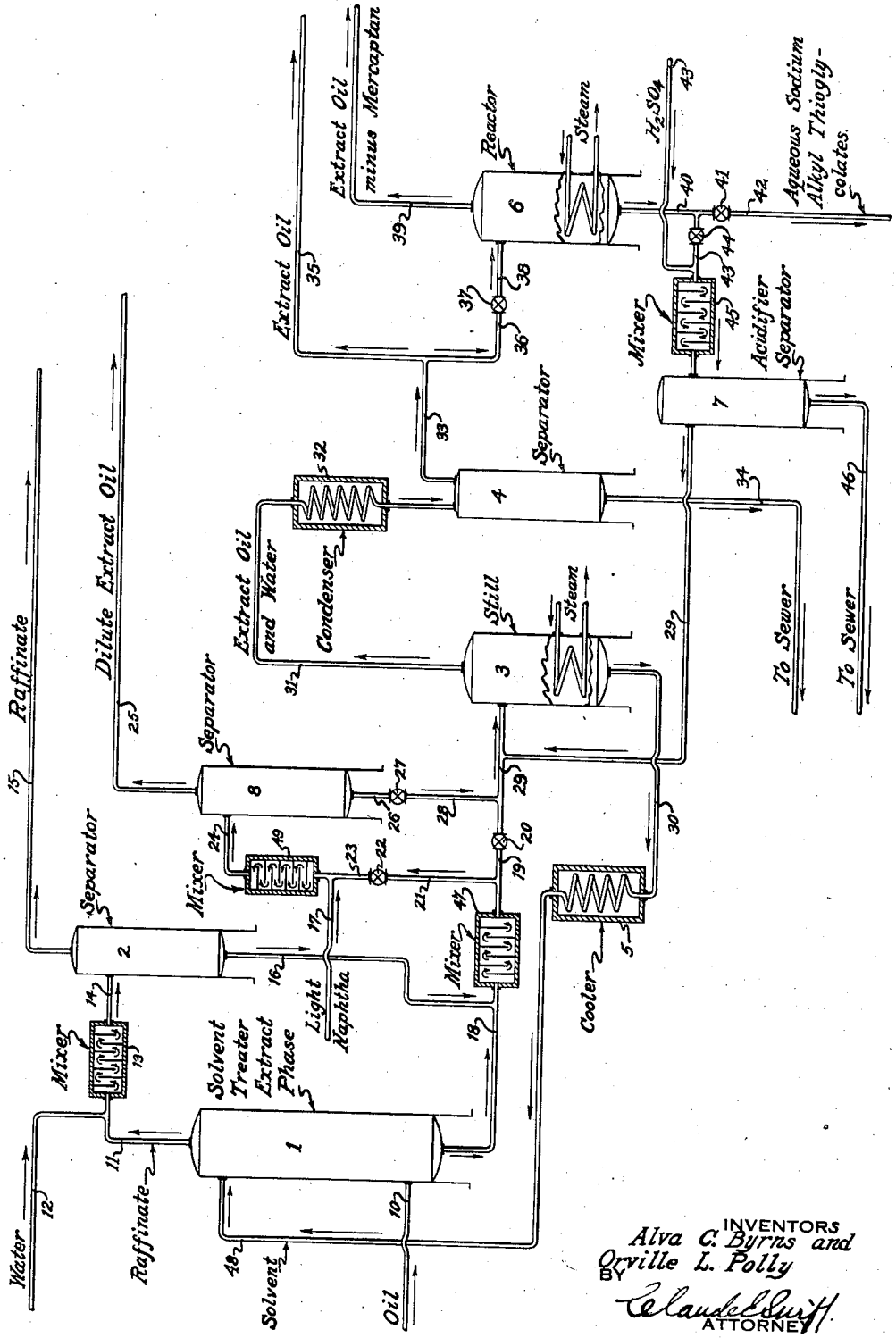
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SOLVENT EXTRACTION OF MINERAL OILS

