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REFINING OF HYDROCARBON OILS

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This invention relates to the treatment of hydrocarbon oils which contain organic sulfur compounds and aromatic hydrocarbons. More particularly, the invention is directed to the treatment of petroleum oils boiling in the heavier-than-gasoline range which contain aromatics and undesirable amounts of organic sulfur compounds. Still more particularly the invention relates to the removal of a separate fraction of low-sulfur aromatics and a separate fraction of essentially organic sulfur compounds from hydrocarbon oils containing these compounds in addition to paraffinic and/or naphthenic compounds.

Practically all hydrocarbon oils derived from natural sources consist of paraffins, naphthenes, aromatics, organic-sulfur compounds and some organic nitrogen and oxygen compounds. For some purposes the presence of aromatics is desirable, e. g., gasolines and high solvency naphthas. For other purposes, the presence of aromatics is objectionable, e. g., burning oils, domestic fuel oils and lube oils. For most common uses of hydrocarbon oils, the presence of organic-sulfur compounds is objectionable even though small amounts are tolerated; for example, 0.15% of sulfur is tolerated in gasoline. The magnitude of the problem is illustrated by the fact that heater oil obtained from West Texas crude contains about 20% of aromatic compounds and about 4% of organic sulfur compounds, its total sulfur content being about 0.7%.

A very large number of processes for reducing sulfur and aromatic content have been developed, such as, sulfuric acid treating, silica gel extraction, liquid SO₂ extraction, etc. These processes either change the chemical nature of the compounds removed, or remove a mixture of aromatic and sulfur compounds which can be separated with difficulty or only at excessive cost. Recently a large demand has arisen for relatively pure organic sulfur compounds, of the type naturally occurring in petroleum oils, as starting materials for synthetic detergents, fungicides, insecticides, etc. At the same time there is great demand for aromatic concentrates and pure aromatic compounds particularly for use in polymeric materials, detergents, super solvency naphthas, etc.

An object of our invention is to refine hydrocarbon oils by substantially reducing the amount of organic sulfur compounds and aromatic compounds present therein. Another object is to produce a domestic fuel oil of good burning quality and odor by removing organic sulfur compounds and aromatic compounds therefrom.

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A particular object is to treat hydrocarbon oils containing organic sulfur compounds and aromatic compounds and recover therefrom a separate fraction of essentially organic sulfur compounds and a separate fraction of essentially aromatic compounds.

We have discovered that a hydrocarbon oil containing aromatic compounds and organic sulfur compounds can be separated into a low sulfur and low aromatic content refined oil, an essentially aromatic hydrocarbon fraction and an essentially organic sulfur compound fraction by a combination process comprising: contacting, in a first extraction step, the feed oil with liquid SO₂ having dissolved therein aromatic compounds and a promoter which increases the organic-sulfur compound solution ability of the liquid SO₂ and has little or no effect on aromatic solubility therein, and separating a low sulfur content first raffinate phase from an essentially organic sulfur compound-liquid SO₂-promoter extract phase; and, in a second extraction step, contacting the first raffinate with liquid SO₂ under conditions resulting in the separation of a low sulfur, low aromatic content second raffinate phase, and an essentially aromatic hydrocarbon-liquid SO₂ extract phase, which extract phase can be, in part, used as the solvent in the first extraction step.

Liquid SO₂ is effective, at temperatures below about +10° C., in removing aromatic compounds from mixtures with paraffinic and naphthenic compounds particularly good results are obtained at temperatures below 0° C. However, liquid SO₂ is not particularly effective in removing organic sulfur compounds. The sulfur-removing powers of liquid SO₂ can be enhanced by adding a promoter, such as, liquid HF, sulfonic acids, etc. Promoters selected from the class of Friedel-Crafts type halides are remarkably effective in liquid SO₂ at these low temperatures. Sufficient liquid SO₂ must be used to exceed the solubility of liquid SO₂ in the oil so as to form a separate phase.

