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HYDROCARBON DESULFURIZATION PROCESS BY REACTING THE SULFUR IN THE HYDROCARBON WITH AN OLEFIN AND A CATALYST, THEN EXTRACTING THE HYDROCARBON WITH SO₂ AND BF₃

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This invention relates to a process for refining hydrocarbon materials containing one or more undesired impurities, such as coloring matter, malodorous materials and organo-sulfur compounds. More particularly, this invention is concerned with a process for desulfurizing mercaptan and other organo-sulfur compound containing hydrocarbon oils, particularly sour petroleum distillates boiling in the heavier-than-gasoline range.

Patent application Serial Number 248,898, filed September 29, 1951, now Patent 2,671,047, entitled "Refining Hydrocarbon Materials with SO₂ and BF₃" by Robert C. Arnold and Arthur P. Lien discloses a process for desulfurizing organo-sulfur compound containing hydrocarbon materials by the treatment thereof with an agent consisting of liquid SO₂ and BF₃. This process gives a markedly greater amount of desulfurization than does an equivalent amount of liquid SO₂ alone. Also, this process converts a sour, i. e., mercaptan containing, oil into an oil that is sweet to the doctor test. These improved results are obtained with substantially no increase in the amount of hydrocarbons taken into the extract phase. However, it has been found that the raffinate oil from this process, although of markedly lower organo-sulfur compound content, contains appreciable amounts of free-sulfur. The free-sulfur is present in the raffinate oil even though none had been present in the sour oil feed to the process. The presence of free-sulfur in hydrocarbon oils such as naphthas, kerosenes, heater oils, or high solvency naphthas has an extremely bad effect on product quality as determined by the copper strip method.

One object of the present invention is to provide a process for refining and desulfurizing hydrocarbon oils containing organo-sulfur compounds. An additional object is to provide a process for decolorizing hydrocarbon materials, particularly hydrocarbon oils. A specific object of the invention is to provide a process for the treatment of a petroleum distillate containing objectionable amounts of organo-sulfur compounds and mercaptans to produce a product oil of low organo-sulfur compound content and also essentially free of free-sulfur. These and other objects of the invention will become apparent from the following description.

It has been discovered that free-sulfur is not present in the product of the treatment of hydrocarbon material containing organo-sulfur compounds with an agent consisting essentially of liquid SO₂ and a promoter selected from the class of Lewis acids (Friedel-Crafts-type halides) when the hydrocarbon oil is treated to substantially eliminate mercaptans prior to undergoing the liquid SO₂-promoter treatment. Thus the combination process of this invention comprises: (1) Treating a hydrocarbon material containing mercaptans and other organo-sulfur compounds to substantially eliminate the mercaptans by treating the oil in the presence of a Friedel-Crafts metal halide catalyst with an olefin in an amount sufficient to substantially eliminate the mercaptans. (2) Contacting said substantially mercaptan-free oil with an agent consisting es-

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entially of liquid SO₂ and a promoter selected from the class of Friedel-Crafts-type halides consisting of BF₃, AlCl₃, FeCl₃, TiCl₄, HgCl₂, BCl₃ and ZnCl₂. At least enough liquid SO₂ is present in the agent to exceed the solubility of liquid SO₂ in the oil undergoing treatment. The temperature of the treatment is below about +10° C.

(3) Separating a raffinate oil of markedly lower organo-sulfur compound content and essentially free of elemental sulfur from an extract phase comprising agent, sulfur compounds and extract hydrocarbons.

The SO₂-promoter process is applicable to various liquid or liquefied hydrocarbon materials which contain organo-sulfur compounds. Thus it is applicable to various petroleum fractions for the purposes of removing sulfur, gums or other resinous materials, colored impurities and odoriferous compounds. Suitable petroleum feed stocks may comprise light naphtha fractions, gasolines, heavy naphthas, kerosenes, transformer oils, heater oils, furnace oils, diesel fuels, gas oils, lube oils and crude oils. Particularly suitable charging stocks are petroleum distillates boiling in the heavier-than-gasoline range, i. e., between about 330° and 675° F.

This process can be applied for the purpose of desulfurizing various petroleum stocks which are to be subsequently treated in refining or conversion operations in which sulfur or sulfur compounds are undesirable, for example, catalytic cracking operations, catalytic reforming operations, catalytic hydrogenation in the presence of sulfur-sensitive catalysts and the like.

