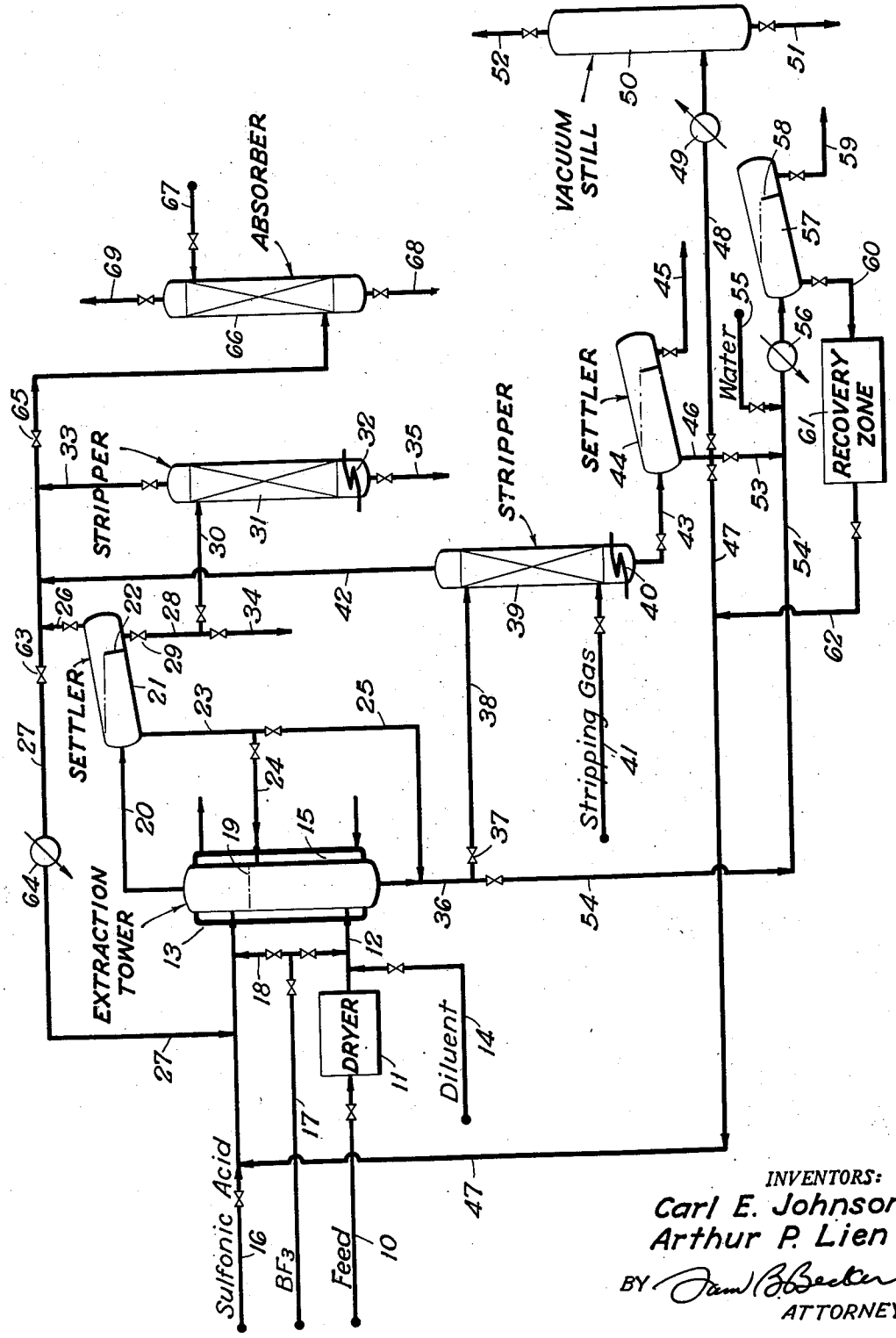
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PROCESS FOR DESULFURIZING HYDROCARBONS USING A MIXTURE OF BORON TRIFLUORIDE AND AN ALKANE SULFONIC ACID AS REAGENT

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PROCESS FOR DESULFURIZING HYDROCARBONS USING A MIXTURE OF BORON TRIFLUORIDE AND AN ALKANE SULFONIC ACID AS REAGENT

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This invention relates to a process for refining organic materials containing one or more undesired impurities, such as coloring matter, malodorous materials and sulfur or sulfur compounds. More particularly, this invention is concerned with a process for refining, and especially for desulfurizing, hydrocarbon materials such as sulfur-containing hydrocarbon oils, e. g. petroleum oil fractions.

