

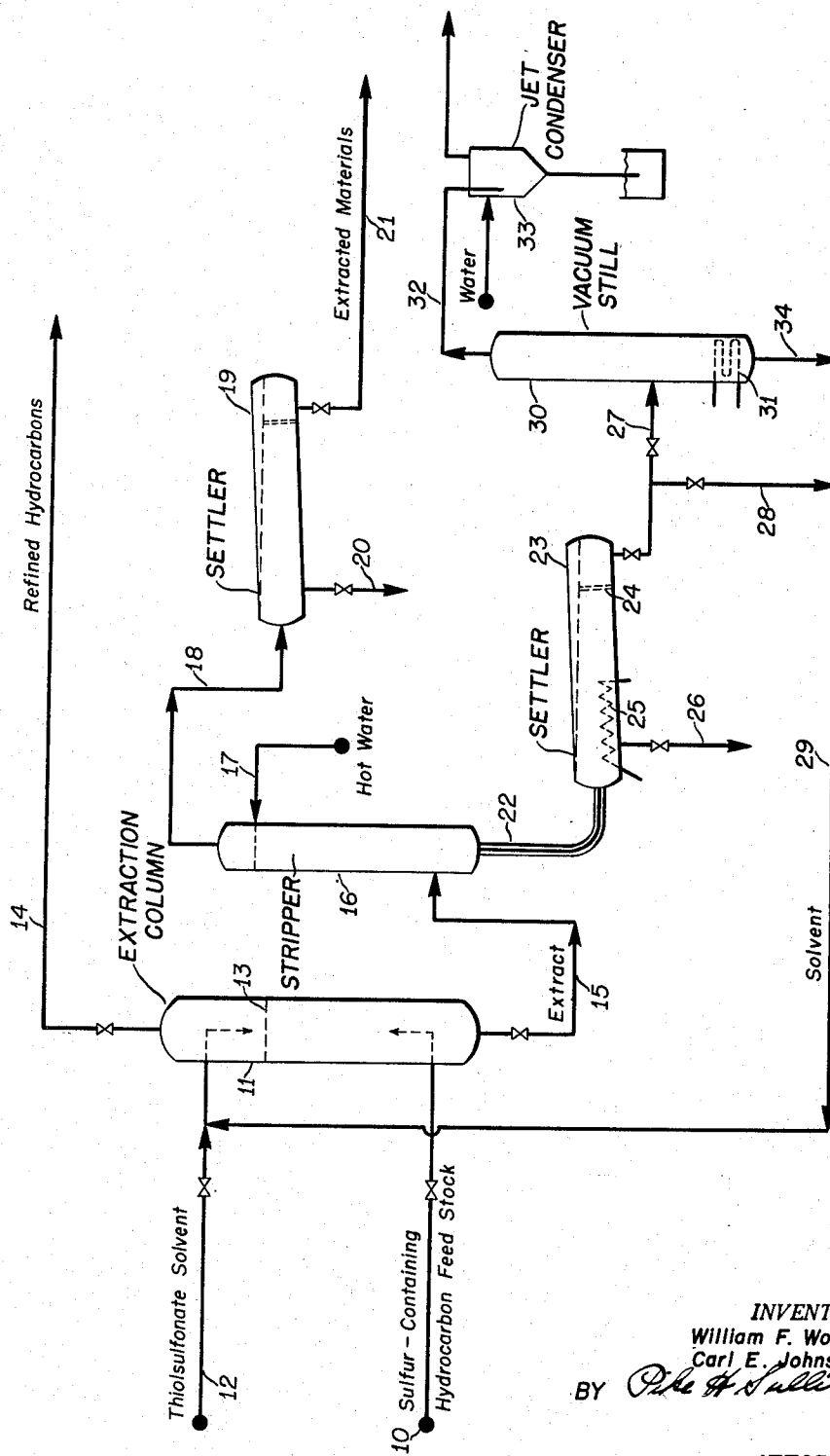
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EXTRACTION OF SULFUR COMPOUNDS WITH THIOISULFONIC ESTERS

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## EXTRACTION OF SULFUR COMPOUNDS WITH THIOLSULFONIC ESTERS

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This invention relates to processes for the extraction of organic sulfur compounds from mixtures thereof with hydrocarbons, for example, such mixtures as occur in various processed or unprocessed petroleum oils. More particularly, this invention relates to processes for the selective extraction of organic sulfur compounds from oils comprising aliphatic hydrocarbons by the employment of certain thioisulfonic esters as selective extraction solvents.