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SOLVENT EXTRACTION OF MINERAL OILS

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23 Claims. (Cl. 196—13)

This invention relates to the refining treatment of hydrocarbon fractions and has as one of its objectives removing sulfur compounds from petroleum or coal tar oils and distillates, or raffinates and extracts obtained from such materials by extraction with liquid sulfur dioxide or other solvents common to the art. More specifically, the invention is a process for preferentially extracting sulfur compounds and/or aromatic hydrocarbons from oils which are predominately olefinic, paraffinic or naphthenic and subsequently recovering the solvent and extracted oil.

The invention is for the fractionation of mineral oil with a new solvent which permits the separation of sulfur compounds and aromatics from olefins, paraffins and naphthenes. The solvent is practically inert chemically and its solvent power is readily controlled by addition or removal of water.

The current art of solvent extraction is toward purifying hydrocarbon oils by the removal of "undesirable" constituents rather than to the resolution of hydrocarbon systems into their typical components with a view to recovering intact the various types of substances separated. Thus it is common practice to treat oils with sulfuric acid. A less drastic treatment may be effected by the use of the lower alkyl sulfonic acids. In either case the extract phase is neither readily nor completely convertible to regenerated solvent and unaltered extract oil. Cracked distillates are particularly susceptible by virtue of their high content of olefins, thiophenes and aromatics which tend to be alkylated, polymerized and sulfonated even at temperatures of 0° C. Thus large losses of solvent and oil occur, and the recovery of valuable sulfur bodies or aromatics is not feasible.

It is clearly an advantage to use a solvent which is practically inert chemically, the solvent power of which can be readily adjusted and which is easily recovered from the extracted oil. We have found that compounds of the general type in which one or more carboxyl groups are substituted for hydrogen in thioethers, such as alkyl sulfides or thiophanes, are useful for preparing solvents with the above-mentioned desirable properties. More specifically, we use ethyl thioglycolic acid and/or its homologs, of which we prefer a mixture resulting from the acid hydrolysis of the reaction product of methyl, ethyl, propyl, butyl and amyl sodiomercaptides with sodium chloroacetate. Such a mixture of sodiomercaptides is usually available as refinery waste-alkali liquors which have been used to remove mercaptans from gasoline distillates.

The ethyl thioglycolic acid which we have produced boils at about 123° C. at 15 mm. pressure and has a specific gravity of 1.148 at 26° C.

The figure accompanying this specification shows a schematic method of carrying out the extraction of mineral oil with our novel solvent.

Referring to the figure, the oil to be extracted is introduced near the bottom of column 1 via line 10. The solvent is introduced near the top of column 1 via line 48. As the solvent passes downwardly through column 1 it dissolves a portion of the oil and eventually the solvent is withdrawn as the extract phase via line 18.

The raffinate phase is withdrawn from column 1 via line 11 and is then mixed with hot water introduced through line 12 in mixer 13. From mixer 13 the raffinate to which the hot water has been added passes to separator 2 where it is allowed to separate into two phases. The upper phase comprising chiefly refined raffinate is withdrawn from the system via line 15. The lower phase comprising most of the solvent originally contained in the fraction and the water introduced via line 12 is withdrawn via line 16 and is mixed with the extract phase recovered from column 1 through line 18 in mixer 47. In the event that the raw stock introduced into line 10 is a heavy material, such as lubricating oil, it is sometimes desirable to employ a light diluent to aid in the separation of the solvent from the extract. In this event the mixture from mixer 47 passes via line 21, valve 22 and line 23 into mixer 49 where it is mixed with light diluent, such as petroleum naphtha introduced by line 17. From mixer 49 the mixture passes through line 24 into separator 8. In separator 8 the mixture separates into two phases, the upper phase consisting chiefly of extract oil diluted with the light petroleum fraction. This phase is withdrawn from separator 8 through line 25. From the bottom of separator 8 an aqueous solution of the solvent is withdrawn through line 26, valve 27 and line 28 and then passed via line 29 into still 3. By the aid of steam introduced into still 3 the extract oil and water are then passed overhead as a distillate through line 31 into condenser 32 where these vapors are condensed and passed as liquids into separator 4. From the bottom of separator 4 the water is withdrawn through line 34 and discarded. From the top of separator 4 the extract oil is withdrawn through line 33 and then may either be withdrawn completely from the system via line 35 or, as an alternative, may be passed by line 36, valve 37 and line 38 to reactor 6 where it is mixed with a concentrated aqueous solution of an alkali, such as sodium hydroxide, containing some sodium alkyl thioglycolate, to extract the mercaptans present in the oil. The addition of sodium hydroxide to the oil containing the mercaptans forms sodium mercaptide which remains in the aqueous layer. The extract oil free from the mercaptans may be withdrawn via line 39