One object of the present invention is to provide a process for refining and desulfurizing hydrocarbon materials containing sulfur and/or organic sulfur compounds. Another object of our invention is to provide a process for substantially deodorizing "sour" or mercaptan-containing hydrocarbon materials. An additional object is to provide a process for decolorizing hydrocarbon materials, particularly hydrocarbon oils. Still another object of our invention is to provide novel mixtures of chemical compounds characterized by a remarkably specific and selective interaction with organic sulfur compounds. These and other objects of our invention will become apparent from the ensuing description thereof.

The problems of refining hydrocarbon materials, particularly of decolorizing, deodorizing and desulfurizing said materials, have assumed increasing importance in the petroleum, coal derivatives and synthetic fuels industries. Attempts have heretofore been made to utilize the refining properties of BF_3 alone and in combination with various complex compounds of BF_3 with oxygenated organic compounds, such as ethers, esters and carboxylic acids, as set forth in U. S. Patent 2,495,851 of Arthur P. Lien and Bernard L. Evering, issued January 31, 1950. Although free BF_3 in combination with various oxygenated organic compounds has substantial utility for desulfurizing hydrocarbon oils, both the extent of desulfurization and selectivity of these combination solvents heretofore known has left something to be desired.

Briefly, we have made the surprising discovery that mixtures of BF_3 and certain organic sulfonic acids, particularly certain hydrocarbon sulfonic acids, exhibit a remarkable refining capacity for hydrocarbon materials containing sulfur or organic sulfur compounds and/or coloring impurities and/or odoriferous materials, particularly mercaptans. Especially remarkable is the ability of mixtures of BF_3 and certain hydrocarbon sulfonic acids to combine selectively with organic sulfur compounds contained in hydrocarbon oils, thereby producing

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solutions of said sulfur compounds in the BF_3-hydrocarbon sulfonic acid mixtures, which solutions are substantially insoluble in the resultant refined hydrocarbon oils at moderate or low temperatures. While the mixtures of BF_3 and certain hydrocarbon sulfonic acids combine with organic sulfur compounds they do not either substantially dissolve or chemically unite with aromatic hydrocarbons or saturated hydrocarbons contained in hydrocarbon oils.

In one particularly desirable aspect, our invention comprises contacting a hydrocarbon oil which is to be refined with a liquid mixture of BF_3 and a sulfonic acid, said mixture being present in an amount sufficient to form a distinct liquid phase upon settling, and thereafter effecting stratification of the contacting mixture into a liquid layer comprising predominantly refined hydrocarbon oil and a second, immiscible layer comprising predominantly a solution or chemical combination of BF_3, sulfonic acid and impurities derived from the hydrocarbon oil charging stock.

To consider the invention in greater detail, the novel refining agent, as has been indicated generally above, comprises certain organic sulfonic acids. Suitable organic sulfonic acids may contain between 1 and 10 carbon atoms, inclusive, in the molecule. We have found hydrocarbon sulfonic acids such as alkanesulfonic acids to be particularly desirable. Although alkanesulfonic acids containing 1 to 10 carbon atoms may be applied for the purposes of our invention, we prefer to employ those acids containing 1 to 5 carbon atoms, inclusive, and more especially 1 to 3 carbon atoms, inclusive, per molecule by reason of their highly selective combination with the organic sulfur compounds contained in hydrocarbon materials, particularly in petroleum oil fractions. Thus, we may employ, in addition to BF_3, alkanesulfonic acids such as methane-, ethane-, propane-, butane-, pentane-, hexane-sulfonic acids and the like. Particularly, we may employ alkanesulfonic acids prepared by nitrogen oxide-catalyzed air oxidation of alkyl disulfides, e. g., as described in U. S. Patent 2,433,395 of Wayne A. Proell et al., patented December 30, 1947, the analyses of which as commercially produced and the properties of which are described by W. A. Proell et al. in a publication in Ind. Eng. Chem. 40, 1129–1132, (June, 1948). It should be understood, however, that we are not limited to the employment of organic sulfonic acids produced by any particular process.

Saturated hydrocarbon sulfonic acids, containing also chloroalkane sulfonic acids or chlorocycloalkanesulfonic acids, can be produced by the so-called Reed Process, which involves treatment of a paraffinic or cycloparaffinic hydrocarbon with mixtures of SO_2 and Cl_2 under ultraviolet irradiation to produce saturated hydrocarbon sulfonyl chlorides, which can be converted to the corresponding sulfonic acids. The Reed Process-derived sulfonic acids may be employed for the purposes of our invention.