Not all the members of the class of compounds known as the Friedel-Crafts type halides can be used in our process. Some members are completely ineffective, for example, aluminum trifluoride, or are only feebly effective, for example, antimony trichloride, aluminum bromide and stannic chloride. A high degree of solubility in the liquid SO₂ is helpful. However, some members of low solubility are good promoters when used in the form of a liquid SO₂-promoter slurry, for example, FeCl₃, HgCl₂, and ZnCl₂. The members of the class which are effective as sulfur removal promoters in liquid SO₂ extraction are,

AlCl_3 , FeCl_3 , TiCl_4 , BF_3 , HgCl_2 , BCl_3 , and ZnCl_2 . Because of its solubility in liquid SO_2 , ease in recovery from the extract phase and excellent desulfurization obtained therewith, we prefer to use BF_3 . (The presence of water is deleterious to the efficacy of the promoter and therefore we use substantially anhydrous material).

An appreciable amount of desulfurization, in excess of that resulting from the use of liquid SO_2 alone, can be obtained by using as little as 0.5 gram mole of promoter per gram atom of sulfur present in the raw oil undergoing treatment. Virtually complete desulfurization can be obtained by using up to about 5 moles of promoter. (It is to be understood that the term "moles of promoter" when used in this specification and attached claims means "gram moles of promoter per gram atom of sulfur present in the raw oil undergoing treatment.") The amount of promoter needed to obtain a certain pre-determined amount of desulfurization will vary with the volumes of liquid SO_2 used in the treatment. However, in general, from about 1 to about 3 moles of promoter will give the desired result.

The amount of liquid SO_2 used may vary from just enough to form two phases to 200 volume percent or more based on raw oil. It is of interest that less than the amount of liquid SO_2 that is merely soluble in the oil can be used, as the presence of the promoter and associated sulfur compounds depresses the solubility of SO_2 in the oil. For example, at -35°C ., about 14% of SO_2 is soluble in a virgin West Texas heater oil; when only 10% of SO_2 and 1 mole of AlCl_3 are added to the oil at this temperature, two phases separate. At a fixed promoter usage, the extent of desulfurization increases markedly with increase in liquid SO_2 usage up to about 25 volume percent of liquid SO_2 ; above this point the gain in desulfurization is small per unit of liquid SO_2 increase and about 100 volume percent appears to be about the practical maximum. In general we prefer to use from at least enough liquid SO_2 to exceed the solubility of SO_2 in the raw oil, and preferably about 25%, to about 100 volume percent of liquid SO_2 based on raw oil.

In our combination process, in the second extraction step the liquid SO_2 is removing essentially only aromatic compounds, so that larger quantities of liquid SO_2 are preferred. In the extraction of the first raffinate, we prefer to use between about 50 and about 200 volume percent of liquid SO_2 based on first raffinate oil.

We have discovered that, when liquid SO_2 -aromatic solution is used, in conjunction with a promoter, for the extraction of raw oil, not only is the extraction of aromatics suppressed somewhat but also the sulfur compounds dissolved into the liquid SO_2 -promoter solution force some of the dissolved aromatics out of the extract phase and into the raffinate phase; thereby the extract phase from this first extraction step consists essentially of sulfur compounds, and the promoter dissolved in liquid SO_2 . We have found that this extraction should use an aromatic compound-liquid SO_2 solvent in the smallest possible volume consistent with desulfurization in order to obtain lowest aromatic content in the sulfur compound fraction; and we prefer to use from about 15 to about 50 volume percent of liquid SO_2 , present in the solvent, based on raw oil. The greater the proportion of aromatics in the liquid SO_2 -aromatic solvent used in the extraction of the raw oil the greater will be the SO_2 requirement in order to obtain two-phase separation.

The effectiveness of the liquid SO_2 -promoter solvent is substantially independent of temperature below about 0°C . Above 0°C ., the desulfurization effectiveness of liquid SO_2 -promoter solvent decreases rapidly; $+10^\circ\text{C}$. is about the highest temperature at which reasonable effectiveness can be maintained. In addition to the effect on desulfurization, the temperature of contacting has an effect on the color of the final oil. At contacting temperatures of about -20°C . and below, final oils of excellent color (nearly water-white) are obtained. The color of the final oil darkens markedly as the temperature of contacting increases until at about 0°C ., no improvement is obtained. Although the extraction steps in our combination process could be operated at different temperatures, we prefer to operate at the same temperature of below about $+10^\circ\text{C}$., and preferably between 0°C . and -40°C .

