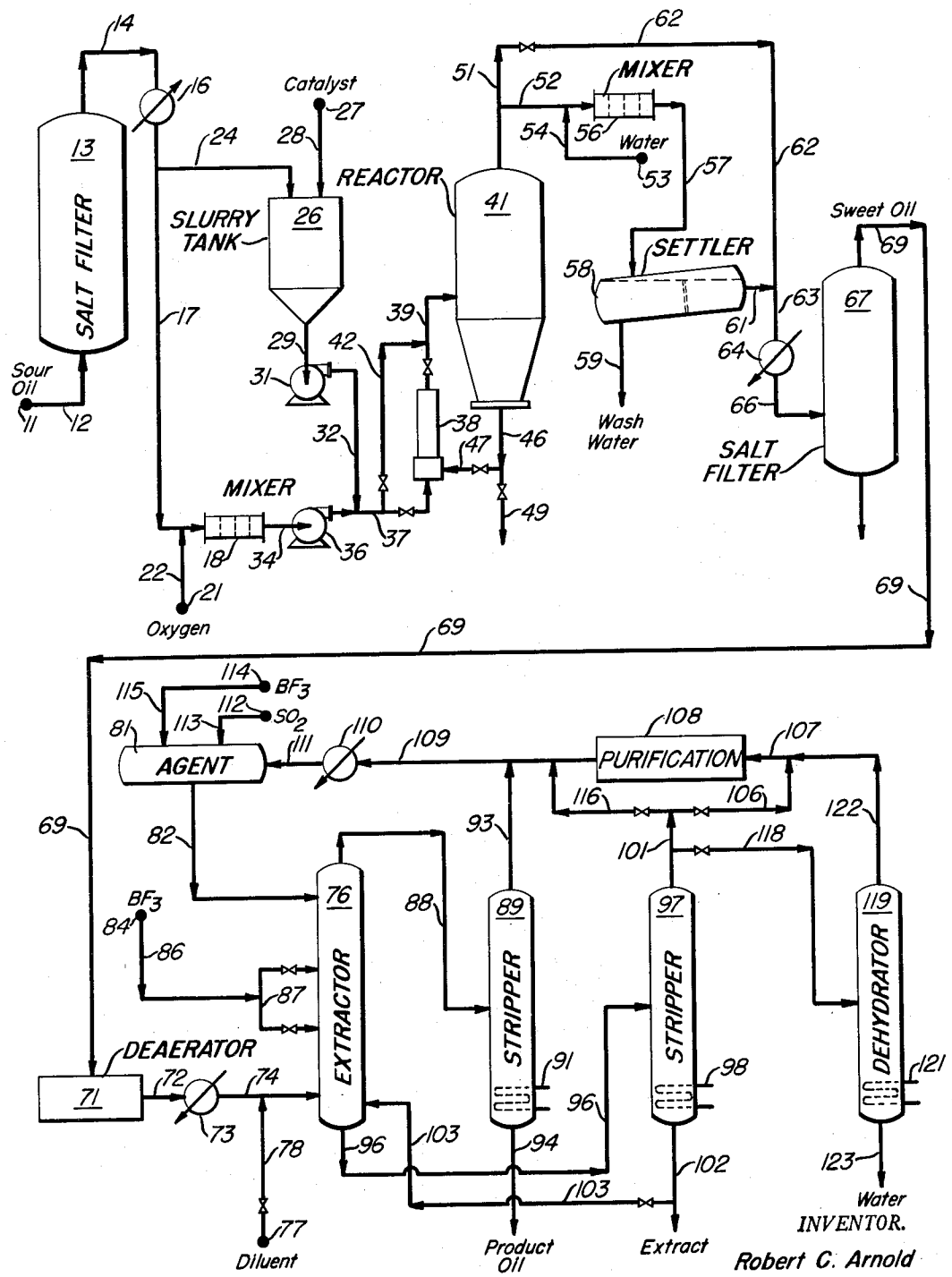
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DESULFURIZATION PROCESS USING ALKALI FOLLOWED BY EXTRACTION WITH LIQUID SULFUR DIOXIDE AND A PROMOTER

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DESULFURIZATION PROCESS USING ALKALI FOLLOWED BY EXTRACTION WITH LIQUID SULFUR DIOXIDE AND A PROMOTER

Robert C. Arnold, Park Forest, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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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 oil distillates boiling in the heavier-than-gasoline range.