We may also employ aromatic-substituted alkanesulfonic acids such as benzylsulfonic, alpha-phenethylsulfonic, beta-phenethylsulfonic, 3-phenylpropanesulfonic acids, and the like. Aromatic sulfonic acids such as benzenesulfonic, toluenesulfonic, xylylsulfonic, ethylbenzenesulfonic, chlorobenzenesulfonic and cumenesulfonic acids also come within the purview of the present invention.

The sulfonic acids which we employ may contain small proportions, between about 0.1 and about 5 percent by weight, of sufuric acid. The sulfonic acids should be substantially anhydrous for the purposes of the present invention, i. e., they should not contain more than about 8 percent by weight of water.

The molar ratio of sulfonic acid to BF_3 in the liquid refining mixtures may vary from about ½ to about 20. Usually we prefer to maintain a molar excess of sulfonic acid with relation to BF_3, viz., to use more than 1 but not more than about 10 mols, preferably about 3 to about 8 mols of sulfonic acid, such as a C_1–C_3 alkanesulfonic acid, per mol of BF_3. We have noted that mixtures of BF_3 and alkanesulfonic acids containing a molar excess of the latter exhibit considerably lower vapor pressures than mixtures in which free or excess BF_3 is present.

Although we have referred to "mixtures" of BF_3 and hydrocarbon sulfonic acids, there is reason to believe that actually chemical compounds or complexes can be formed upon absorption of BF_3 in these acids. For example, measurements of the absorption of BF_3 in methanesulfonic acid at 30° C. indicate the formation of the complex compound $BF_3.2CH_3SO_3H$. Aromatic sulfonic acids exhibit a decreased tendency to form BF_3 complexes in the absence of sulfur compounds such as mercaptans, thioethers, etc., but in the presence of the latter, complexes containing BF_3, aromatic sulfonic acid and probably a sulfur compound such as a thioether or the like appear to be readily formed.

The BF_3-organic sulfonic treating agent is usually employed in proportions between about 5 and about 200 percent by volume, based on the volume of the hydrocarbon material which is employed as the charging stock. The minimum proportion of the refining agent is determined by the minimum amount required in a specific instance to exceed its solubility in the hydrocarbon material being treated; that is to say, the minimum amount of refining agent should be at least sufficient under the treating conditions to form a distinct liquid phase in a quiescent system. The maximum proportion of refining agent will depend upon the extent of refining desired to be effected and, to some extent, by the other conditions of treatment, for example, intimacy of contacting, temperature and time. In refining processes primarily conducted for the desulfurization of hydrocarbon oils, it is desirable to use a sufficient proportion of the combination refining agent to obtain a molar ratio of BF_3 to the organic sulfur compounds in the oil of at least about 0.5, and preferably one or even more when thoroughgoing desulfurization is desired.

Although certain sulfonic acids which may be employed for the purposes of the present invention are solid or semi-solid materials at room temperature or the desired refining temperatures, we have noted that the addition of BF_3 thereto lowers their melting or solidification points and readily permits their use for the purposes of the present invention. Moreover, the absorption of sulfur compounds and other impurities from a hydrocarbon oil by the BF_3-organic sulfonic acid refining agent serves further to reduce its softening or solidification point. If desired, a slurry of the organic sulfonic acid in a saturated hydrocarbon diluent may be employed for the purposes of this invention and combined with BF_3 prior to the refining operation to produce at least partial liquefaction. A slurry of organic sulfonic acid in a saturated hydrocarbon diluent can be contacted simultaneously with the hydrocarbon material to be refined and with BF_3.

The present refining process may be conducted at temperatures within the range of about −30 to about 120° C. For reasons of economy, efficiency and convenience, however, we usually prefer to employ temperatures between about 10° C. and about 60° C.

The present refining process is ordinarily conducted under pressure sufficient at least to maintain the BF_3-organic sulfonic acid refining agent substantially in the liquid phase, although it should be understood that the present process may, if desired, be conducted under such conditions that a substantial partial pressure of BF_3 exists in the vapor phase of the refining zone. We should like to point out, however, that one of the principal advantages of the present refining agent and process, in comparison with prior art processes which have utilized BF_3 or BF_3 in combination with BF_3-organic compound complexes, is that the present process can be operated very effectively even at atmospheric pressure, with little or no partial BF_3 pressure in the vapor space of the refining zone. Thus, when at least about 1 mol, preferably at least about 2 mols, of organic sulfonic acid is employed per mol of BF_3 in the refining agent, the refining agent is characterized by a relatively low partial pressure of free BF_3 in the vapor phase in equilibrium with the liquid phase, at moderate temperatures. In general, the present process permits the utilization of pressures which are common in the design of commercial process equipment, for example, between about 15 and about 500 p. s. i. g., although, more usually, process equipment for use in connection with this invention will be designed for operating pressures in the range of about 15 to about 100 p. s. i. g.

