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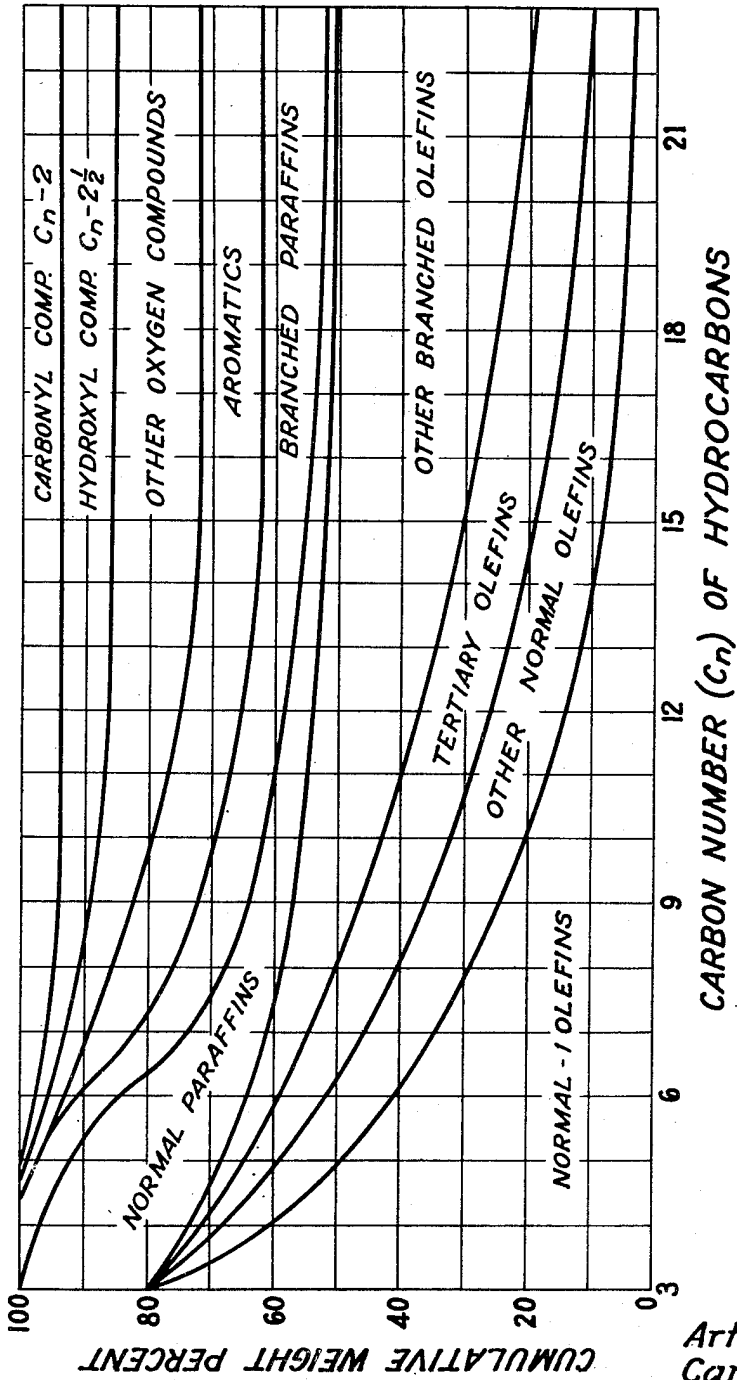
A. A. HARBAN ET AL