Patent application Serial Number 248,898, filed September 29, 1951, now Patent No. 2,671,047, entitled "Refining Hydrocarbon Materials with SO_2 and BF_3" 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 essentially of liquid SO_2 and BF_3. This process gives a markedly greater amount of desulfurization than does an equivalent amount of liquid SO_2 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 elemental sulfur. The elemental sulfur is present in the raffinate oil even though none had been present in the sour oil feed to the process. The presence of elemental 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 to produce a product oil of low organo-sulfur compound content and also essentially free of elemental sulfur. These and other objects of the invention will become apparent from the following description.

It has been discovered that elemental sulfur is not present in the product of the treatment of hydrocarbon material containing organo-sulfur compounds with an agent consisting essentially of liquid SO_2 and a promoter selected from the class of Lewis acids (Friedel-Crafts halides) when the hydrocarbon oil is treated to substantially eliminate mercaptans prior to undergoing the liquid SO_2-promoter treatment. Thus the process of this invention comprises (1) treating a hydrocarbon material containing mercaptans and other organo-sulfur compounds to substantially eliminate the mercaptans, either by physical removal or conversion to the corresponding disulfides. (2) Contacting said substantially mercaptan-free oil with an agent consisting essentially of liquid SO_2 and 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 $ZnCl_2$. At least enough liquid SO_2 is present in the agent to exceed the solubility of liquid SO_2 in the oil undergoing treatment. The temperature of the treatment is below about 10° C. (3) A raffinate oil of markedly lower organo-sulfur compound content and essentially free of elemental sulfur is separated from an extract phase comprising agent, sulfur compounds and extract hydrocarbons.

The SO_2-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 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.

Any method which produces a substantially sweet oil may be utilized in the process of this invention. Although the mechanism is not understood, the mercaptans present in the feed oil appear to be the cause of the formation of elemental sulfur in the SO_2-promoter process. A product oil that is free of elemental sulfur can be obtained if the mercaptans are eliminated from the oil.

Any conventional process for the physical removal of mercaptans may be utilized, e. g., the sour oil may be contacted with an aqueous caustic-organic solvent solution. The organic solvent may be a monohydric alcohol such as methanol or ethanol; a dihydric alcohol such as ethylene glycol; or a dihydric alcohol containing ether linkages such as diethylene glycol or triethylene glycol. Other organic solvents such as water-soluble aliphatic amines or alkanolamines may be used. The various solutizer processes may be used. In these processes the solution consists of aqueous caustic and a solubility promoter such as phenolic compounds, lower molecular weight fatty acids, wood tar oils, and tannins.

Any conventional process for the conversion of the mercaptans to the corresponding disulfides wherein the disulfides are dissolved in the oil may be used. Examples of these processes are: Contacting the sour oil with concentrated aqueous caustic solution in the presence of free-oxygen. Contacting the sour oil with aqueous caustic solution, free-oxygen and catalysts for the oxidation of mercaptans such as hydroquinone, pyrogallol,

tannin, petroleum phenols, etc. Contacting the sour oil with concentrated aqueous caustic solution and free-oxygen in the presence of active copper catalysts such as $CuSO_4$ and $CuCl_2$.

The most widely used processes for sweetening sour oils by the conversion of mercaptans to disulfides are the doctor process and the copper chloride process. In the doctor process the sour oil is contacted with an aqueous caustic solution containing dissolved litharge and free-oxygen in the presence of elemental sulfur. In the copper chloride process the sour oil is contacted with free-oxygen in the presence of a catalyst mass consisting essentially of copper chloride, water and an inert support.

It is to be understood that any process which results in the production of a substantially sweet oil may be utilized and the process of this invention is not limited to the processes listed above.

In general, the proportion of liquid sulfur dioxide used varies depending upon 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 elemental 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 in 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° 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, countersolvents or co-solvents can be employed in the present process in addition to the refining agent. Especially in the case of viscous or relative high pour point hydrocarbon charging stocks it may be desirable to dilute said charging stocks with diluents or countersolvents 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 with 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 substantially 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 employed 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. Numerous pumps, valves and other items of equipment have been omitted from this embodiment since these items may be readily added thereto by those skilled in the art.