The time period required in the present refining process will be dependent, naturally, upon the intimacy of contacting with the refining agent of the hydrocarbon material being treated and upon the operating temperature. Ordinarily, the time period is selected between about ½ and about 30 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. Although the present process has been referred to as a refining or extraction process, there is rea-

son to believe that the actual mechanism of refining in the present process is a chemical or quasi-chemical union of organic sulfur compounds, colored impurities and the like with the highly acidic, chemically reactive, BF_3-organic sulfonic acid refining agent.

The present refining process is applicable to various liquid or liquefied hydrocarbon materials. Thus, it is applicable to various petroleum fractions for the purposes of removing sulfur, gums or other resinous materials, colored impurities and odoriferous compounds, particularly mercaptans. Suitable petroleum feed stocks may comprise light naphtha fractions, gasolines, heavy naphthas, kerosenes, heater oils, furnace oils, diesel fuels, gas oils, cycle stocks from thermal or catalytic cracking operations, reduced crude oils and crude oils. The present refining 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 hydroforming operations, catalytic hydrogenation in the presence of sulfur-sensitive catalysts and the like.

We have noted that the BF_3-hydrocarbon sulfonic acid refining agents exert a remarkable specificity in their interaction with organic sulfur compounds to the exclusion of complex formation with both low boiling and high boiling aromatic hydrocarbons, examples of the former being m-xylene or mixtures of m- and p-xylene and an example of the latter being the high boiling aromatic hydrocarbons contained in gas oils. The selectivity of interaction of the BF_3-hydrocarbon sulfonic acid refining agents to the exclusion of reaction with aromatic hydrocarbons is even greater than that of an active silica gel. So far as we are aware, the BF_3-hydrocarbon sulfonic acid refining agents have the highest sulfur selectivity of any treating reagent, including even liquid hydrogen fluoride which had the highest sulfur selectivity factor of any treating reagent known to us. It will be apparent, accordingly, that the BF_3-sulfonic acid refining agents may be applied to the desulfurization of aromatic hydrocarbon fractions, for example, sulfur-containing benzol, toluol, xylol or naphthalene fractions, or the like.

The present 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 present refining agents serve not only to remove organic sulfur compounds from the feed stock, but also to remove oxygen compounds and nitrogen compounds. It should be understood that the above specific examples of charging stocks which may be refined in accordance with the present invention are illustrative only and are not intended to limit the field of applicability of the process of the present invention.

When substantial proportions of olefins are contained in the charging stock and it is not desired to remove them from said stock, it is desirable to carry out the refining operations in the presence of cognate or added alkylatable hydrocarbons, for example, isoparaffins such as isobutane, isopentane or the like; cycloalkanes containing a tertiary hydrogen, for example, methylcyclopentane, methylcyclohexane, ethylcyclohexane, and the like; aromatic hydrocarbons such as benzene, toluene, xylenes, ethylbenzene, naphthalene or the like.

The present process can be carried out in batch, continuous or semi-continuous operating cycles, 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 BF_3-organic sulfonic acid 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.

In order more fully to describe one specific embodiment of our invention, reference is made to the annexed figure. The feed stock, for example, a sulfur-bearing hydrocarbon material such as a straight run heater oil derived from distillation of a West Texas crude oil, is passed through valved line **10** into a drying zone **11**, wherein it is substantially dehydrated, thence through line **12** into the refining equipment, which in the figure is depicted as an extraction tower **13**. Drying zone **11** may comprise conventional drying reagents and equipment and may, for example, take the form of a vessel packed with excelsior, fiber glass, a commercial magnesium silicate drying agent (Florisil), alumina gel or the like. If desired, the viscosity of the hydrocarbon feed stock can be reduced by dilution with a saturated hydrocarbon diluent such as n-pentane, isopentane, n-octane, petroleum ether, methylcyclopentane, cyclohexane or the like, which may be introduced into line **12** through valved line **14**.

Extraction tower **13** may, if desired, be packed with suitable corrosion-resistant packing material, for example, 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. The extraction or chemical combination of sulfur compounds with the refining agent is slightly exothermic. Accordingly, it may be desirable to provide a cooling coil, cooling jacket or other means of heat removal in the extraction zone. A cooling jacket **15** is depicted in the figure. When a low boiling hydrocarbon diluent such as n-pentane is employed, at least partial heat removal from the extraction zone can be effected by the evaporation of the diluent.