In addition the refining agents of the present invention may be applied to the desulfurization and decolorization of sour aromatic hydrocarbon fractions, for example, crude benzols, toluols, xylols, naphthalene fractions or the like.

The process may also be applied to the refining of various coal tar fractions and coal tar distillates. In the refining of shale oil fractions the refining agents serve not only to remove organic sulfur compounds from the feed stock, but also to remove oxygen compounds and nitrogen compounds.

It is to be understood that the above specific examples of charging stocks which may be refined by the present invention are illustrative only and are not intended to limit the field of applicability of the process.

Although the mechanism is not understood, the mercaptans present in the feed oil appear to be the cause of the formation of free-sulfur in the SO₂-promoter process. A product oil that is free of free-sulfur can be obtained if the mercaptans are eliminated from the oil.

The sweetening process is believed to involve the reaction of a mercaptan and an olefin in the presence of a catalyst. Although any olefinic hydrocarbon can be utilized, sterically hindered olefins, such as tetramethylethylene, are not especially suitable. It is preferred to use the lower molecular weight olefin, such as ethylene, propylene and butylene.

In general, at least about one mol of olefin is used per mol of mercaptan present in the sour oil. Somewhat less than this amount may be used, as it is not necessary to produce an oil that is sweet to the doctor test. A substantially sweet oil, i. e., an oil having a mercaptan number below about 5, can be treated by the SO₂-promoter process without the introduction of amounts of free-sulfur that can be detected by the reverse doctor test. The presence of olefin in excess of the about 1 mol minimum amount has a beneficial effect on the rate of sweetening. A large excess of olefin is undesirable because of the introduction of side reactions, such as polymerization.

The sweetening process can be carried out at temperatures as low as -60° C. and as high as +50° C. or higher. Low temperatures have an adverse effect on the rate of sweetening. Elevated temperatures, in the presence of

very active catalysts such as BF_3 , introduced undesirable side reactions. It is preferred to operate at about the same temperature as the subsequent SO_2 -promoter process.

The rate of sweetening is dependent upon the amount of olefin, the temperature, the catalyst and the degree of agitation. In general the higher the temperature the faster the rate of sweetening. At the preferred conditions of operation, the sweetening time may be between about 5 minutes and 60 minutes. In any event, the contacting must be maintained for a time long enough to substantially sweeten the sour oil feed.

The catalyst for the olefin-mercaptan reaction may be any Lewis acid. However, it is preferred to use those Friedel-Crafts-type halides which are also effective desulfurization promoters for liquid SO_2 . As little as trace amounts of catalyst may be used. In order to increase the rate of sweetening (decrease contact time), it is desirable to use more than this amount, for example, about 1 mol of catalyst per mol of mercaptan in the sour oil. In some cases, all of the promoter needed in the SO_2 -promoter process, may be introduced into the olefin-sour oil-catalyst contacting zone. The "catalyst" may be different from the "promoter" but it is preferred to operate using the same "catalyst-promoter" in each process step of the combination process of this invention.

In general, the proportion of liquid sulfur dioxide used in the liquid SO_2 -promoter process varies with the specific hydrocarbon material being treated and the treating conditions, especially the temperature. The relative miscibility of liquid sulfur dioxide and hydrocarbon charging stocks varies with temperature, greater mutual miscibilities being encountered at higher temperatures and lower miscibilities at lower temperatures. At least a sufficient amount of sulfur dioxide is used to exceed its solubility in the hydrocarbon material being treated at the particular treating temperature, thereby forming two distinct liquid phases, i. e., a predominantly hydrocarbon liquid phase containing a relatively small proportion of dissolved sulfur dioxide or raffinate layer and a predominantly sulfur dioxide liquid phase or extract layer. Ordinarily, liquid sulfur dioxide is employed in the process in amounts between about 15 percent and about 200 percent by volume or more, based on the volume of hydrocarbon charging stock. Preferably, between about 25 and 75 volume percent of liquid SO_2 is used.