The time period required in our refining process will be dependent upon the intimacy of contacting with the solvent and also upon the contacting temperature. Ordinarily, the time period will be between $\frac{1}{2}$ minute and about 60 minutes, and preferably about 5 minutes.

When the raw oil is very viscous or of relatively high pour point, it may be desirable to dilute the raw oil with a low boiling material such as butane, pentane, hexane, petroleum ether, etc., which is inactive toward the liquid SO_2 and the promoter.

Our refining process can be used for various petroleum feed stocks, such as naphtha, kerosene, heater oil, gas oils, and lube oils. Also the process can be used on the oils from various conversion processes, for example, thermal cracking, coking, catalytic cracking, products of other solvent extraction processes, etc. While thermally cracked oils can be utilized in our process, the high olefin content interferes somewhat with the separation and the polymers formed contaminate the extract fractions. Catalytically cracked oils are particularly suitable feed for our process because they contain large amounts of sulfur compounds and aromatic compounds. Any hydrocarbon oil made up of a mixture of paraffins, naphthenes, aromatics and organic sulfur compounds is a suitable feed for our process.

In some instances, the aromatic and organic-sulfur compounds may be of more value than the refined oil produced and the process may be operated even though more refined oil is made than is required. In such a case, the refined oil makes an excellent feed to a catalytic cracking process, since it is low in the two materials that are objectionable in catalytic cracking feed. The catalytic cracking operation builds up aromatics and refractory organic sulfur compounds; therefore, the gas oil produced from catalytic cracking of our refined oil is a good charging stock to our process. This sequence of operations may be continued until the original raw oil is completely converted.

The following data are supplied as illustrative of advantageous results attainable by the use of our process.

RUN I

A virgin West Texas heater oil (obtained by distillation from a high sulfur West Texas crude) with the following characteristics was treated with liquid SO_2 and BF_3 .

$^\circ\text{API}$	40.9
Sulfur (wt. percent)	0.61
n_D^{20}	1.4558

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Color, Saybolt	-----	+13
Mercaptan No.	-----	57
ASTM distillation:		
IBP	-----°F	330
50%	-----°F	450
Max.	-----°F	555

Liquid SO₂, 500 ml., was added to 500 ml. of the heater oil contained in a reactor provided with a cooling jacket and mechanical agitator. The temperature of the reactor contents was maintained at -20° C. BF₃, in the amount of 2 gram moles per gram atom of sulfur in the heater oil, was metered into the closed reactor. At this point a pressure of from 10 to 100 p. s. i. g., due largely to BF₃, existed in the reactor; this pressure fell quickly to about 0 p. s. i. g. when agitation was started. Agitation was continued for 5 minutes; the reactor contents were allowed to settle for 30 minutes before the raffinate phase and extract phase were withdrawn. The raffinate phase was washed with water, then with 10% aqueous caustic, again with water, and then dried. This procedure removed all traces of the SO₂ and BF₃ which were dissolved in the treated oil. The SO₂ was flashed from the extract phase and the BF₃ complex decomposed by heating, followed by a caustic wash. The yield of raffinate oil was 85 volume percent; this treated oil had the following characteristics: sulfur, 0.086%; refractive index of n_D^{20} , 1.4468; mercaptan number, doctor sweet. The extract oil had a sulfur content of 4.3%.

RUN II

A sample of the heater oil described in Run I was treated in a series of batchwise steps in order to simulate equilibrium countercurrent contacting. Raw oil was treated with 100 volume percent of liquid SO₂ at -20° C., the extract phase was used in conjunction with BF₃ to treat more raw oil; the raffinate from the extract phase-BF₃ solvent treat was then contacted with liquid SO₂ alone.

Raw oil was contacted with 28 volume percent of extract phase, which contained 26 parts of liquid SO₂ and 2 parts of aromatic compounds, and 2 mols of BF₃ per gram atom of sulfur in the raw oil at a temperature of -20° C. for 5 minutes. The first raffinate was separated from the first extract phase; this first raffinate was then contacted with 100 volume percent of liquid SO₂ at -20° C. for 5 minutes; the second raffinate was separated and washed with caustic and water to remove dissolved SO₂. The SO₂ was removed from the second extract phase. Although an equilibrium equivalent to countercurrent contacting was not reached in this particular instance, the following results were obtained.