The hydrocarbon sulfonic acid, e. g., a mixture of C_1–C_3 alkanesulfonic acids, is introduced into tower **13** through valved line **16**. Boron trifluoride is passed through valved line **17** into a manifold **18**, whence all or a portion thereof may be passed into line **16**, or into line **12** to join the hydrocarbon feed stock. The proportion of combined treating reagent to the hydrocarbon oil may be, for example, about 30 to about 50 volume percent, based on the hydrocarbon oil, and the treating reagent may contain between about 2 and about 5 mols of the sulfonic acid per mol of BF_3.

Contacting in tower **13** may, for example, be effected at about 20 to about 30° C. at pressures between about 15 and about 50 p. s. i. g. Tower **13** may be operated raffinate-rich or extract-rich, but we prefer the latter mode of operation. Meniscus **19** is shown in the figure as the separation boundary between a lower liquid extract

phase and a supernatant liquid raffinate phase comprising predominantly refined hydrocarbon stock. The contacting period in tower 13 can be varied between about ½ and about 30 minutes and may be, for example, about 5 minutes.

Raffinate is withdrawn from tower 13 through line 20 into a separating vessel 21 provided with a weir 22. Occluded refining agent or extract separates in the lower portion of vessel 21 whence it is withdrawn through valved line 23 and can be recycled through valved line 24 into tower 13 below the meniscus or interface 19. Optionally, all or part of the material in line 23 may be passed through valved line 25 to be treated with extract derived from the lower portion of tower 13. Any gases which separate in drum 21 can be vented through valved line 26 into manifold 27 for recycle to tower 13 or for passage to an absorber, the operation of which will be described hereinafter.

Hydrocarbon raffinate collects in the upper portion of drum 21 in advance of weir 22 and is discharged through line 28, and pressure reducing valve 29 through line 30 into the upper portion of a stripping tower 31, which is provided with a reboiler coil 32 and suitable contacting or packing material. Any BF_3 which may have been occluded with the raffinate is vaporized and passes overhead of stripper 31 through line 33 into line 27. If desired, all or part of the raffinate passing through line 30 may be diverted therefrom through valved line 34 and either removed from the treating system or subjected to such further treatments as desired, for example, washing with caustic alkalies or the like. Stripped raffinate is withdrawn from tower 31 through valved line 35.

A liquid extract layer comprising predominantly the BF_3-hydrocarbon sulfonic acid refining agent containing sulfurous and other impurities derived from the hydrocarbon charging stock, is withdrawn from tower 13 through line 36 and may be treated by alternative, but not necessarily mutually exclusive, processing methods which will be described hereinafter.

If desired, all or part of the extract materials may be diverted from line 36 through pressure reducing valve 37 and line 38 into stripping tower 39, which may be provided with suitable packing material and a reboiler coil 40. Stripping gases such as flue gases, nitrogen, methane, ethane, propane, natural gas, air or the like may be introduced into the lower portion of tower 39 through valved line 41 to aid in the stripping operations. Temperatures between about 50 and about 250° C. and pressures between about 5 and about 50 p. s. i. a. can be maintained in tower 39 to effect decomposition of the various complex compounds containing BF_3 which may be present in the extract materials, thereby liberating BF_3-containing gases which pass overhead through line 42 into manifold 27. More or less hydrogen sulfide may also be generated by decomposition of sulfur compounds at the temperatures attained in the operation of stripping tower 39, thereby contaminating the BF_3 gas stream passing overhead through line 42.

The stripped extract materials are withdrawn from the lower portion of tower 39 through valved line 43 into settling drum 44. As a result of substantial or complete removal of BF_3 from the extract layer, the extract layer can be separated by settling, centrifuging or the like into one liquid layer comprising predominantly hydrocarbon sulfonic acid and a second liquid layer comprising predominantly sulfur compounds and/or other impurities derived from the hydrocarbon charging stock. The impurities are withdrawn through valved line 45. The sulfonic acid may be withdrawn from the lower portion of drum 44 through line 46, thence through valved line 47 for recycle to line 16 and refining tower 13. Optionally, part or all of the sulfonic acid may be diverted from line 46 through valved line 48 and heater 49 into a vacuum still 50, provided with residue draw-off line 51 and distillate draw-off line 52. Depending upon the boiling points of the residual contaminants which may be present in the sulfonic acid and the boiling point of the sulfonic acid, one or the other may be separated as a distillate and the other as a residue. The vacuum distillation treatment improves the quality of the sulfonic acid and fits it for further recycle (by lines not shown) to refining tower 13.