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. Since this feed is to be sweetened by the copper chloride process, it should be H_2S-free. The H_2S has been removed by washing with a dilute aqueous caustic solution. Other methods of removing H_2S may be used. (Some sweetening methods do not require removal of the H_2S).

Caustic reacts with the copper catalyst and deactivates it. Therefore, it is necessary to remove any caustic which may be present in the feed. The sour oil feed in this illustration is passed from source **11** through line **12** into salt filter **13**. Salt filter **13** consists of a cylindrical vessel filled with crushed rock salt. The rock salt removes any aqueous caustic that may be occluded in the feed. Instead of using a salt drum, a vessel filled with steel wool, gravel, sand or other coalescing medium may be used.

The feed is passed out of salt filter **13**, through line **14**, into heat exchanger **16**. In heat exchanger **16** the temperature of the sour oil is raised to about 80° F. In general, the temperature of operation should be between about 60° and 100° F. From heat exchanger **16** the sour oil is passed by way of line **17** into mixer **18**. Mixer **18** may be any form of agitating device. In this case mixer **18** is provided with knothole orifice plates. Free-oxygen from source **21** is passed through line **22** into line **17** where it meets the main stream of sour oil. The free-oxygen and the sour oil are thoroughly intermingled in mixer **18**.

Theoretically, the amount of free-oxygen needed in the process to insure substantially complete regeneration of the catalyst is 1 mol for each 4 mols of mercaptan present. However, normally a 100 or 200% excess is desirable.

A side stream of the sour oil is withdrawn from line **17** by way of line **24** and is passed into slurry tank **26**. Slurry tank **26** is a cone-bottomed vessel provided with an agitator not shown. Fresh catalyst from source **27**

is added by way of line **28** to slurry tank **26**. The slurry of catalyst and oil is passed from tank **26** through line **29** by way of pump **31** into line **32**. The main stream of sour oil is passed from mixer **18** by way of line **34** and pump **36** into line **37** where it meets the makeup catalyst slurry from line **32**.

The catalyst comprises $CuCl_2$, water and a carrier. The carrier consists essentially of a finely powdered mixture, having a screen size of less than about 80 mesh of fuller's earth. Adsorbed on the carrier is an aqueous solution of $CuCl_2$. Based on the total catalyst, the catalyst should contain between about 5 and 30 weight percent of water and between about 1 and 25 weight percent of $CuCl_2$. (However, the $CuCl_2$ may be made by reacting in aqueous solution cupric sulfate and sodium chloride or ammonium chloride. When forming the $CuCl_2$ by this reaction, it is preferred to use a small excess of the chloride salt.)

The sour oil-oxygen-catalyst dispersion in line **37** is passed into eductor **38** and from eductor **38** it is passed through line **39** into reactor **41**. In some cases the eductor may be by-passed and the dispersion passed into line **39** by way of by-pass line **42**. In reactor **41** the sour oil and the catalyst are maintained in the dispersed condition until the oil is substantially sweet.

Reactor **41** has a conical shaped lower portion into which the catalyst settles. The dense slurry of catalyst and oil is withdrawn from the bottom of reactor **41** through line **46** and is passed into eductor **38** by way of line **47**. In eductor **38** the recycle catalyst meets the stream of sour oil and makeup catalyst. When the catalyst has become substantially inactive, catalyst is sent to recovery by way of lines **46** and **49**.

The substantially sweet oil contains a very slight amount of catalyst. The oil is withdrawn from reactor **41** through line **51** and is passed into line **52** where it meets water from source **53** and line **54**. The amount of wash water used is dependent upon the amount of catalyst carried over from the reactor. In general, the amount of wash water may be between about 10 and 100 volume percent based on oil. The mixed stream of water and oil is passed into mixer **56**. From mixer **56** the stream of oil and water is passed by way of line **57** into settler **58**. The wash water separates in settler **58** and is sent to a sewer by way of line **59**. The washed oil from settler **58** is passed into line **61**. In some cases the washing operation is not necessary and the operation may be by-passed by way of lines **51** and **62**.