and the aqueous sodium mercaptide may then be heated with steam and reacted with sodium chloroacetate to form sodium alkyl thioglycolates according to the reaction:

$$RSNa + ClCH_2CO_2Na \rightarrow NaCl + RSCH_2CO_2Na$$

The aqueous solution of sodium alkyl thioglycolates in reactor **6** may be withdrawn through line **40**, valve **41** and line **42** from the system or, as an alternative, this aqueous solution may be diverted through valve **44**, line **43** into mixer **45** where it is mixed with sulfuric acid and then passed through separator **7**. In the bottom of separator **7** an aqueous solution of sodium sulfate is withdrawn through line **46** and is discarded. The top layer in separator **7**, which is largely alkyl thioglycolic acid and contains some water, is passed through line **29** into still **3** where the water is distilled off through line **31**.

The substituted thioglycolic acid recovered as the bottom fraction in still **3** is withdrawn therefrom through line **30** and is passed through cooler **5** and thence through line **48** back to the extraction column.

In the above description of the process we have described the auxiliary diluent introduced via line **17** into the mixture of extract oil and solvent in order to obtain optimum separation between the oil layer and the aqueous layer in separator **8**. In many instances it is unnecessary to use the auxiliary diluent to obtain proper phase separation between the water and the extract oil and in those cases we simply close valves **22** and **27** and open valve **20** to permit the mixture in mixer **47** to flow via line **19**, valve **20** and line **29** directly into still **3** where the solvent is separated from the extract oil in the manner described above.

Obviously, the extract oils or the raffinates may be subjected to a second stage of extraction by a repetition of the procedure we have outlined, by employing the solvent at the same or different concentrations.

The strength of acid employed as solvent will vary with the particular nature of the stock to be extracted. For example, it may be desirable to separate thiophenes from aromatics. We have found this to be possible with our method, but such a separation is more difficult than the separation of thiophenes or aromatics from olefins. In the former case we employ a relatively dilute acid. In any event the acid concentration used would not be below 40% by volume, with a preferred range of 50% to 90% acid by volume. In some cases it will be useful to incorporate a third component in the aqueous acid employed as solvent. Thus we may use a polar substance mutually soluble in both the water and alkyl thioglycolic acid, as for example only, ethylene glycol or the sulfone of our substituted mercaptoacetic acid, in order to modify the selectivity of the solvent. Such addition imposes no limitations on the procedure already proposed for operating our process.

As would be anticipated, lowering the operating temperature improves the selectivity of our solvent. However, since the selectivity is readily adjusted by varying the acid concentration we prefer to operate the process simply at atmospheric temperature but we do not wish to imply any restriction to such temperature of operation. For example, where the extraction is being applied to a wet stock, such as a gas oil distillate, it may be found advantageous to operate at a somewhat higher temperature than atmospheric, to offset the effect of dilution of the solvent. On the other hand, conditions may obtain where it is desired to employ substantially anhydrous alkyl thioglycolic acid at a temperature sufficiently low to produce phase separation.