An optional treatment for sulfonic acid containing residual contaminants and, in fact, a treatment to which the entire extract phase may be subjected if desired, involves dilution with water to separate contaminant materials derived from the hydrocarbon charging stock. In this mode of operation, the sulfonic acid is diverted from line 46 through valved line 53 into line 54, whence it is joined by water, for example, in proportions between about 10 and about 200 volume percent, introduced through valved line 55. If desired, part or all of the extract layer may be diverted from line 36 into valved line 54. The resultant aqueous mixture may be passed through heat exchanger 56 into settling drum 57 provided with weir 58. In drum 57, gravity separation is effected between extract materials, i. e., sulfur compounds and other contaminants derived from the hydrocarbon feed stock and an aqueous solution of the components of the refining agent. Extract materials may be removed from drum 57 through valved line 59 and the aqueous refining agent may be removed from drum 57 through valved line 60 into concentration or recovery equipment schematically depicted at 61, employing conventional methods and equipment, thence through valved line 62 into line 47 for recycle through valved line 16 to refining tower 13.

Manifold 27 contains gases comprising BF_3, relatively low boiling saturated hydrocarbons employed as a diluent in refining tower 13 and/or as stripping gases introduced through tower 39, together with more or less hydrogen sulfide derived from decomposition of organic sulfur compounds in tower 39. Part or all of the stream in manifold 27 may be passed through valve 63 and heat exchanger 64 into line 16 for recycle to refining tower 13. Preferably, part or all of the gas stream in manifold 27 is passed through valve 65 into an absorption tower 66, there to be countercurrently contacted with liquid hydrocarbon sulfonic acid, introduced through valved line 67, which selectively absorbs and complexes the BF_3 component of the gas stream to produce a solution which is withdrawn through valved line 68 and can suitably be recycled (by lines not shown) to refining tower 13. Unabsorbed diluent gases pass overhead from absorber 66 through valved line 69. In order to increase the extent and efficiency of BF_3 recovery it may be desirable to charge sulfur compounds, particularly alkyl thioethers or a portion of the sulfur-containing hydrocarbon feed stock into the upper portion of tower 66, preferably through line 67.

The following specific examples are intended

to be illustrative but not unduly limitative of the present invention.

Example 1

The charging stock was a West Texas heater oil having a sour odor, orange-yellow color, 332 to 548° F. A. S. T. M. boiling range, sulfur content of 0.78 weight percent and 48 mercaptan number. The oil (151 ml.) was contacted with 23.5 percent by volume of a BF_3-methanesulfonic acid liquid mixture containing 0.488 mol of methanesulfonic acid and 0.1075 mol BF_3 at room temperature (20–25° C.) and atmospheric pressure by shaking for 5 minutes in a glass vessel. Upon cessation of shaking, the contents of the vessel separated into a supernatant liquid raffinate phase and a lower extract phase comprising the BF_3-methanesulfonic acid refining agent. The raffinate phase amounted to 96.7 percent by volume of the initial heater oil charging stock and contained 0.29 weight percent sulfur, indicating that 62.9 percent desulfurization occurred. The raffinate layer was separated from the extract and washed with water. The raffinate thus treated had a very light yellow color, a sweet odor and a mercaptan number of 16. The mercaptan number is the number of milligrams of mercaptan sulfur per 100 ml. of sample. The extract layer was diluted with water, whereupon it separated into an aqueous phase comprising the refining agents and a supernatant layer of 5 ml. (3.3 volume percent of feed) of a dark brown, foul-smelling oil which contained 12.4 percent by weight of sulfur. Therefore, the sulfur selectivity factor of the refining agent

$$\frac{(\%\ \text{desulfurization} \times 10)}{\%\ \text{extract}}$$

in the above-described operation was 190.

By way of comparison, the treatment of a West Texas furnace oil (1.46 percent sulfur; 438–632° F. A. S. T. M. boiling range) with 34 g. BF_3 per 640 g. of oil at room temperature and 100 p. s. i. g. resulted in only 17.8 percent desulfurization. These results are in sharp contrast to the above example. The proportion of BF_3 based on feed in the above example was 5.6 weight percent whereas it was 5.3 weight percent based on feed in the instance in which methanesulfonic acid was not employed. The desulfurization data are, therefore, reasonably comparable.

Attention is likewise drawn to Example 4, Table 1 of U. S. Patent 2,495,851 wherein treatment of West Texas furnace oil (1.46 percent sulfur) with 20 volume percent of BF_3-ethyl ether complex resulted in only 9.9 percent desulfurization. It will, thus, be apparent that whereas free BF_3 is essential to activate the BF_3 complexes described in U. S. Patent 2,495,851, no free BF_3 is essential in the present process, since, as shown by the above example, 4.35 mols of methanesulfonic acid were present for each mol of BF_3 employed.

