. Sulfur determinations were then made on the original charge, the raffinate, and the extract. The original charge showed a sulfur content of 0.11% by weight while the sulfur content of the raffinate was 0.025% and the sulfur content of the extract was 0.2%. It was also found that the mercaptan sulfur content of the charge was 18 mg. per 100 ml., that of the raffinate was 0, and the mercaptan sulfur content of the extract was 16 mg. per 100 ml. indicating that the mercaptan sulfur had all been concentrated in the extract.

The present invention may be employed in conjunction with conventional solvent extraction processes. For example, sulfur dioxide and/or similar solvents may be employed to remove aromatic constituents from naphthas and a poly-olefin glycol extraction may follow the sulfur dioxide extraction to remove sulfur compounds from the substantially aromatic-free raffinate resulting from the extraction with sulfur dioxide.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A process for removing sulfur and its compounds from a non-aromatic hydrocarbon fraction containing them which comprises contacting the sulfur-containing fraction with a poly-olefin glycol having a molecular weight in the range between 400 and 4,000 under conditions to form a raffinate phase and an extract phase, and recovering substantially sulfur-free hydrocarbons from said raffinate phase.

2. A method for removing sulfur and its compounds from a non-aromatic hydrocarbon boiling below 175° F. containing them which comprises contacting said hydrocarbon with a poly-olefin glycol having a molecular weight in the range between 400 to 4,000 under conditions to form a raffinate phase and an extract phase, separating said phases, and recovering substantially sulfur-free hydrocarbons from said raffinate phase.

3. A method for removing sulfur and its compounds from non-aromatic hydrocarbons containing them which comprises heating a sulfur-containing non-aromatic hydrocarbon fraction boiling in the range between 100° F. and 600° F. to a temperature no lower than 120° F. and no higher than 50° F. above the boiling point of the heaviest hydrocarbon in said non-aromatic hydrocarbon fraction, contacting said heated hydrocarbon fraction with a poly-olefin glycol having a molecular weight in the range between 1,000 and 4,000 under conditions to form a raffinate phase and an extract phase, separating said phases, and recovering a substantially sul-

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fur-free hydrocarbon from said raffinate phase.

4. A method in accordance with claim 3 in which the sulfur-containing non-aromatic hydrocarbon fraction is a solvent raffinate of a crude petroleum fraction.

5. A method in accordance with claim 3 in which the sulfur-containing non-aromatic hydrocarbon fraction is a petroleum distillate boiling below 175° F.

6. A method in accordance with claim 3 in which the poly-olefin glycol is a polyethylene glycol.

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