The sulfur-removing powers of liquid SO_2 are remarkably enhanced by the addition thereto of a promoter selected from the class of Lewis acids (Friedel-Crafts-type halides). Not all the members of the class of compounds known as the Friedel-Crafts-type halides can be used in this 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 SO_2 is helpful. However, some members of low solubility are good promoters when used in the form of a liquid SO_2 -promoter slurry, for example, FeCl_3 , HgCl_2 , and ZnCl_2 . The members of the class which are effective as sulfur removal promoters in liquid SO_2 extraction are AlCl_3 , FeCl_3 , TiCl_4 , BF_3 , HgCl_2 , BCl_3 , and ZnCl_2 . With the exception of BF_3 these promoters do not appear to give complete sweetening when a sour oil is contacted with the SO_2 -promoter agent. However, a sufficient amount of sweetening occurs with all the promoters to produce a deleterious amount of free-sulfur in the product oil if the sour oil is not sweetened prior to contacting with the SO_2 -promoter agent. Because of its solubility in liquid SO_2 , ease of recovery from the extract phase and superior desulfurization obtained therewith, BF_3 is preferred.

The amount of promoter employed in the process will usually fall within the range of about 0.5 to about 5 mols per gram atom of sulfur contained in the hydrocarbon charging stock. The proportions of promoter to sulfur within the above range, when employed with liquid

sulfur dioxide, are sufficient not only to effect substantial desulfurization of sulfur-containing hydrocarbon materials but also to effect additional refining, particularly decolorization. For purposes of desulfurization it has been discovered that the optimum desulfurization can be effected by the employment of between about 1 and about 3 mols of promoter per gram atom of sulfur contained in the hydrocarbon charging stock. (It is to be understood that at least a sufficient amount of liquid sulfur dioxide to form a liquid phase distinct from the raffinate hydrocarbon material is also present in the contacting zone.)

The SO_2 -promoter process may be conducted at temperatures between about $+10^\circ \text{C}$. and -85°C . The preferred temperature range is between about -10°C . and -40°C . The optimum temperature will vary not only with the type of charging stock but also with the desired product, i. e., maximum desulfurization and maximum color improvement may require different temperatures at otherwise constant conditions of operation.

The SO_2 -promoter process is conducted under pressure sufficient at least to maintain a substantial proportion of the sulfur dioxide in the liquid state and likewise sufficient at least to maintain a substantial proportion of the gaseous promoters dissolved in the liquid phase. In the presence of liquid sulfur dioxide, BF_3 forms extremely stable addition compounds with organo-sulfur compounds and, as a result, a substantial proportion of BF_3 which is originally introduced into the refining zone as a gas is rapidly absorbed. The partial pressure of BF_3 in equilibrium with said BF_3 -sulfur compound addition compounds is very low at temperatures of 0°C . or less. In general, the SO_2 -promoter process can be operated at pressures which are commonly encountered in commercial process equipment, for example, between about 1 and about 300 p. s. i. g., although usually pressures between about 1 and about 15 p. s. i. g. are sufficient for the present purposes.

The contacting time required in the SO_2 -promoter process is dependent upon the intimacy of contacting with the refining agent of the hydrocarbon material being treated and upon the operating temperature. Ordinarily, the contacting time may be between about 1 and 60 minutes. The operating temperature will, to some extent, affect the intimacy of contacting by determining the liquid viscosities in the refining system and, probably to a more important extent, by determining the rate of interaction of sulfur compounds and other impurities in the feed stock with the refining agent.

Various diluents, countsolvents or co-solvents can be employed in addition to the refining agent. Especially in the case of viscous or relatively high pour point hydrocarbon charging stocks it may be desirable to dilute said charging stocks with diluents or countsolvents such as liquefied propane, butanes, pentanes, hexanes, saturated naphthas or the like. The use of various co-solvents, particularly benzol with liquid sulfur dioxide, is well known and these co-solvents may find application in the process.