To compare the action of a sulfonic acid alone, 10 ml. of a West Texas heater oil, containing 0.78 weight percent of sulfur, were contacted with 4 ml. of mixed C_1–C_4 alkanesulfonic acids by stirring for 145 minutes at room temperature. The mixture was then allowed to stratify into an upper, hydrocarbon layer and a lower, acid layer, and the layers were separated. The hydrocarbon layer was washed with 10 ml. of water, then with a solution of 1 ml. of concentrated ammonia in 10 ml. water and finally with 10 ml. of distilled water. The treated hydrocarbon layer contained 0.77 weight percent of sulfur, indicating that essentially no desulfurization occurred.

In order to compare the BF_3-sulfonic acid refining agents of the present invention with BF_3-carboxylic acid refining agents, a heater oil containing 0.73 percent by weight of sulfur was treated with $BF_3.2CH_3CO_2H$ in the proportion of 57 ml. of complex per 182 ml. of heater oil at atmospheric pressure, 20 to 25° C. and 5 minutes of contact. Only 8 percent desulfurization of the feed was thus obtained.

Example 2

The West Texas heater oil of Example 1 (0.78 percent sulfur) was contacted at atmospheric pressure and 0 to 5° C. with 31.3 volume percent of a BF_3-methanesulfonic acid liquid mixture by occasional shaking over a 30 minute period. The refining agent contained 0.782 mol of methanesulfonic acid and 0.214 mol of BF_3 and was used to treat 182 ml. of feed. The contacting mixture was then allowed to settle, forming a two-liquid layer system. The upper, raffinate hydrocarbon layer was separated and washed with water; it was found to constitute 96.2 percent by volume of the heater oil charging stock and to contain 0.16 percent sulfur. The refractive index (n_D^{20}) of the feed was 1.4602 and of the raffinate, 1.4582. The extract material was characterized by a sulfur content of 11.9 percent and refractive index of 1.5090. Since 79.5 percent desulfurization of the feed had occurred with a 3.8 volume percent loss of oil on extraction, the sulfur selectivity factor in this operation was 215.

Example 3

A West Texas gas oil (A. S. T. M. boiling range, 432–650° F.; sulfur content of 1.50 weight percent; n_D^{20} of 1.4825) was extracted at room temperature and atmospheric pressure with 31.2 percent by volume of a BF_3-methanesulfonic acid liquid mixture containing 4.04 mols of methanesulfonic acid per mol of BF_3, and the mixture worked up as described in previous examples. As a result, 51.3 percent desulfurization was obtained at an extract volume equal to 9.1 volume percent of the feed stock. Accordingly, the sulfur selectivity factor in this operation was 56.4.

Example 4

The gas oil charging stock of Example 3 was extracted by the same procedure with 30 volume percent of a liquid mixture containing 1 mol of BF_3 per 3.36 mols of methanesulfonic acid. Desulfurization of the charging stock occurred to the extent of 46 percent accompanied by a 7.5 volume percent loss of the feed to extract. The sulfur selectivity factor in this operation was 61.3.

Example 5

A West Texas virgin heavy naphtha (170 ml.) containing 0.32 percent by weight of sulfur, was contacted with 46.5 ml. of a BF_3-methanesulfonic acid liquid mixture containing 3.34 mols of sulfonic acid per mol of BF_3 at room temperature and atmospheric pressure. Raffinate and extract phases were separated and worked up as in previous examples. The refining treatment produced less than 2 volume percent of extract, based on the naphtha charged, and the raffinate was found to contain only 0.07 percent of sulfur, corresponding to 78 percent desulfurization of

the naphtha. The sulfur selectivity factor in this operation, accordingly, was somewhat over 400.

Example 6

A mixture of 160 ml. of toluene and 20 ml. of thiophene was contacted with 46 ml. of the BF_3-methanesulfonic acid refining agent described in Example 5. As a result, appreciable quantities of heat were evolved, the contacting mixture darkened and viscous resinous materials were produced. A supernatant raffinate layer was formed on settling the contacting mixture and was separated. The raffinate contained 2.41 percent by weight of sulfur, while the charging stock analyzed 4.48 percent by weight of sulfur. As a result of the treatment, 46.2 percent desulfurization of the charging stock occurred.

Example 7

A West Texas heater oil containing 0.78 weight percent of sulfur (152 ml.) was mixed with commercial p-toluenesulfonic acid and BF_3 was bubbled through the resultant mixture at room temperature. The volume ratio of extractant to oil was 0.30 and the extraction mixture contained 0.346 mol of sulfonic acid and 0.0826 mol of BF_3. Upon standing, the extraction mixture separated into an upper, hydrocarbon layer and a lower, acid layer. The hydrocarbon layer (raffinate) was found to contain 0.44 weight percent of sulfur, indicating that the extraction treatment had resulted in 43.6 weight percent desulfurization of the heater oil. The extract was estimated as 3 percent by volume, based on feed. The sulfur selectivity factor was therefore about 145 in this operation.