The washed oil from line **61** is passed through line **63**, through cooler **64** and line **66** into salt filter **67**. Cooler **64** lowers the temperature of the washed oil in order to reduce the amount of water dissolved in the oil, and salt filter **67** dehydrates the washed oil. Brine from vessel **67** is passed to the sewer by way of line **68**. Salt filter **67** is similar in construction to salt filter **13**.

Dehydrator **67** may comprise other 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.

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 oil is passed through line **69** into deaeration equipment **71** 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 processes of liquid sulfur dioxide refining of hydrocarbon oils can be employed. The deaerated oil is passed through line 72 into heat exchanger 73 wherein the temperature of the stock is lowered to the desired treating temperature.

The oil thus pretreated is introduced by way of line 74 into the lower portion of extraction tower 76. The extraction tower 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 extraction tower 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.

If desired, the viscosity of the hydrocarbon charging stock 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 77 may be introduced by way of valved line 78 into line 74.

In extractor 76 the oil is contacted with liquid sulfur dioxide and BF_3. If desired the combined reagents may be introduced into the upper portion of tower 76 from storage drum 81 through line 82. Alternatively, liquid sulfur dioxide alone may be introduced through line 82 and BF_3 may be introduced into the extraction zone from source 84 by way of line 86 and manifold 87.

Contacting in extractor 76 is effected at a temperature of −10° C. and at a pressure of about 50 p. s. i. g. The amount of liquid sulfur dioxide introduced into extractor 76 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. Tower 76 may be operated raffinate-rich or extract-rich; the latter mode of operation is preferred. The contacting time in extractor 76 is about 5 minutes.

The raffinate phase is withdrawn from the upper end of extractor 76 through line 88 into stripping tower 89 which is provided with internal reboiler 91. Stripper 89 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 89 and are withdrawn through line 93 for reuse. Product oil is withdrawn through line 94 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 76 through line 96 for treatment to separate extract materials and the components of the agent, respectively. Herein the extract phase is passed from line 96 into stripper 97 which is provided with internal reboiler 98. Stripper 97 is similar in construction to stripper 89. The extract phase is subjected to a sufficiently high temperature in stripper 97 to vaporize essentially its entire content of sulfur dioxide and BF_3. Such temperatures fall within the range of about 50° C. to about 250° C. Sufficient pressure must be maintained in stripper 97 to prevent vaporization of the lower boiling portions of the extract. The sulfur dioxide and BF_3 are passed overhead from stripper 97 by way of line 101.

Stripped extract is withdrawn from stripper 97 and is passed to storage not shown by way of line 102. A portion of the extract may be recycled by way of valved line 103 to a lower point of extractor 76 as a reflux stream.

The SO_2 and BF_3 are passed from line 101 through valved line 106 and line 107 into purification zone 108. Here non-condensible gases, H_2S, etc. are removed by means well known to the liquid SO_2 extraction art. The purified SO_2 and BF_3 are passed into line 109 where they meet the material from line 93 and the combined stream is passed by way of condenser 110 and line 111 in storage drum 81.

Makeup SO_2 from source 112 is passed by line 113 and makeup BF_3 from source 114 is passed by line 115 into storage drum 81.

When the stream in line 101 contains little or no H_2S, the purification zone may be by-passed and the SO_2 and BF_3 passed by way of valved line 116 directly to line 109.

It is desirable from time to time to dehydrate at least a portion of the stream passing through line 101. A part of this stream is passed by way of valved line 118 into dehydrator 119 which is provided with internal reboiler 121. Dehydrated SO_2 and BF_3 are withdrawn overhead through line 122 and are passed by way of line 107 to purification zone 108. A liquid bottoms fraction comprising water, sulfur dioxide and BF_3 hydrates is withdrawn from the lower portion of dehydrator 119 by way of line 123 for discharge from the system.

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 SO_2—BF_3 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	0.62
Mercaptan Number	48.1
Color, Saybolt	16
Color, aged, Saybolt	12
ASTM distillation, °F.:	
Initial	332
10%	390
50%	446
90%	502
Max.	565

The aged color is a measure of the storage stability of an oil. The aged color is determined by exposing 100 ml. of the oil to the atmosphere in an open beaker for 20 hours at a temperature of 200° F. The color of the oil at the end of the exposure is the "aged color."