Numerous so-called selective solvents have been proposed for removing organic sulfur compounds from their solutions in various hydrocarbon oils, particularly for the refining of lubricating oil stocks, burning oils and the like. While a number of selective solvents are in actual commercial use, no solvent has been found to be sufficiently satisfactory for all purposes to retard the general search for improved selective solvents.

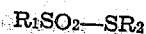
We have discovered that certain esters of thioisulfonic acids are surprisingly effective selective solvents for organic sulfur compounds in admixture with hydrocarbons, notably in certain petroleum oil fractions. We have further found that said thioisulfonic esters can be prepared relatively cheaply, have relatively mild corrosive properties permitting their employment in conventional equipment, are characterized by surprisingly low or negligible solubility thereof in the raffinate phase produced by the extraction process, are readily recoverable, and have physical properties which permit their employment as selective extraction solvents for organic sulfur compounds at readily attainable temperatures and pressures. Moreover, the molecular weight and chemical constitution of the thioisulfonic esters can be varied to obtain "tailor-made" extraction solvents best suited for the particular extraction operations as they arise.

It is an object of this invention to provide a process for the selective extraction of organic sulfur compounds from their mixtures with hydrocarbons. Another object of this invention is to provide the art of selective extraction of organic sulfur compounds with novel solvents, viz., certain thioisulfonic esters. An additional object of our invention is to provide solvents for selective extraction processes characterized by high selectivity for organic sulfur compounds while at the same time exhibiting little or no solvent capacity for aliphatic hydrocarbons, both saturated and unsaturated. A further object of our invention is to provide the art with novel selective extraction processes and solvent recovery procedures. These and other objects of

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our invention will be readily discerned from the ensuing description thereof and from the appended drawing which is a schematic flow sheet illustrating our process.

The novel solvents employed in the selective extraction process of this invention are thioisulfonic esters containing between 2 and 20 carbon atoms, inclusive, per molecule and having the general formula:



wherein  $R_1$  and  $R_2$  may be the same or different and are selected from the class consisting of hydrocarbon radicals and substituted hydrocarbon radicals. Ordinarily, it is preferred to employ thioisulfonic esters wherein  $R_1$  and  $R_2$  are unsubstituted hydrocarbon radicals containing no aliphatic unsaturation, i. e., wherein  $R_1$  and  $R_2$  are selected from the class consisting of saturated hydrocarbon radicals and aromatic hydrocarbon radicals. Thus, the hydrocarbon radical may be an alkyl radical, a cycloalkyl radical, a cycloalkyl-alkyl radical, an aralkyl radical, aryl, alkaryl or cycloalkyl-aryl radical. The  $R_1$  and  $R_2$  radicals in the above formula may contain negative substituents such as halogen atoms, nitro groups, amino groups or the like.

Examples, given by way of illustration and not necessarily for limitative purposes, of suitable  $R_1$  or  $R_2$  alkyl radicals are: methyl, ethyl, n-propyl, isopropyl, n-butyl, amyl, octyl, nonyl, hexadecyl and octadecyl. Illustrative examples of suitable  $R_1$  or  $R_2$  cycloalkyl radicals include cyclopentyl, methylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, ethylcyclopentyl, and endomethylenecyclohexyl (bicyclo[2,2,1]heptyl) and 2-methylbicyclo[2,2,1]heptyl. Examples of suitable  $R_1$  or  $R_2$  aralkyl radicals in the above general formula include benzyl, 2-phenylethyl, 2-phenylpropyl, w-xylyl, naphthomethyl, and the like. Examples of suitable  $R_1$  or  $R_2$  cycloalkyl-alkyl radicals include cyclohexylmethyl, cyclohexylethyl, cyclopentylpropyl, and the like. Examples of suitable  $R_1$  or  $R_2$  aryl radicals include phenyl, naphthyl and derivatives containing nuclearly substituted chlorine atoms, nitro groups, etc. Examples of suitable  $R_1$  or  $R_2$  alkaryl radicals for substitution in the above general formula are tolyl, xylyl, dimethylphenyl, ethylphenyl, isopropylphenyl, butylphenyl, methylnaphthyl, dimethylnaphthyl, and the like. Examples of suitable  $R_1$  or  $R_2$  cycloalkyl-aryl radicals include cyclohexylphenyl, methylcyclopentylphenyl, cyclohexyltolyl, and the like.