It is possible to heat the total extract phase from the process until substantially all the SO_2 has been vaporized off without substantially decomposing the promoter-sulfur compound adduct, if the temperature of the extract phase does not exceed about 50°C . When using BF_3 as the promoter, the free BF_3 , i. e., the BF_3 existing in simple solution in the extract phase, passes off along the gaseous SO_2 . Partial removal of the SO_2 results in the separation of a second raffinate layer and the yield of the second raffinate reaches a maximum when substantially all the SO_2 has been removed. When substantially all the SO_2 has been removed from the first extract phase, the second raffinate consists essentially of all the aromatic hydrocarbons extracted from the feed stock and some sulfur compounds, as evidenced by the sulfur content thereof; and the second extract phase consists sub-

stantially of an adduct of promoter and sulfur compounds. The amount of SO_2 present in the second extract phase may vary from about 1 to about 15 volume percent depending upon the temperature at which the first extract phase was heated in order to remove SO_2 and free BF_3 . The sulfur content of the aromatic hydrocarbon containing second raffinate obtained by this SO_2 removal technique is less than the sulfur content of the total extract materials; and may be in some cases as low as 0.1 weight percent.

When the extract phase is treated so as to remove substantially all the SO_2 , the second extract material appears to consist essentially of organo-sulfur compounds. Treatment of a West Texas heater oil containing 0.6 weight percent sulfur with 2 mols of BF_3 per mol of sulfur dissolved in 25 volume percent of liquid SO_2 , separation of the resultant extract phase, removal of the SO_2 and free BF_3 from the extract phase at about 25°C . gave a second extract material with a sulfur content of 12.1%. The second raffinate consisted of aromatic hydrocarbons and enough organo-sulfur compounds to give a sulfur content of 4%.

The SO_2 -promoter process can be carried out in batch, continuous or semi-continuous operating cycles, and in one or more stages, employing contacting and separation equipment such as has heretofore been employed in the selective solvent refining of petroleum lubricating oil stocks or in effecting the alkylation of isoparaffinic hydrocarbons with olefins in the presence of liquid acid catalysts. It should be understood that the specific equipment forms no part of the present invention and that any equipment adaptable for the purposes of contacting the refining agent with the hydrocarbon charging stock and thereafter separating spent refining agent from the refined charging stock can be employed for the purposes of the invention.

The invention is illustrated by one embodiment shown in the annexed drawing which forms a part of this specification. The feed stock to the process is a heater oil derived by distillation from West Texas crude. This feed boils between 375° and 560°F . and has a mercaptan number of 90. The feed should be H_2S -free and herein the H_2S has been removed by washing with a dilute aqueous caustic solution. Other methods of removing H_2S may be used.

The feed is passed from source 11 by way of line 12 into line 13. The olefins in this illustration are refinery mixed butylenes. The butylenes from source 16 are passed by way of line 17 into line 13. Herein 1 mol of butylenes is added per mol of mercaptans in the feed. The combined streams are passed by way of line 13 into dryer 19.

Dryer 19 may comprise conventional equipment and drying reagents, for example, a vessel packed with calcium chloride, excelsior, fiber glass, magnesium silicate drying agents (Florisil), alumina gel or the like. Drying of the oil can also be effected by distillation, for example, vacuum distillation prior to the addition of a dry butylene stream.

It should be understood that the specific drying treatment forms no part of the present invention and that any drying treatment may be used which substantially eliminates water from the charging stock. The presence of water in the charging stock and in the treating system is extremely undesirable since water combines with BF_3 to form hydrates, which complicates the recovery of BF_3 , and since the corrosive tendencies of the SO_2 -promoter agent tend to increase with increasing water concentration in the refining system.

The dried stream is passed through line 21 into deaeration equipment 22 wherein air dissolved in or entrained in the charging stock is substantially removed. The specific deaeration process and equipment form no part of the present invention. Vacuum deaeration equipment such as is ordinarily employed in commercial proc-

esses of liquid sulfur dioxide refining of hydrocarbon oils can be employed. The deaerated oil is passed through line 23 into heat exchanger 24 wherein the temperature of the stream is adjusted to the desired sweetening temperature.

The temperature of the butylene-feed stream is reduced to -20°C . by means of exchanger 24. The cooled stream is passed by way of line 26 into reactor 27. Reactor 27 herein is a vertical vessel designed to give intimate contacting of a gas and a liquid. Other methods of contacting may be employed.

BF_3 is introduced by way of line 28 into reactor near the point of butylene-feed entry. Herein about 1 mol of BF_3 per gram atom of sulfur present in the feed is employed. The BF_3 -butylene-feed is maintained at about -20°C . in reactor 27 for about 15 minutes.