2,522,619

EXTRACTION OF OXYGENATED COMPOUNDS

Filed Sept. 30, 1949

2 Sheets-Sheet 1



COMPOSITION OF ALKALI WASHED HCS LIQUID

Fig. 1

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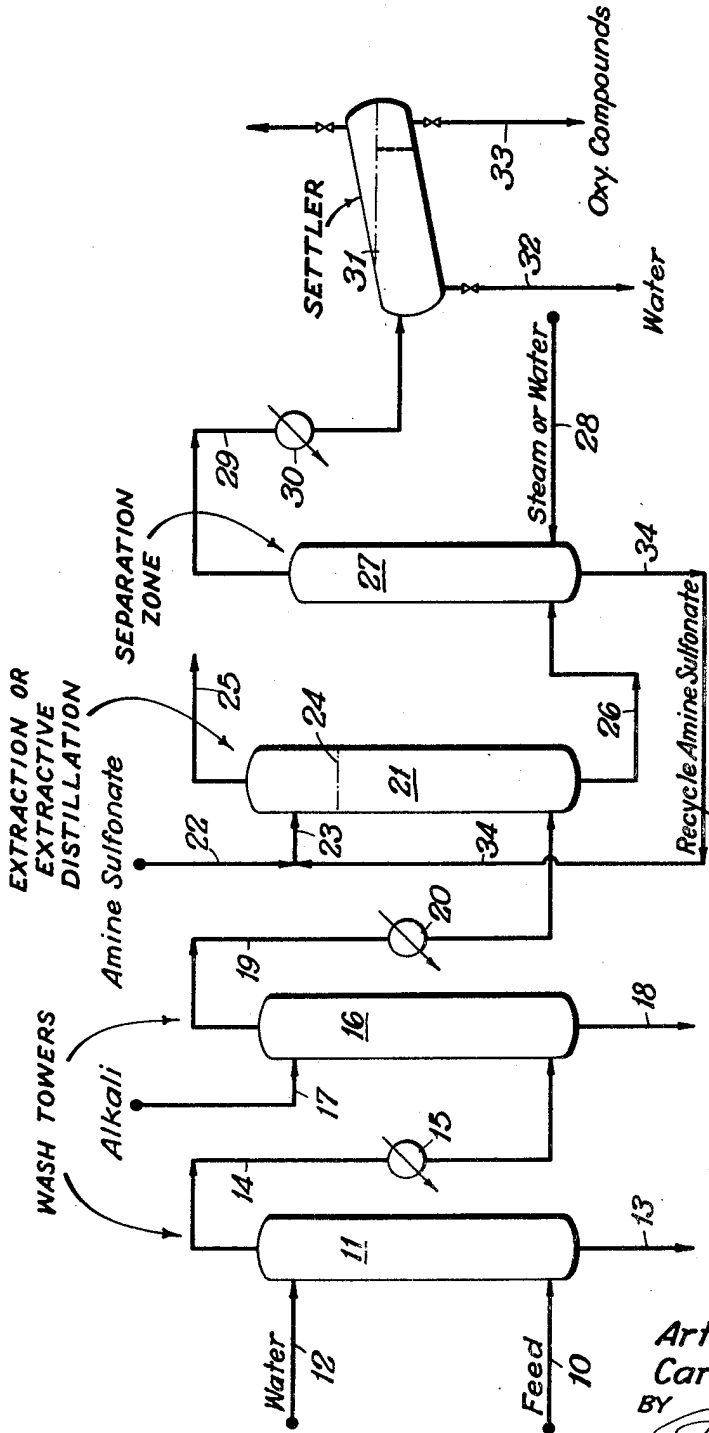


Fig. 2

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# UNITED STATES PATENT OFFICE

2,522,619

## EXTRACTION OF OXYGENATED COMPOUNDS

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Application September 30, 1949, Serial No. 113,746

15 Claims. (Cl. 260—450)

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This invention relates to the extraction of oxygenated compounds from mixtures thereof with aliphatic hydrocarbons. More particularly, this invention relates to processes for the selective extraction of oxygenated organic compounds, particularly neutral oxygenated organic compounds, from oils comprising aliphatic hydrocarbons by the employment of certain amine salts of sulfonic acids as selective extraction solvents.

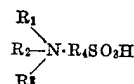
We have discovered that certain amine sulfonates are surprisingly effective selective solvents for neutral, oxygenated organic compounds, as well as aromatic hydrocarbons and sulfur compounds, in admixture with aliphatic hydrocarbons, e. g., certain natural or synthetic hydrocarbon oil fractions. We have further found that said amine sulfonates can be prepared relatively cheaply, have relatively low toxicity, and have relatively mild corrosive properties, which permits their employment in conventional equipment. The amine sulfonate solvents employed in the process of the present invention 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 enable them to be employed as selective extraction solvents for various oxygenated compounds at readily attainable temperatures and pressures. Moreover, said amine sulfonates are characterized by surprisingly great thermal stability, which permits their use in high temperature extraction processes such as extractive distillation processes.

It is an object of this invention to provide a process for the selective extraction of neutral, oxygenated organic compounds from their mixtures with aliphatic hydrocarbons, including both acyclic and alicyclic hydrocarbons which may be completely saturated or may contain one olefinic unsaturation per molecule. Another object of this invention is to provide a process for the selective extraction of one or more neutral, oxygenated, oil-soluble organic compounds, such as alcohols, ethers, aldehydes, ketones, esters, lactones, acetals and the like having at least 4 carbon atoms in the molecule, from their solutions in hydrocarbon oils, such as the solutions produced by the catalytic reduction of carbon monoxide (HCS or Hydrocarbon Synthesis process), solutions produced by the modified HCS process known as the Synol process, solutions produced by the oxidation of various aliphatic hydrocarbon fractions, or from hydrocarbon fractions derived from shale oils. Another object of this invention is to provide the art of selective extrac-

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tion of oxygenated compounds with novel solvents, viz., certain amine sulfonates. An additional object of our invention is to provide solvents for selective extraction processes characterized by high selectivity for neutral, oxygenated organic compounds, aromatic hydrocarbons and 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 a novel selective extraction process. These and other objects of our invention will be readily discerned from the ensuing description thereof and from the appended figures.

The novel solvents employed in the selective extraction process of this invention are amine sulfonates having the general formula:



wherein  $R_1$  and  $R_2$  are selected from the class consisting of hydrogen and saturated hydrocarbon radicals,  $R_3$  is a saturated hydrocarbon radical, and  $R_4$  is selected from the class consisting of saturated hydrocarbon radicals and aromatic hydrocarbon radicals.