The action of this solvent, when applied to the treatment of olefinic gasolines, is illustrated by the following examples, which in themselves are not intended to delineate or limit the general application of our process in any way.

Example 1

A 100 ml. sample of cracked gasoline of 51.3° A. P. I. and containing 3.46% sulfur was agitated two minutes with 50 ml. of a mixture of 80% ethyl thioglycolic acid in water at room temperature (about 70° F.) and allowed to settle two minutes. The extract was drawn off, treated with water, and the extract oil recovered.

A second 100 ml. sample was treated twice consecutively with 50 ml. of 80% acid, as outlined above.

A third 100 ml. sample was treated three times with 50 ml. portions of 80% acid, as above. The raffinites from each run were washed with water until neutral and analyzed for sulfur. The results are presented in the following table:

Table I

Volume of solvent per cent of oil volume	Volume per cent yield of raffinate	Weight per cent sulfur in raffinate	Weight per cent sulfur extracted
0	----------	3.46	----------
50	97.5	3.15	11.6
100	93.0	3.0	19.8
150	91.5	2.47	35.4

The raffinates were improved in color and odor.

Example 2

A series of batchwise extractions similar to those above were made with 100 ml. of a heavier cracked distillate of 41.2° A. P. I. gravity containing 3.6% sulfur. At the end of the sixth stage, using 50 ml. of 80% ethyl thioglycolic acid at each stage, the sulfur content of the washed raffinate was 2.57%, and 21.5% of the oil had been removed as extract, for which an analysis showed 10.6 weight percent sulfur.

Example 3

The specificity of the solvent is shown by the percentage increase above the original volume of solvent when the solvent is shaken with an equal volume of a 20% blend of the indicated substance in hexane. The results are tabulated below:

Table II

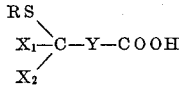
	Acid concentration per cent ethyl thioglycolic acid in water			
	84	91	95	98
	Per cent increase in volume of solvent layer			
2,5; dimethyl thiophene	8	16	26	100
Crude xylene	8	14	24	100
C_6 thiophane	8	13	20	60
Di-isobutylene	4	8	12	22
Methyl cyclohexane	2	8	12	20
Pure hexane	4	8	10	20

The solubilities of the above substance fall into two well defined classes; thiophenes, thiophanes and aromatics, versus olefins, naphthenes and paraffins at each concentration of solvent. Greater specificity is shown by the more dilute solvents.

The invention may then be described as residing in the use of a novel solvent for the separation of oil into fractions. More specifically, the invention may be stated as residing in the use of a mercapto-substituted carboxylic acid containing one or more carboxyl groups, as for example, the compound may be a mercapto-substituted mono carboxylic acid, such as butyric or propionic acid or it may be a mercapto-substituted poly carboxylic acid, such as succinic acid or adipic acid.

Furthermore, while we have specifically shown that ethyl thioglycolic acid and its homologs, methyl, propyl, butyl and amyl thioglycolic acids or mixtures thereof, may be used, it is to be understood that we may also use thioglycolic acids in which the alkyl group specified above may be substituted by aryl groups or aralkyl groups.

Our invention also embraces mercapto carboxylic acids of the following type:



Where X_1 and X_2 are alkyl groups, unsaturated radicals derived from alkyl groups by loss of hydrogen, aralkyl groups, hydrogen, carboxylic groups, heterocyclic rings or RS groups the same or different from the RS— groups shown and where R represents an alkyl, aralkyl, carbocyclic or heterocyclic group, or an unsaturated radical derived from an alkyl group by loss of hydrogen and Y represents $(CH_2)_n$ where $n=0$ or an integer which may be as high as 5 or higher.

The above is simply descriptive of the scope of our invention it is not to be understood as to be limiting the novel process and solvent which we have discovered.