The treated oil (second raffinate) was obtained in 83.5 volume percent yield and had a sulfur content of 0.07 wt. percent; a refractive index of n_D^{20} , 1.4450; and an API gravity of 44.1. The first extract oil, which was comprised substantially of organic-sulfur compounds, represented 7.0 volume percent of the raw oil and had a sulfur content of 6.87 wt. percent and a refractive index n_D^{20} , 1.5188. The second extract oil represented 9.5 volume percent of the raw oil and had a sulfur content of 1.0 wt. percent and a refractive index of n_D^{20} , 1.5134. It contained more than 95% of aromatic compounds.

RUN III

In this run there was treated a light recycle catalytic gas oil obtained by distillation of the

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product from the cracking of a mixture of various virgin gas oils at about 900° F. in the presence of a silica-alumina catalyst. This light cat gas oil had the following characteristics:

°API	-----	30.1
Sulfur (wt. percent)	-----	1.34
n_D^{20}	-----	1.4963

ASTM distillation:

IBP	-----°F	415
50%	-----°F	460
Max.	-----°F	525

Liquid SO₂, 250 ml., was added to 250 ml. of the recycle oil contained in a reactor provided with a cooling jacket and mechanical agitator. The temperature of the reactor contents was maintained at -20° C. by a Dry Ice acetone bath. AlCl₃, in the amount of 2 gram moles per gram atom of sulfur in the heater oil, was added into the reactor and the reactor closed. Agitation was continued for about 2 minutes. The mixture was allowed to settle and the two phases therein separately withdrawn. The raffinate phase was water and caustic washed to remove dissolved SO₂ and AlCl₃. The SO₂ was flashed from the extraction phase and the AlCl₃-oil allowed to stand until it separated into an aromatic oil containing about 4% sulfur and an AlCl₃ sludge. This sludge was hydrolyzed to yield a very high sulfur, viscous, tarry liquid with drying oil properties. The raffinate oil represented 65% of the raw oil, and had the following characteristics: sulfur, 0.13%, n_D^{20} , 1.4656.

RUN IV

A sample of the light cat cycle oil was treated in a manner similar to Run II in order to simulate countercurrent contacting. In the first extraction step 64 volume percent, based on raw oil, of second extract phase which contained about 51 parts of liquid SO₂ and 13 parts of aromatic compounds, and 2 moles of AlCl₃ per gram atom of sulfur in the raw oil, were contacted at a temperature of -20° C. for 5 minutes. The treated oil (second raffinate) had a sulfur content, 0.04%; n_D^{20} , 1.4505; and an API gravity, 43.1. The first extract oil had a sulfur content 5.6%. The second extract oil had a sulfur content, 0.54% and a n_D^{20} , 1.5428.

The above runs do not represent the equilibrium attainable in countercurrent operations and therefore do not give as good separations as can be obtainable with the more efficient operation. They do illustrate this fact: Our process operating with no more of the solvent than the conventional single tower processes can produce a refined oil in the same yields and quality as the conventional process, a relatively low sulfur aromatic hydrocarbon fraction, and a fraction consisting substantially entirely of organic sulfur compounds.

In order to more fully describe a specific embodiment of our invention, reference is made to the accompanying drawing which constitutes a part of this specification and in which a schematic flow diagram of our process is shown.

The feed stock, for example, a virgin heater oil from a West Texas crude, is passed through line 11 into a drying zone 12 wherein it is substantially dehydrated. The presence of water in the treating system is extremely undesirable because water combines with BF₃ to form hydrates, which hydrates complicate the recovery of BF₃; and the presence of water increases the corrosive tendencies of the SO₂ refining agent. Drying zone

12 comprises conventional equipment such as, for example, a vessel packed with calcium chloride, alumina gel, or the like.

The dried raw oil is passed through line 13 into deaeration equipment 14, wherein air dissolved or entrained in the feed oil is substantially removed. Conventional deaeration equipment such as is ordinarily employed in commercial processes of liquid SO₂ refining of hydrocarbon oils may be employed. The dried deaerated feed oil is passed through line 16 into heat exchanger 17, wherein the temperature of the feed oil is lowered to the desired treating temperature.