Specific examples of selective solvents for em-

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ployment in the extraction process of the present invention include the following esters of methanethiolsulfonic acid: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-amyl, octyl, dodecyl, hexadecyl, octadecyl; the corresponding esters of ethanethiolsulfonic acid; the corresponding esters, not however containing more than 20 carbon atoms per molecule, of 1-propanethiolsulfonic acid, 2-propanethiolsulfonic acid, butanethiolsulfonic acid, pentanethiolsulfonic acid, hexanethiolsulfonic acid, octanethiolsulfonic acid, dodecanethiolsulfonic acid, etc. Other specific examples include methyl benzenethiolsulfonate, methyl-p-toluenethiolsulfonate, ethyl benzenethiolsulfonate, phenyl benzenethiolsulfonate, chlorophenyl chlorobenzenethiolsulfonate, benzyl benzenethiolsulfonate, phenyl, 3,5-dinitrobenzenethiolsulfonate, ethyl bis-benzenedithiolsulfonate, etc. It should be understood that we may employ mixtures of esters rather than individual esters. Because of their high selectivity and cheapness, we prefer to employ esters of the above general formula wherein  $R_1$  and  $R_2$  are  $C_1$ - $C_4$  alkyl radicals.

Although there has been some dispute concerning the chemical structure of thiolsulfonic esters, sometimes called disulfoxides, the consensus of evidence favors the general formula which we have given above. The structures  $CH_3SO_2-SCH_3$  and  $C_2H_5SO_2-SC_2H_5$  have, for example, been assigned by us on the basis of infrared spectra showing strong absorption bands at 7.6 and 8.8 microns, due to the  $-SO_2-$  group and the absence of absorption in the region of 9.1-10.0 microns, indicating the absence of the  $-SO-$  group. Structure assignment has also been based upon the discovery by us of a new acid-catalyzed addition reaction of thiolsulfonates to olefins to yield 1,4-sulfonethioethers, rather than the 1,4-disulfoxides which would be the reaction products expected from the symmetrical disulfoxide structure  $R_1-SO-SO-R_2$ . The selective solvents which we prefer to designate as esters of thiolsulfonic acid are prepared preferably by the oxidation of the corresponding disulfide. They can be prepared non-catalytically with dilute nitric acid, that is, about 40% nitric acid or with hydrogen peroxide as oxidizing agents at ambient temperatures up to about 80° C. Other oxidizing agents may be used. The disulfides also may be oxidized catalytically using air or oxygen as the oxidizing agent and the higher oxides of nitrogen as catalyst as taught in U. S. 2,433,395. The esters of thiolsulfonic acid may also be prepared by other methods well known in the art.

It is not intended to imply that all the thiolsulfonates contemplated for use in this invention are precisely equivalent. However, they are all generally useful and suitable for the purposes of the claimed invention.

The thiosulfonates defined by the above general formula are either normally liquid or relatively low melting solids and may usually be used for the purposes of the present invention without auxiliary solvents or diluents. However, because of their solubility in hot water, methanol, ethanol, benzol, etc., it may be desirable to employ the solvents of the present invention together with more or less of such diluents or co-solvents in order to modify the selectivity of the thiolsulfonates, to lower their melting points, or for other reasons. The amount of auxiliary solvents employed can be selected with reference to specific cases; ordinarily, only between about 1 and about 20 weight per cent based on the thiolsulfonate will

be employed. Anti-solvents or diluents may also be employed in the practice of the present invention. Thus, diluents such as saturated hydrocarbons may be added to the feed stock to be desulfurized or introduced directly into the extraction zone. In the process of the present invention the selective solvent is employed as a liquid, melt or solution; the feed stock may be charged to the process as a liquid or solution.