We claim:

1. A process for the separation of mineral oil into fractions which comprises extracting said oil with a mercapto-substituted carboxylic acid thereby forming a raffinate phase and an extract phase and separating said phases.

2. A process for the extraction of mineral oil which comprises commingling said oil with an alkyl thioglycolic acid thereby forming a raffinate and an extract phase and separating said phases.

3. A process for the extraction of mineral oil which comprises commingling said oil with a substituted mercapto acetic acid, settling the mixture of oil and a substituted mercapto acetic acid thereby forming an upper raffinate phase and a lower extract phase and separating said phases.

4. A process for the fractionation of a mineral oil which comprises mixing said oil with ethyl thioglycolic acid and thereby forming a raffinate phase and an extract phase and separating said phases.

5. A process for the separation of mineral oil which comprises commingling said oil with a mixture of alkyl thioglycolic acids of different molecular weights thereby forming a raffinate phase and an extract phase and separating said phases.

6. A process for the separation of sulfur compounds from petroleum stocks containing said sulfur compounds and one of the members selected from the group consisting of paraffins, naphthenes and olefins which comprises commingling said stock with a substituted thioglycolic acid containing an organic substituent thereby dissolving the sulfur compounds contained therein and separating the solution of sulfur compounds from the remaining stock.

7. A process for the fractionation of a mixture containing sulfur compounds and olefins which comprises commingling said mixture with an alkyl thioglycolic acid and thereby forming a raffinate phase containing the olefins and an extract phase containing the sulfur compounds and separating said phases.

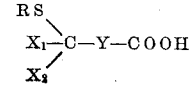
8. A process for the separation of aromatics from olefins which comprises commingling a mixture containing said compounds with an alkyl thioglycolic acid thereby forming a raffinate phase containing one of said compounds and an extract phase containing the other of said compounds and separating said phases.

9. In the process of extracting oil into fractions with a selective solvent comprising an alkyl thioglycolic acid the step of regulating the solvent power of the solvent by the addition to the solvent of an agent adapted to modify the solvent power of the solvent for certain constituents of the oil.

10. A process according to claim 9 in which the agent employed is water.

11. A process for the separation of a hydrocarbon mixture into fractions of different character, which comprises commingling said mixture with a selective solvent comprising a sulfur compound of the class consisting of thioethers, alkyl sulfides and thiophanes in which at least one carboxyl group is substituted for a hydrogen group, and thereby forming two liquid phases from which hydrocarbon fractions may be recovered.

12. A process for the separation of a hydrocarbon mixture into fractions of different character, which comprises commingling said mixture with a selective solvent so as to form two phases, separating said phases from each other, and separating a hydrocarbon fraction from each of said phases; said selective solvent comprising a mercapto-substituted carboxylic acid having the general formula



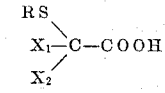
where X_1 and X_2 are alkyl groups, unsaturated radicals derived from alkyl groups by loss of hydrogen, aralkyl groups, hydrogen, carboxylic groups, heterocyclic rings or RS groups the same or different from the RS groups shown and where R represents an alkyl, aralkyl, carbocyclic or heterocyclic group, or an unsaturated radical derived from an alkyl group by loss of hydrogen, and Y represents $(CH_2)_n$, where $n=0$ or an integer.

13. A process according to claim 12 in which the selective solvent comprises a mercapto-substituted mono-carboxylic acid from the class consisting of acetic, propionic and butyric acid.

14. A process according to claim 12 in which the selective solvent comprises an alkyl thioglycolic acid having the general formula RS—CH_2—COOH, where R is an alkyl group from the class consisting of methyl, ethyl, propyl, butyl and amyl.

15. A process according to claim 12 in which

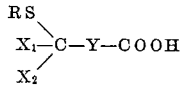
the selective solvent comprises an alkyl thioglycolic acid having the general formula



in which R is an alkyl group from the class consisting of methyl, ethyl, propyl, butyl and amyl, and X_1 and X_2 are hydrogen or alkyl groups from the class consisting of methyl, ethyl, propyl, butyl, and amyl.