In the case of very viscous hydrocarbon feed oils, the viscosity of the oil can be reduced by dilution with a paraffinic hydrocarbon such as butane, pentane, petroleum ether, etc. The diluent may be introduced into line 16 through valved line 18.

The dried deaerated (diluted) feed oil is introduced into the lower portion of treating or extraction tower 19. The extraction tower may be packed with corrosion-resisting materials, or may be of modified bubble cap type construction. In tower 19 the feed oil is contacted with BF₃ and a solvent consisting of liquid SO₂ that is substantially saturated with aromatic compounds derived from the particular feed oil being treated. If desired, the BF₃ and solvent may be combined and introduced into the upper portion of tower 19 as one stream. In this type of operation BF₃ is withdrawn from storage drum 21 through line 22 and valved line 23, and is passed into line 24. Alternatively, solvent alone may be introduced through line 24 and BF₃ may be introduced into the extraction tower through line 22 and manifold 26.

Contacting in extraction tower 19 may be effected at temperatures between about 0° C. and about -60° C., preferably at about -20° C. and at pressures between 0 and about 100 p. s. i. g.; sufficient pressure must be maintained on the system to keep the SO₂ in the liquid state. The amount of liquid SO₂ contained in the solvent introduced into tower 19 may be between about 15 and about 50 volume per cent based on the feed oil. It is desirable to keep the amount of liquid SO₂ that is introduced into this first extraction step as low as the desired degree of desulfurization will permit. With large quantities of liquid SO₂ the effectiveness of the BF₃ in selectively removing sulfur compounds to the exclusion of aromatics is somewhat impaired. Thus the smaller the volume of liquid SO₂ added to first extraction step, the smaller the amount of aromatic compounds carried out of the system into the organic sulfur compound fraction product. Thus we prefer to use such an amount of solvent that the amount of liquid SO₂ will be between about 15 and 35 volume per cent and preferably be about 25 volume per cent based on feed oil.

The amount of BF₃ may be between about 0.5 and about 5 moles per gram atom of sulfur in the feed oil. Preferably, the amount of BF₃ used should be between 1 and 3 moles.

The contacting period in tower 19 may be varied between about 1/2 and about 60 minutes and is preferably about 5 minutes.

The first raffinate is withdrawn from the upper part of tower 19 through line 27 and valved line 28 into stripping tower 29. Stripping tower 29 may contain packing material, bubble trays, or even be unpacked. In order to maintain the proper temperature for removing dissolved BF₃

and SO₂ from the first raffinate, tower 29 is provided with a reboiler 31. The stripped first raffinate is passed from stripper 29 into cooler 32 and through valved line 33 and line 34 into extraction tower 36. Ordinarily it will not be necessary to remove dissolved BF₃ from the first raffinate as the amount of this material will be too slight to affect treating in the second extraction step. However, to eliminate the possibility that excessive amounts of BF₃ may be carried over into the second extraction step, stripping tower 29 has been provided; SO₂ and BF₃ pass out of stripper 29 by line 30. When stripper 29 is not being used the first raffinate may be bypassed by means of valved line 37 into line 34 and thence into extraction tower 36. In extraction tower 36 the first raffinate is contacted with liquid SO₂ which is withdrawn from storage 38 and passed through line 39 into the upper portion of extraction tower 36. The amount of liquid SO₂ introduced into tower 36 may be between about 15 and about 200 volume per cent by volume of first raffinate, preferably between about 25 and 100 volume per cent, while the temperature and pressure maintained in tower 36 may be different from that in tower 19. We prefer to operate the second extraction step at about the same temperature, i. e. about -20° C. and same pressure as that maintained in the first extraction step. The second raffinate is withdrawn from tower 36 and passes through line 41 to stripper 42, which stripper is similar in construction to stripper 29. The temperature of the second raffinate oil is raised high enough by means of reboiler 43 to remove the SO₂ dissolved therein. The SO₂ stripped from the second raffinate passes out of the stripper 42 through line 40. The treated oil (SO₂-free second raffinate oil) passes out of stripper 42 by line 46 to storage or further treatment. The extract phase from tower 36 passes out of the tower through line 47; a suitable portion of the extract is passed through valved line 48 to line 24 for use as solvent in the first extraction step. That portion of the extract phase from tower 36 not needed for the first extraction step in tower 19 passes through valved line 49 into stripper 51, which is similar in construction to strippers 29 and 42. In stripper 51 the SO₂ is removed from the extract oil by means of heat provided by reboiler 52. The SO₂ passes out of stripper 51 through line 53 and the aromatic compound fraction passes from stripper 51 by line 54 to storage or further treatment.