An overall comparison of the above examples indicates that the sulfur selectivity factors tend to decrease somewhat with increasing average molecular weight or boiling range of the hydrocarbon charging stock subjected to the refining process of the present invention.

The extracts produced in the process of the present invention are in themselves useful compositions of matter. Thus, they may be caused to react with olefinic or terpenic compounds to produce derivatives of the sulfur compounds therein contained. Treatment with olefins may be employed to convert mercaptans in the extracts to thioethers. Moreover, condensation reactions may be effected in the extract and hydrogen sulfide evolved by subjecting the extracts to elevated temperatures. If desired, the extract materials may be treated to recover substantially pure sulfur compounds, employing the water dilution method described in connection with the annexed figure, optionally followed by vacuum distillation of the sulfur compounds thus liberated.

It will be apparent that the refining process of the present invention can be employed in combination with other refining processes.

Having thus described our invention, what we claim is:

1. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with a BF_3-hydrocarbon sulfonic acid mixture in an amount sufficient at least to form a separate liquid phase, and separating a refined hydrocarbon material and an extract phase comprising BF_3, hydrocarbon sulfonic acid and a sulfur compound.

2. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with a BF_3-hydrocarbon sulfonic acid mixture in an amount sufficient at least to form a separate liquid phase at a temperature between about −30° C. and about 120° C., and separating a refined hydrocarbon material and an extract phase comprising BF_3, hydrocarbon sulfonic acid and a sulfur compound.

3. The process of claim 2 in which said contacting is effected at a temperature between about 10° C. and about 60° C.

4. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with between about 5 and about 200 percent by volume of a liquid mixture of BF_3 and a hydrocarbon sulfonic acid containing 1 to 10 carbon atoms, inclusive, per molecule, at a temperature between about −30° C. and about 120° C., and separating a refined hydrocarbon material and an extract phase comprising BF_3, hydrocarbon sulfonic acid and a sulfur compound.

5. The process of claim 4 in which the proportion of the liquid BF_3-hydrocarbon sulfonic acid, based on said hydrocarbon material, is between about 20 percent and about 100 percent by volume.

6. The process of claim 4 in which the proportion of the liquid BF_3-hydrocarbon sulfonic acid, based on said hydrocarbon material, is between about 20 percent and about 100 percent by volume, and in which said contacting is effected at a temperature between about 10° C. and about 60° C.

7. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with between about 5 and about 200 percent by volume of a liquid mixture of BF_3 and an alkanesulfonic acid containing 1 to 3 carbon atoms, inclusive, per molecule, at a temperature between about −30° C. and about 120° C., and separating a refined hydrocarbon material and an extract phase comprising BF_3, alkanesulfonic acid and a sulfur compound.

8. The method of removing mercaptans from a mercaptan-containing hydrocarbon oil which comprises contacting said hydrocarbon oil with between about 5 and about 200 percent by volume of a liquid mixture of BF_3 and an alkanesulfonic acid containing 1 to 3 carbon atoms, inclusive, per molecule at a temperature between about −30° C. and about 120° C., and separating the contacting mixture into an extract layer and a refined hydrocarbon oil layer containing a substantially reduced quantity of mercaptans.

9. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with a liquid mixture comprising BF_3 and a hydrocarbon sulfonic acid in substantial molar excess, based on the amount of BF_3, the amount of said liquid being sufficient at least to form a distinct liquid phase, and separating a refined hydrocarbon material and an extract phase comprising BF_3, hydrocarbon sulfonic acid and a sulfur compound.

10. The process of claim 9 wherein said liquid mixture contains from about 3 to about 8 mols of hydrocarbon sulfonic acid per mol of BF_3.

11. The method of desulfurizing a sulfur-bearing hydrocarbon material which comprises contacting said material with between about 5 and about 200 percent by volume of a liquid mixture comprising essentially BF_3 and an alkanesulfonic acid containing 1 to 3 carbon atoms, inclusive, per molecule, the molar ratio of said alkanesulfonic acid to said BF_3 in said liquid mixture being

between about 3 and about 8, at a temperature between about −30° C. and about 120° C., and separating a refined hydrocarbon material and an extract phase comprising BF_3, said alkanesulfonic acid and a sulfur compound.

12. The process of claim 11 wherein the alkanesulfonic acid is methanesulfonic acid and wherein said contacting is effected at a temperature between about 10° C. and about 60° C.

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