In general, the extraction operations of the present invention are conducted at temperatures between about -20° C. and about 150° C., the particular extraction temperature depending upon the specific thiosulfonate solvent, the melting point of the solvent, whether or not it is used alone or with an auxiliary solvent or diluent, the degree and selectivity of extraction sought to be effected, etc.

The volume of selective solvent employed depends, among other things, upon the organic sulfur content of the feed stock, the temperature of operation and desired efficiency, but will generally fall within a range of about 0.2 to about 10 volumes of thiosulfonate per volume of charging stock. Ordinarily, we prefer to employ between about 0.5 and about 2 volumes of solvent per volume of feed stock. Usually, pressures within the range of about 0 to 100 p. s. i. g. are sufficient for this purpose, it being appreciated that the particular pressure necessary in a given case can readily be determined. The extractive process of the present invention is conducted under essentially neutral or slightly alkaline operating conditions.

Numerous hydrocarbon oil fractions derived from petroleum, coal, shale, etc., are known to contain organic sulfur compounds whose removal is desired in order to produce refined hydrocarbon oils. Such oils may boil within the boiling ranges of (and be generally characterized as) gasoline, naphtha, kerosene, gas oil, heater oil, furnace oil, diesel fuel, transformer oil, crude oil, lubricating oil, etc. The process of the present invention is applicable to the refining of gasoline boiling range hydrocarbon oils containing organic sulfur compounds, particularly thioethers or, in the case of sweetened gasolines, alkyl disulfides, and is applicable to such oils containing a substantial proportion of mono-olefinic hydrocarbons, as in the case of sweetened or unsweetened gasolines produced from sulfur-bearing crude oils, such as West Texas crude oil, by cracking or coking processes. 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 or dehydrogenation in the presence of sulfur-sensitive catalysts and 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 delimit the field of applicability of the process of the present invention.

The present invention 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 isoparaflinic 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 solvent with the hydrocarbon charging stock and thereafter separating an extract phase from the refined charging stock can be employed for the purposes of the invention. The data in the table afford a comparison of the performance of methyl methanethiolsulfonate in cracked cycle stock extraction with that of nitromethane, furfural, dimethylformamide, SO<sub>2</sub>, and diethylsulfoxide, which are among the most highly regarded solvents for the extraction of sulfur compounds from the type of feed stock here under consideration. As a measure of the selectivity of the solvents for the extraction of sulfur compounds, the so-called sulfur selectivity factor (SSF) is determined in accordance with the following equation:

$$SSF = \frac{\text{percent S in feed} - \text{percent S in raffinate}}{\text{Volume percent extracted}} \times 104$$

TABLE

Solvent	Volume percent extract on 100% treat	Sulfur selectivity factor
Methyl methanethiolsulfonate	16	240
Nitromethane	13	200
Furfural	26	220
Dimethyl formamide	40	160
Sulfur dioxide	35	210
C <sub>2</sub> H <sub>5</sub> -SO-C <sub>2</sub> H <sub>5</sub>	36	160

Thus, methyl methanethiolsulfonate was superior in sulfur selectivity to all of the excellent liquid solvents.

The light catalytic cycle stock employed in certain of the examples was derived from the catalytic cracking of West Texas gas oil in the presence of natural clay catalyst and had the following properties:

A. S. T. M. distillation

Volume percent distilled:	B. P., ° F	
I. B. P.	B. P., ° F	429
10	B. P., ° F	455
20	B. P., ° F	465
30	B. P., ° F	473
40	B. P., ° F	482
50	B. P., ° F	492
60	B. P., ° F	502
70	B. P., ° F	511
80	B. P., ° F	523
90	B. P., ° F	540
E. P.	B. P., ° F	578
<i>n</i> <sub>D</sub> <sup>20</sup>		1.4967
Weight percent S		1.10
Specific dispersion		156
Bromine number		11
° A. P. I.		29.3

The following examples are intended to illustrate but not necessarily to limit the invention:

Example 1

Light catalytically cracked cycle oil having the properties set forth in the above table was agi-

tated at room temperature and atmospheric pressure with an equal volume of methyl methanethiolsulfonate and the mixture was allowed to settle. The treatment of 50 volumes of cycle stock yielded 58 volumes of a dark-colored bottom or extract layer and 42 volumes of a top or raffinate layer of much lighter color than the feed stock. The raffinate layer was washed briefly with boiling water and was found to contain 0.72 weight per cent sulfur as against 1.10 weight per cent sulfur in the feed stock; this corresponds to 35% desulfurization of the feed stock with the production of 16% of extract, or a sulfur selectivity factor of about 220. When a further portion of the raffinate layer was washed with cold aqueous caustic solution, then with water and filtered, its sulfur content was reduced to 0.65 weight per cent, corresponding to 41% desulfurization or an overall sulfur selectivity factor of about 255.

Example 2

A mixture of equal volumes of the above described catalytic cycle stock and phenyl benzenethiolsulfonate was agitated to obtain contact over a period of five minutes at room temperature after which it was permitted to separate to form two layers. The extractant phenyl benzenethiolsulfonate was prepared by oxidizing diphenyl disulfide with hydrogen peroxide and was used in this experiment as a super cooled liquid. Upon separation of the mixture, a raffinate layer amounting to 30% of the total volume of the mixture was purified by crystallization of a minor amount extractant therefrom. This raffinate had a sulfur content of 0.66% as contrasted with a sulfur content of 1.10% for the raw unextracted catalytic cycle stock. Thus a yield of about 60% of 40% desulfurized oil was obtained. A sulfur selectivity factor of 100 is indicated.

Example 3

A mixture of equal volumes of methyl disulfide and normal heptane was agitated for 10 minutes at room temperature with an equal volume of methyl methanethiolsulfonate. From 5 volumes of charging stock there was obtained a raffinate layer of 2.7 volumes. Two volumes of the raffinate layer were then treated with concentrated (37.7%) aqueous hydrochloric acid to remove 0.1 volume of the solvent which was present therein. The raffinate thus obtained had a refractive index of *n*<sub>D</sub><sup>20</sup> 1.4159 while the refractive indices of the feed stock and of n-heptane were 1.4543 and 1.3879, respectively. Thus, about 55% desulfurization was obtained with about 48% extraction of the feed stock into the extract layer, corresponding to a sulfur selectivity factor of about 115.

An illustrative flow process and equipment are indicated in the figure. The hydrocarbon mixture to be extracted, containing sulfur compounds, for example, a light cycle stock from silica-alumina cracking of a West Texas gas oil, is passed through valved line 10 into the contacting zone 11. The feed stock is preferably dried and, if it contains hydrogen sulfide, is treated to effect its removal, e. g., by washing with caustic, ethanalamine, dimethylethanalamine, etc.

We may employ conventional contacting and separation equipment such as has heretofore been employed in effecting selective solvent extraction of lubricating oils, illuminating oils, etc., or in the processes for the extractive distillation of hydrocarbon oils. The contacting equipment

may comprise a vertical tower, which is preferably provided with packing or spacing materials to insure thorough contacting of the hydrocarbon feed stock and the thioisulfonate solvent. Suitable materials of construction for the contacting zone are aluminum and stainless steel, although it should be understood that we may employ other construction materials, for example, glass-, ceramic- or carbon-lined iron towers. Suitable spacing materials comprise shaped fragments, for example, Berl saddles or Raschig rings made of carbon, porcelain, glass, aluminum, stainless steel, etc.; stainless steel jack chain; stainless steel or aluminum screens which may be shaped, for example, in the form of Scofield, McMahon or Stedman packing, etc. If desired, the contacting tower may be jacketed or provided with heat exchange coils to permit maintenance of the desired temperature.

In a desirable method of operation, the feed stock is passed into the lower portion of zone 11 against a counter-flow of a thioisulfonate, for example, methyl methanethioisulfonate, which is introduced into the upper portion of tower 11 through valved line 12. Diluents, e. g., pentane or hexane, or modifying solvents, e. g. ethanol or benzol, may be introduced with the feed stock, the thioisulfonate solvent or separately through a line not shown, into zone 11. Alkaline conditions during extraction can be maintained by introducing ammonia (gas) into zone 11 (by a line not shown).