The first extract phase from tower 19 passes out of the tower through line 56 into stripper 57 which may be similar in construction to strippers 29, 42, and 51. The first extract phase may be subjected to a sufficiently high temperature by means of reboiler 58 to vaporize substantially all the SO₂ and BF₃ present therein. Such temperatures fall within the range of about 50° C. to about 250° C. The SO₂ and BF₃ free extract oil, consisting essentially of organic-sulfur compounds, is withdrawn from stripper 57 through line 59 to storage or further treatment. The SO₂ and BF₃ pass overhead from stripper 57 through line 61.

From time to time, it may be necessary to send the SO₂ or SO₂-BF₃ streams from the strippers to a dehydration operation for the removal of water which tends to build up in the system. In such event, the streams in lines 30 and 40 may pass through valved lines 62, 63 and 64; the stream from line 53 may pass through lines 63 and 64; and the stream in line 61 may pass

through line 64 to dehydrator 66. From dehydrator 66, the SO_2 , BF_3 and some H_2S which forms during the high temperature dissociation of the BF_3 -sulfur compound complexes, pass through line 67 to a purification system 68. The streams from strippers 29, 42 and 51 may be passed directly to purification system 68 by way of lines 62 and 69.

The purification system 68 separates the SO_2 , BF_3 and H_2S ; fractional liquifaction may be used because of the spread between the boiling points of these compounds. From system 68, the BF_3 passes through line 71, compressor 72 and cooler 73 to BF_3 storage 21. Some losses are inevitable, so additional BF_3 may be added from source 74. From system 68, the SO_2 passes by line 76, compressor 77, and cooler 78 to SO_2 storage 38; make-up SO_2 may be added from source 79.

It should be understood that many details of process technique have been omitted in the above specific embodiment of our process. Common expedients which have been employed in commercial SO_2 refining processes will suggest themselves to those skilled in the art; such expedients are within the purview of the present invention.

The invention disclosed herein is an improvement on the inventions disclosed and claimed in our application No. 182,613, filed August 31, 1950, and now abandoned, and in our application No. 201,174, filed December 16, 1950, now U. S. Patent 2,646,390.

We claim:

1. A process for refining a hydrocarbon oil which contains both aromatic and sulfur compounds, which process comprises extracting said oil in a first extraction zone with an aromatic compound-liquid SO_2 solvent and an effective amount of an added promoter selected from the class of Friedel-Crafts halides consisting of BF_3 , AlCl_3 , FeCl_3 , TiCl_4 , HgCl_2 , BCl_3 and ZnCl_2 , and the amount of liquid SO_2 being sufficient to effect formation of a separate phase in the presence of the oil and promoter whereby a first extract phase which contains liquid SO_2 , promoter and predominantly organic-sulfur compounds and a first raffinate phase are obtained, extracting said first raffinate phase in a second extraction zone with liquid SO_2 , in the absence of any substantial amount of said promoter, to obtain a second raffinate phase substantially reduced in both aromatic and organic-sulfur compound content and a second extract phase which contains liquid SO_2 , predominantly aromatic hydrocarbons and a minor amount of organic-sulfur compounds, removing SO_2 and promoter from said first and second extract phases respectively and removing SO_2 from said second raffinate phase.

2. The process of claim 1 wherein the contacting in each of the extraction steps is effected at a temperature in the range of $+10^\circ\text{C}$. to -60°C .

3. The process of claim 1 wherein the amount of promoter used in said first extraction zone is between about 0.5 and 5 gram moles per mole of sulfur in said oil.

4. The process of claim 1 wherein the amount of said solvent used in said first extraction step contains from about 15 to about 50 volume per cent of liquid SO_2 , based on said oil.

5. The process of claim 1 wherein the amount of liquid SO_2 used in said second extraction zone is between about 15 and 200 volume per cent, based on said first raffinate oil.