A substantially sweet oil is withdrawn from the top of reactor 27 and is passed by way of line 29 into heat exchanger 31.

If desired, the viscosity of the oil may be reduced by dilution with a saturated hydrocarbon such as n-pentane, isopentane, n-octane, petroleum ether, methylcyclopentane, cyclohexane or the like. Diluent from source 33 may be introduced by way of valved line 34 into line 29. No diluent is used in this embodiment.

The substantially sweet oil is adjusted to a temperature of -20°C . in exchanger 31 and is then introduced by way of line 36 into the lower portion of extraction tower 37. The extractor may be packed with suitable corrosion-resistant packing materials to increase the efficiency of contacting of the charging stock and refining agents. For example, the extractor can be packed with structural carbon in the form of Berl saddles, glass or porcelain spheres, Monel metal fragments, mild carbon steel jack chain or the like, or may be provided with mechanically- or magnetically-actuated agitators.

In extractor 37 the oil is contacted with liquid sulfur dioxide and BF_3 . If desired the combined reagents may be introduced into the upper portion of extractor 37 from storage drum 38 through line 39. Alternatively, liquid sulfur dioxide alone may be introduced through line 39 and BF_3 may be introduced into the extraction zone from source 41 by way of valved line 42 and manifold 43.

Contacting in extractor 37 is effected at a temperature of -20°C . and at a pressure of about 50 p. s. i. g. The amount of liquid sulfur dioxide introduced into extractor 37 is 70 percent by volume, based on the volume of oil. The amount of BF_3 is 2.5 mols per gram atom of sulfur contained in the oil. Extractor 37 may be operated raffinate-rich or extract-rich; the latter mode of operation is preferred. The contacting time in extractor 37 is about 10 minutes.

The raffinate phase is withdrawn from the upper end of extractor 37 through line 46 into stripping tower 47 which is provided with internal reboiler 48. Stripper 47 may be unpacked or may optionally contain bubble trays, packing materials or other fractionating devices. Relatively small amounts of liquid SO_2 and BF_3 which have been occluded in the raffinate are vaporized in stripper 47 and are withdrawn through line 49 for reuse. Product oil is withdrawn through line 51 to storage not shown.

Further treatment of the product oil may be desired, for example, treatment with concentrated sulfuric acid or with selective solvents, alkali treatment, clay treatment, water washing or other refining treatment. If diluent has been used, this may be removed by distillation.

The extract phase is withdrawn from the lower portion of extractor 37 through line 52 for treatment to separate extract materials and the components of the agent, respectively. Herein the extract phase is passed from line 52 into stripper 53 which is provided with internal reboiler 54. Stripper 53 is similar in construction to stripper 47. The extract phase is subjected to a sufficiently high temperature in stripper 53 to vaporize essentially its entire content of sulfur dioxide and BF_3 . Such tempera-

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tures fall within the range of about 50° C. to about 250° C. Sufficient pressure must be maintained in stripper 53 to prevent vaporization of the lower boiling portions of the extract. The sulfur dioxide and BF₃ are passed overhead from stripper 53 by way of line 56.

Stripped extract is withdrawn from stripper 53 and is passed to storage not shown by way of line 58. A portion of the extract may be recycled by way of valved line 59 to a lower point of extractor 37 as a reflux stream.

The SO₂ and BF₃ are passed from line 56 through valved line 61 and line 62 into purification zone 63. Here non-condensable gases, H₂S, etc. are removed by means well known to the liquid SO₂ extraction art. The purified SO₂ and BF₃ are passed into line 66 where they meet the material from line 49 and the combined stream is passed by way of condenser 67 and line 68 in storage drum 38.

Makeup SO₂ from source 71 is passed by line 72 into storage drum 38.

When the stream in line 56 contains little or no H₂S, the purification zone may be by-passed and the SO₂ and BF₃ passed by way of valved line 74 directly to line 66.

It is desirable from time to time to dehydrate at least a portion of the stream passing through line 56. A part of this stream is passed by way of valved line 76 into dehydrator 77 which is provided with internal reboiler 78. Dehydrated SO₂ and BF₃ are withdrawn overhead through line 81 and are passed by way of line 62 to purification zone 63. A liquid bottoms fraction comprising water, sulfur dioxide and BF₃ hydrates is withdrawn from the lower portion of dehydrator 77 by way of line 83 for discharge from the system.