The contacting of the thioisulfonate and hydrocarbon feed stock results in the production of raffinate and extract phases whose common boundary or interface is indicated at 13. The countercurrent extraction zone may be operated with either the feed stock or solvent as the continuous phase. In the mode of operation, illustrated in the drawing, the extract phase is shown as the continuous phase through which the hydrocarbon feed stock is introduced as the dispersed phase.

The raffinate phase forms a supernatant layer above interface 13 in zone 11 whence it is discharged, together with the diluent employed, from said zone through valved line 14. The raffinate phase is characterized by a substantially reduced content of organic sulfur compounds as compared with the feed stock. It should be understood, however, that the raffinate phase may be further treated to reduced its content of organic sulfur compounds, if it is so desired. For this purpose, a portion at least of the raffinate phase may be recycled from line 14 by a line not shown to re-enter zone 11 with fresh feed stock. Alternatively, or in addition, the raffinate in line 14 may be sent to another contacting zone, identical in all substantial respects with zone 11, for treatment in a second stage with fresh solvent, which may be the same thioisulfonate or a different thioisulfonate from that passing into line 12, or may be an entirely different type of solvent, e. g. liquid hydrogen fluoride,  $\text{HF}-\text{BF}_3$ , liquid  $\text{SO}_2$ , phenol, furfural, dimethylformamide, bis-(beta-chloroethyl) ether, etc. It should be noted that further extraction of the raffinate passing through line 14 with solvents different from the thioisulfonate passing through line 12 is greatly facilitated by the fact that the thioisulfonate is substantially insoluble in said raffinate, averting the necessity of special procedures for the removal of thioisulfonate from said raffinate. Small amounts of thioisulfonate entrained in the raffinate can

be removed by washing with hot water or aqueous hydrochloric acid.

The extract phase, a solution of organic sulfur compounds in the thioisulfonate solvent, is withdrawn from the lower end of tower 11 through valved line 15, whence it is passed into separation zone 16. If desired, a part of the extract phase may be recycled from line 15 to feed line 10 by means of a line not shown in the drawing. Zone 16 may be a separating vessel into which hot water or aqueous extractants are introduced by valved line 17, in suitable amounts, e. g. between about 0.5 and about 3.0 volumes per volume of extract, at temperatures between about 20 and about 100° C. to effect the resolution of the extract into an aqueous thioisulfonate layer and a layer containing organic sulfur compounds and co-solvent employed in the extraction operation. Methyl methanethioisulfonate is soluble to the extent of about 15 g. per 100 g. of water at 65° C. and about 6 g. per 100 g. of water at 20° C.; its solubility in 37.7% hydrochloric acid is about 10 times its solubility in water at the same temperature and the HCl solution of the thioisulfonate can be resolved into two layers by blowing off HCl gas. Alternatively, the separation zone 16 may take the form of a distillation vessel, preferably a steam distillation vessel in which the sulfur compounds are vaporized and pass overhead, usually as azeotropes with water, through line 18 into a settling vessel 19, whence the water layer is withdrawn through valved line 20 and sulfur compounds are withdrawn through valved line 21. The extracted materials may be employed as plasticizers for vinyl resins, natural and synthetic rubber, asphalts, etc.

A bottoms fraction containing the thioisulfonate is withdrawn from zone 16 through valved, insulated line 22 into a settler 23 provided with weir 24 and cooling coil 25. The temperature of the aqueous solution of thioisulfonate in settler 23 is reduced to about room temperature or even to a lower temperature, e. g., down to about 10° C. in order to reduce the solubility of the thioisulfonate solvent in said aqueous phase. If desired,  $\text{CaCl}_2$ ,  $\text{NaCl}$  or other salts may be added to the aqueous phase in settler 23 in order to reduce the solubility of the thioisulfonate solvent therein. Two immiscible liquid layers are produced in settler 23, one of which is water or an aqueous salt solution and the other of which comprises essentially the thioisulfonate solvent. The thioisulfonates are in general of higher specific gravity than water but may be of lower specific gravity than aqueous salt solutions. The two layers are separately withdrawn from settler 23 at the appropriate points. For illustrative purposes, in the figure, an aqueous salt solution is shown being withdrawn from settler 23 through valved line 26 and the thioisulfonate solvent through valved line 27, whence it may be recycled wholly or in part through valved line 28 and manifold 29 to line 12 and thence to extraction column 11. Preferably, at least a portion of the thioisulfonate solvent is directed from line 27 into a distillation column 30 provided with a heating or reboiler coil 31. Column 30 can suitably be a vacuum still from which steam can be separated from the wet solvent and removed overhead through line 32 into a barometric condenser 33. The dried solvent is discharged as bottoms through line 34 into manifold 29 for recycle to the extraction zone 11.