6. The process of claim 1 wherein a part of the second extract phase with its contained SO_2 is

employed to supply both liquid SO_2 and aromatic compounds to said first extraction zone.

7. A process for refining petroleum oils that contain objectionable amounts of organic sulfur compounds and of aromatic compounds which process comprises contacting in a first extraction step said oil with from about 0.5 to about 5 moles of a promoter selected from the class of Friedel-Crafts halides consisting of BF_3 , AlCl_3 , FeCl_3 , TiCl_4 , HgCl_2 , BCl_3 and ZnCl_2 and a solvent containing from about 15 to about 50 volume per cent of liquid SO_2 , based on said oil, and SO_2 soluble constituents, which solvent is derived from a second extraction step, separating a first raffinate phase from a first extract phase, contacting in a second extraction step the first raffinate phase with from about 15 to about 200 volume per cent of liquid SO_2 , based on first raffinate oil, separating a second raffinate phase from a second extract phase and passing the requisite amount of said second extract phase to said first extraction step, wherein the temperature of contacting in said extraction steps is maintained between about 0°C . and -60°C .

8. The process of claim 7 wherein the temperature of contacting is below about -20°C .

9. The process of claim 7 wherein the promoter is BF_3 .

10. The process of claim 9 wherein each extraction step is conducted in a countercurrent tower and wherein the solvent to the first extraction step is introduced near the top of the tower and the BF_3 is introduced intermediate the point of oil entry and the point of solvent entry.

11. The process of claim 9 wherein the first extract phase is separated to recover SO_2 and BF_3 , the second extract phase is separated to recover SO_2 and the SO_2 and BF_3 are recycled to the process.

12. The process of claim 7 wherein the promoter is AlCl_3 .

13. A process for reducing the organic-sulfur compound and aromatic compound content of a sulfur and aromatic containing virgin petroleum distillate boiling above the gasoline range which process comprises contacting in a first extraction step said distillate with from about 1 to about 3 moles of BF_3 per mole of sulfur in said distillate and with a solvent containing liquid SO_2 and SO_2 -soluble constituents which solvent is derived from a second extraction step and which solvent is used in such amounts that from about 15 to about 35 volume percent of liquid SO_2 , based on said distillate, is present in said first extraction step, separating a first raffinate phase from a first extract phase, contacting the first raffinate oil in a second extraction step with from about 25 to about 100 volume percent of liquid SO_2 , based on said first raffinate, separating a second raffinate phase from a second extract phase, passing the requisite amount of said second extract phase to said first extraction step to supply said solvent therefor, wherein said extraction steps being conducted at a temperature not higher than about -20°C . and wherein the time of contact in each extraction step is from about 5 minutes to 1 hour, removing the SO_2 and BF_3 from said first extract phase to recover a fraction consisting essentially of organic sulfur compounds, removing the SO_2 from the second raffinate phase to recover an oil low in both aromatics and organic-sulfur compounds, removing the SO_2 from the second extract phase to recover an oil consisting of aromatic compounds and a minor amount of organic-sulfur compounds

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and recycling the SO_2 and BF_3 to the extraction steps.

14. A process for refining a hydrocarbon oil which contains both aromatic and organic sulfur compounds which process comprises contacting in a first extraction zone said oil with a solvent, containing liquid SO_2 and added aromatic compounds, and an effective amount of a promoter for increasing the solubility of said organic-sulfur compounds in liquid SO_2 , which promoter is selected from the class of Friedel-Crafts halides consisting of BF_3 , AlCl_3 , FeCl_3 , TiCl_4 , HgCl_2 , BCl_3 and ZnCl_2 , wherein the amount of liquid SO_2 used is sufficient to form two phases, separating a first extract phase consisting essentially of liquid SO_2 , substantially all the added promoter and rich in organic-sulfur compounds from a first raffinate phase, contacting said first raffinate phase in a second extraction zone with liquid SO_2 , in the absence of added amounts of promoter, to form a second extract

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phase consisting essentially of liquid SO_2 , small amounts of organic-sulfur compounds and rich in aromatic compounds and a second raffinate phase substantially reduced in both aromatic and organic-sulfur compound content.

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