Some BF₃ and some gaseous SO₂ are withdrawn from drum 38 and are passed through line 86 in gas-liquid separator 87. BF₃, free of SO₂, is passed from separator by way of lines 88 and 28 to reactor 27. Liquid SO₂ is passed from separator 87 by way of line 89 back to drum 38.

Makeup BF₃ may be introduced from source 41 by way of valved line 91 into line 28 and/or by way of valved line 92 in line 39.

The extract may be subjected to various refining operations. For example, it can be given a catalytic hydrofining treatment, employing a conventional catalyst, e. g., cobalt molybdate, and conventional operating conditions. The extract is a surprisingly good feed to a catalytic cracking operation; a high yield of very high octane gasoline is obtained, which gasoline has the remarkably low sulfur content of less than 0.1 weight percent.

Numerous pumps, valves, heat exchangers and other engineering details have been omitted from the combined operation in the interests of simplifying the description. Common engineering process expedients, particularly those which have heretofore been employed in processes of refining hydrocarbon oils with liquid sulfur dioxide will readily suggest themselves to those skilled in the art; it is to be understood that such engineering expedients are within the purview of the present invention.

The results obtainable with the process of this invention are illustrated by the following comparative experiments. The charging stock used in all the experiments below was a West Texas virgin heater oil distillate, characterized as follows:

°API	40
Sulfur (total), wt. percent	0.56
Mercaptan number	57.1
Color, Saybolt	16
Free sulfur	None

ASTM Distillation, °F.:

Initial	332
10%	390
50%	446
90%	502
Max.	565

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The extraction procedure consisted of adding liquid sulfur dioxide to oil contained in a reactor provided with a cooling jacket and mechanical agitator. The temperature of the reactor contents was maintained at -20° C.

When used, BF₃ was metered into the reactor and the reactor was closed. At this point a pressure of from 10 to 100 p. s. i. g., due largely to BF₃, prevailed in the reactor, but when agitation was started, the pressure fell rapidly to about 0 p. s. i. g. Agitation was continued for 20 minutes at -20° C. followed by a 30-minute settling period to furnish ample time for the extract and raffinate phases to separate. The extract phase was drawn off at the bottom of the reactor and the raffinate phase was washed with water and then with 10% caustic. Finally the raffinate was again washed with water and dried.

Run 1

In this run the feed was contacted with liquid SO₂ alone (50 volume percent of liquid SO₂). The oil from the raffinate phase was sour to the doctor test. About one-half of the mercaptans has been removed by the extraction. A reverse doctor test indicated that the product oil contained no free-sulfur.

Run 2

In this run 400 ml. of sour oil, 200 ml. of liquid SO₂ and 8.0 g. of BF₃ were charged to the reactor. The product oil had a total sulfur content of 0.17 weight percent (69% reduction in sulfur content) and was sweet to the doctor test. However, the product oil had a free-sulfur content of 14 milligrams per 100 ml. of oil.

Run 3

The conditions of this run were identical with those of Run 2 except that 40 g. of diisobutylene were also added to the reactor. The product oil had a total sulfur content of 0.08 weight percent (86% reduction in sulfur content) and was doctor sweet. The free-sulfur content was 4 mg. per 100 ml. of oil.

Run 4

In the first step, 400 ml. of sour oil, 8.5 g. of BF₃ and 21.0 g. of propylene were charged to the reactor. The contents were agitated at -20° C. for 1 hour. A sample was withdrawn and tested for mercaptan content; the oil was doctor sweet.

In the second step, 200 ml. of liquid SO₂ was added to the reactor containing the sweet oil, BF₃ and some propylene. The contents were treated according to the extraction procedure above. The product oil was doctor sweet and contained no free-sulfur, as determined by the reverse doctor test.

These runs show that the presence of free-sulfur can be avoided if the mercaptan containing oil is first rendered substantially doctor sweet prior to treatment with liquid SO₂-BF₃ agent.