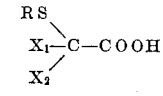
16. A process according to claim 12 in which the selective solvent is an aqueous solution containing between about 50% and about 90% of ethyl thioglycolic acid having the formula $CH_3—CH_2—S—CH_2—COOH$.

17. A process for the separation of a hydrocarbon mixture containing organic sulfur compounds, which comprises commingling said mixture with a selective solvent so as to form an extract phase containing a hydrocarbon extract fraction richer in said organic sulfur compounds, and a raffinate phase containing a hydrocarbon raffinate fraction poorer in said organic sulfur compounds, separating said extract phase from said raffinate phase, and recovering said hydrocarbon fractions from each phase; said selective solvent comprising a mercapto-substituted carboxylic acid having the general formula



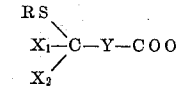
where X_1 and X_2 are alkyl groups, unsaturated radicals derived from alkyl groups by loss of hydrogen, aralkyl groups, hydrogen, carboxylic groups, heterocyclic rings or RS groups the same or different from the RS groups shown and where R represents an alkyl, aralkyl, carbocyclic or heterocyclic group, or an unsaturated radical derived from an alkyl group by loss of hydrogen, and Y represents $(CH_2)_n$, where $n=0$ or an integer.

18. A process according to claim 17 in which the selective solvent comprises an alkyl thioglycolic acid having the general formula



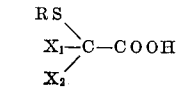
in which R is an alkyl group from the class consisting of methyl, ethyl, propyl, butyl and amyl, and X_1 and X_2 are hydrogen or alkyl groups from the class consisting of methyl, ethyl, propyl, butyl, and amyl.

19. A process for the separation of a hydrocarbon mixture containing aromatic type hydrocarbons, which comprises commingling said mixture with a selective solvent so as to form an extract phase containing a hydrocarbon extract fraction richer in said aromatic type hydrocarbons, and a raffinate phase containing a hydrocarbon raffinate fraction poorer in said aromatic type hydrocarbons, separating said extract phase from said raffinate phase, and recovering said hydrocarbon fractions from each phase; said selective solvent comprising a mercapto-substituted carboxylic acid having the general formula



where X_1 and X_2 are alkyl groups, unsaturated radicals derived from alkyl groups by loss of hydrogen, aralkyl groups, hydrogen, carboxylic groups, heterocyclic rings or RS groups the same or different from the RS groups shown and where R represents an alkyl, aralkyl, carbocyclic or heterocyclic group, or an unsaturated radical derived from an alkyl group by loss of hydrogen, and Y represents $(CH_2)_n$, where $n=0$ or an integer.

20. A process according to claim 19 in which the selective solvent comprises an alkyl thioglycolic acid having the general formula



in which R is an alkyl group from the class consisting of methyl, ethyl, propyl, butyl and amyl, and X_1 and X_2 are hydrogen or alkyl groups from the class consisting of methyl, ethyl, propyl, butyl, and amyl.

21. A process according to claim 17 in which the organic sulfur compounds include mercaptans, and a portion of said mercaptans is recovered from the hydrocarbon extract fraction and converted to a mercapto-substituted carboxylic acid which may be employed as a selective solvent.

22. A process for the separation of sulfur compounds from petroleum stocks containing said sulfur compounds and one of the members selected from the group consisting of paraffins, naphthenes and olefins which comprises commingling said stock with a substituted thioglycolic acid containing a hydrocarbon constituent thereby dissolving the sulfur compounds contained therein and separating the solution of sulfur compounds from the remaining stock.

23. A process according to claim 1 in which the hydrocarbon group attached to the S atom of the mercapto substituent group is selected from the class consisting of alkyl, aryl, and aralkyl groups.

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