Alternatively, the recycle stream of solvent may be dehydrated in column 30 by azeotropic

distillation of water therefrom with various azeotropic agents, e. g. benzene, toluene, n-heptane, ethyl acetate, etc.

Although the drawing represents a continuous countercurrent extraction operation, it will be apparent that the process of the present invention is amenable to batch processing, multi-unit operation, concurrent flow of solvent and feed stock, the use of knot-hole or other mechanical mixers for feed and solvent in series with one or more settling zones and other variations that will no doubt occur to those skilled in the art without departing from the spirit of this invention.

Having thus described the process of our invention, what we claim is:

1. A process for the extraction of an organic sulfur compound from a mixture thereof with hydrocarbons, which process comprises contacting said mixture with an ester of a thiolsulfonic acid containing 2 to 20 carbon atoms per molecule and separating a raffinate phase from an extract phase comprising said ester and said organic sulfur compound.
2. The process of claim 1 wherein said mixture comprises a cracked gas oil containing organic sulfur compounds.
3. A process for the extraction of an organic sulfur compound from a mixture thereof with hydrocarbons, which process comprises contacting said mixture with an ester of a thiolsulfonic acid containing 2 to 20 carbon atoms per molecule in liquid condition at a temperature between about  $-20^{\circ}$  C. and about  $150^{\circ}$  C., and separating a raffinate phase from an extract phase comprising said ester and said organic sulfur compound.
4. The process of claim 3 wherein said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.
5. The process of claim 3 wherein said mixture comprises a cracked gas oil containing organic sulfur compounds and said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.
6. The process of claim 3 wherein said mixture comprises essentially a saturated hydrocarbon and said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.
7. A process for the extraction of an organic sulfur compound from a mixture thereof with hydrocarbons, which process comprises contacting said mixture with an ester of a thiolsulfonic acid containing 2 to 20 carbon atoms per molecule in liquid condition, separating a raffinate layer from an extract layer containing said ester

and said sulfur compound, selectively extracting said ester from said extract layer with an aqueous extractant at a temperature between about 20 and about  $100^{\circ}$  C. to produce an aqueous ester, drying said aqueous ester and recycling the resultant dried ester to further contact with said mixture.

8. The process of claim 7 wherein said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.

9. The process of claim 7 wherein said mixture comprises a cracked gas oil and said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.

10. A process for the extraction of a cognate organic sulfur compound from its mixture thereof with a hydrocarbon, which process comprises contacting said mixture in the absence of a strongly alkaline metal hydroxide with an ester of a thiolsulfonic acid containing 2 to 20 carbon atoms per molecule, and separating a refined, substantially desulfurized hydrocarbon liquid layer from an insoluble extract liquid layer comprising said ester and said organic sulfur compound.

11. The process of claim 10 wherein said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.

12. The process of claim 10 wherein said mixture comprises a cracked gas oil containing organic sulfur compounds and said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.

13. The process of claim 10 wherein said mixture comprises a sweetened gasoline.

14. The process of claim 10 wherein said mixture comprises a sweetened gasoline and said ester has the formula  $R_1SO_2-SR_2$  wherein  $R_1$  and  $R_2$  are alkyl radicals containing 1 to 4 carbon atoms.

15. The process of claim 10 wherein said mixture comprises a thioether.

16. The process of claim 10 wherein said mixture comprises a disulfide.

WILLIAM F. WOLFF.  
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