Thus having described the invention, what is claimed is:

1. A process for refining a mercaptan-containing hydrocarbon oil, which process comprises (1) contacting said oil with at least an effective amount of an olefinic hydrocarbon, in the presence of at least a catalytic amount of a Friedel-Crafts-type halide, for a time at least sufficient to render said oil substantially mercaptan-free, (2) contacting said substantially mercaptan-free oil with an agent consisting essentially of liquid SO₂ and a promoter, wherein the liquid SO₂ is present in an amount at least sufficient to form an extract phase and the promoter is selected from the class of Friedel-Crafts halides consisting of AlCl₃, FeCl₃, TiCl₄, BF₃, HgCl₂, BCl₃ and ZnCl₂ at a temperature below about +10° C. and (3) separating a refined raffinate containing essentially no free-sulfur from an extract phase.

2. The process of claim 1 wherein at least about 1 mol of olefin is present per mol of mercaptan in said oil.

3. The process of claim 1 wherein said mercaptan

elimination process is carried out at a temperature below about $+50^{\circ}\text{C}$.

4. The process of claim 3 wherein said olefin is propylene.

5. The process of claim 1 wherein said olefin is diisobutylene.

6. The process of claim 1 wherein said olefin is a butylene.

7. The process of claim 1 wherein said catalyst is BF_3 .

8. The process of claim 1 wherein said catalyst is AlCl_3 .

9. The process of claim 1 wherein said catalyst is FeCl_3 .

10. A process for refining a hydrocarbon oil containing mercaptans and other organo-sulfur compounds, which process comprises (1) contacting said oil with at least about 1 mol of olefinic hydrocarbons per mol of mercaptan in said oil, in the presence of at least a catalytic amount of a Friedel-Crafts halide selected from the class consisting of AlCl_3 , FeCl_3 , TiCl_4 , BF_3 , HgCl_2 , BCl_3 and ZnCl_2 , at a temperature between about -60° and $+50^{\circ}\text{C}$. for a time sufficient to render said oil substantially odor sweet, (2) contacting the substantially sweet oil from step (1) with an agent consisting essentially of liquid SO_2 , in an amount between about 15 and 200 volume percent based on oil, and a promoter selected from the class of Friedel-Crafts halides consisting of AlCl_3 , FeCl_3 , TiCl_4 , BF_3 , HgCl_2 , BCl_3 and ZnCl_2 , in an amount between about 0.5 and 5 mols per gram atom of sulfur in the oil, at a temperature between about -10° and -40°C ., (3) separating a raffinate phase from an extract phase, and (4) recovering a product oil markedly reduced in organo-sulfur compound content and containing essentially no free-sulfur as measured by the reverse doctor test from said raffinate phase.

11. The process of claim 10 wherein said hydrocarbon oil is a petroleum distillate boiling in the heavier-than-gasoline range.

12. The process of claim 10 wherein said promoter is BF_3 and the BF_3 is present in an amount between about 1 and 3 mols per gram atom of sulfur in the oil.

13. The process of claim 10 wherein the oil from step (1) has a mercaptan number below about 5.

14. The process of claim 10 wherein said catalyst is present in an amount of about 1 mol per mol of mercaptan.

15. The process of claim 10 wherein the temperature of step (1) is substantially the same as the temperature in step (2).

16. The process of claim 10 where the catalyst of step (1) is the promoter of step (2).

17. The process of claim 16 wherein the promoter is BF_3 .

18. A process for refining a sour petroleum distillate boiling in the heavier-than-gasoline range which also contains other organo-sulfur compounds, which process comprises (1) contacting said distillate with at least 1 mol of a lower molecular weight olefin per mol of mercaptans in said distillate, in the presence of between about 1 and 3 mols of BF_3 per gram atom of sulfur in said distillate, at a temperature between about -10° and -40°C . for a time sufficient to reduce the mercaptan number of said distillate to below about 5, (2) contacting the substantially sweet oil with between about 25 and 75 volume percent, based on said oil, of liquid SO_2 and between about 1 and 3 mols of BF_3 per gram atom of sulfur in said oil, at a temperature between about -10° and -40°C . for a time sufficient to effect a substantial amount of desulfurization, (3) separating a raffinate phase from an extract phase, and (4) recovering from said raffinate phase a sweet oil containing essentially no free-sulfur.

19. The process of claim 18 wherein said olefin is propylene.

20. The process of claim 18 wherein said olefin is diisobutylene.

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