The extraction procedure consisted of adding 375 ml. of liquid sulfur dioxide to 750 ml. of 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, 1.7 mols of BF_3 per gram atom of sulfur in the oil were 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 BF_3, 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 SO_2 alone. 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 the feed was contacted with liquid SO_2-BF_3 agent. The product oil was sweet to the doctor test. However, the reverse doctor test indicated that free-sulfur was present.

Run 3

In this run the feed was contacted at 120° F. with a 50% aqueous KOH solution (2% based on feed) and air until the mercaptan number of the oil had been reduced to 4.8. The Saybolt color of the substantially sweet oil was −4; the aged oil was a tan color falling in the lower value of the ASTM-Union scale. No change had taken place in the total sulfur content and the oil contained no free-sulfur.

Run 4

The substantially sweet oil from Run 3 was treated with liquid SO_2 alone. An 88 volume percent yield of product oil was obtained. The product oil contained 0.36 weight percent sulfur (41% reduction in sulfur content). The Saybolt color was 17 and the aged color was 9. The product oil was sour and contained no free-sulfur.

Run 5

The substantially sweet oil from Run 3 was treated with liquid SO_2—BF_3 agent. An 86% yield of product oil was obtained. The product oil contained 0.11 weight percent sulfur (82% reduction in sulfur content). The Saybolt color was 25 and the aged color was 21. The product oil was sweet and contained no free-sulfur.

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 SO_2—BF_3 agent. Further, the runs show that a remarkable improvement in color stability is obtained by treating an aqueous caustic-air sweetened oil with liquid SO_2—BF_3 agent as compared with treating said oil with liquid SO_2 alone.

Thus having described the invention, what is claimed is:

1. A process for refining a mercaptan-containing hydrocarbon oil, which process comprises (1) treating said oil to substantially eliminate the mercaptans therefrom, (2) contacting said substantially mercaptan-free oil with an agent consisting essentially of liquid SO_2 and a promotor, wherein the liquid SO_2 is present in an amount at least sufficient to form an extract phase and the promoter is selected from the class of Friedel-Crafts metal halides consisting of $AlCl_3$, $FeCl_3$, $TiCl_4$, BF_3, $HgCl_2$, BCl_3 and $ZnCl_2$ 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 said mercaptan elimination process comprises contacting said oil with a catalyst comprising $CuCl_2$ in the presence of free-oxygen.

3. The process of claim 1 wherein said mercaptan elimination process comprises contacting said oil with a catalytic amount of an aqueous caustic solution in the presence of free-oxygen.

4. The process of claim 3 wherein said contacting is carried out in the presence of a mercaptan oxidation catalyst.

5. The process of claim 1 wherein said mercaptan elimination process comprises the doctor process.

6. The process of claim 1 wherein the mercaptan elimination process comprises contacting said oil with a reagent solution comprising aqueous caustic and methanol and separating a substantially mercaptan-free oil from a mercaptide-reagent solution phase.

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

8. The process of claim 1 wherein said promoter is $AlCl_3$.

9. The process of claim 1 wherein said promoter is $FeCl_3$.

10. A process for refining a hydrocarbon oil containing mercaptans and other organo-sulfur compounds, which process comprises (1) treating said hydrocarbon oil by a process that produces a substantially mercaptan-free and elemental sulfur-free oil, (2) contacting the 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 metal 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. A process for refining a high organo-sulfur compound containing sour petroleum distillates boiling in the heavier-than-gasoline range, which process comprises (1) contacting said distillate with a catalytic amount of an aqueous caustic solution in the presence of free-oxygen under conditions to reduce the mercaptan number of said distillate to below about 5, (2) separating the substantially sweet distillate from the aqueous caustic solution, (3) contacting, under substantially anhydrous conditions, said substantially sweet distillate with between about 25 and 75 volume percent, based on said distillate, of liquid SO_2 and 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., (4) separating a raffinate phase from an extract phase, and (5) recovering from said raffinate phase a sweet oil containing essentially no free-sulfur.

15. The process of claim 14 wherein said petroleum distillate is a heater oil boiling between about 330° and 575° F.

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