Thus, the saturated hydrocarbon radicals may be alkyl radicals, cycloalkyl radicals, cycloalkyl-alkyl and aralkyl radicals. The amine sulfonate solvents of this invention contain between 4 and 20 carbon atoms, inclusive, per molecule.

Examples, given by way of illustration and not necessarily for limitative purposes, of suitable alkyl radicals are: methyl, ethyl, n-propyl, isopropyl, n-butyl, amyl, octyl, nonyl, hexadecyl and octadecyl.

Illustrative examples of suitable cycloalkyl radicals include cyclopentyl, methylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, ethylcyclopentyl, endomethylene-cyclohexyl (bicyclo[2,2,1]heptyl) and 2-methyl-bicyclo[2,2,1]heptyl.

Examples of suitable cycloalkyl-alkyl radicals include cyclohexylmethyl, cyclohexylethyl, cyclopentylpropyl, and the like.

Examples of suitable aralkyl radicals in the above general formula include benzyl, 2-phenylethyl, 2-phenylpropyl, w-xyllyl, naphthomethyl and the like.

$R_4$  may be an alkyl, cycloalkyl, cycloalkyl-alkyl, aralkyl, aryl, alkaryl or cycloalkyl-aryl radical. Examples of suitable  $R_4$  aryl radicals include phenyl, naphthyl and derivatives containing nonclearly-substituted chlorine atoms, etc.

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Examples of suitable R<sub>4</sub> alkaryl radicals for substitution in the above general formula are tolyl, xylyl, dimethylphenyl, ethylphenyl, isopropylphenyl, butylphenyl, methylnaphthyl, dimethylnaphthyl, and the like.

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

Certain properties of some of the amine sulfonates which are useful for the purposes of the present invention are shown in the following table:

TABLE I

Amine Radical	Sulfonic Acid Radical	Melting Point, °C.
Triethylamine.....	Methane.....	35
Do.....	Ethane.....	43
Mono-n-butylamine.....	do.....	40-60
Tri-n-butylamine.....	do.....	40-60
Triethylamine.....	Mixed C <sub>1</sub> -C <sub>4</sub> .....	-48
Mono-n-butylamine.....	do.....	30-60

We have found that equal volumes of the salts of Table I and the following solvents are miscible at 20-25° C.: methanol, 95% ethanol, acetone and benzene, and that the salts are insoluble in hexane.

We have discovered that certain triethylamine sulfonates are particularly desirable for the purposes of the present invention because they are relatively non-viscous, non-volatile liquids at normal temperatures, exhibit high selectivity for neutral, oxygenated organic compounds, aromatic hydrocarbons and sulfur compounds, and are characterized by relatively little change in viscosity with temperature. Certain properties of triethylamine salts of the lower alkanesulfonic acids which are particularly desirable for employment in the claimed process are set forth in Tables II and III.

TABLE II

*Properties of triethylamine salts of alkanesulfonic acids*

Sulfonic Acid	d <sub>4</sub> <sup>20</sup>	Viscosity, SSU <sup>1</sup>			V. I.	Pour Point, °F.	Flash Point, °F.
		100° F.	130° F.	210° F.			
Methane.....	1.120	256.7	144.7	53.9	127	-70	415
Ethane.....	1.100	259.6	143.8	54.4	128	-45	430
Mixed (C <sub>1</sub> -C <sub>4</sub> )	1.108	274.4	143.1	55.1	126	-55	400

<sup>1</sup> Period of efflux in seconds from Saybolt Universal viscosimeter.

TABLE III

*Effect of added water on the viscosity of triethylamine (C<sub>1</sub>-C<sub>4</sub>) alkanesulfonates*

	0% H <sub>2</sub> O	2% H <sub>2</sub> O	5% H <sub>2</sub> O	20% H <sub>2</sub> O
Vis. at 100° F., SSU.....	274.4	245.0	174.9	71.5
Vis. at 130° F., SSU.....	143.1	128.3	100.2	51.6
Vis. at 210° F., SSU.....	55.1	52.8	47.7	35.5
Viscosity Index.....	126	126.5	133.5	21.8
Pour Point, °F.....	-55	-50	-50	-65

The amine sulfonates defined by the above general formula are either normally liquid or relatively low melting solids and may be used for the purposes of the present invention without auxiliary solvents or diluents. However, because of

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their solubility in water, methanol, ethanol, etc., it may be desirable to employ the amine sulfonate solvents of the present invention together with more or less of such diluents or co-solvents, to modify the selectivity of the amine sulfonates, lower their melting point, 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 amine sulfonate will be employed. If desired, the amine sulfonates may be employed together with between about 1 and about 20 per cent of sulfonic acid, preferably the sulfonic acid that is combined in the amine sulfonate.

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, solution or vapor. The present invention, therefore, relates to liquid-liquid or liquid-vapor extraction processes employing the above defined amine sulfonate solvents. When the feed stock is charged to the process as a vapor, the process is one of extractive distillation.

By the term "extraction," as employed in the appended claims, it is intended to include not only liquid-liquid extraction processes, but also extractive distillation processes employing the above defined solvents. It is well appreciated that these processes differ somewhat from each other in efficiency or applicability in specific instances, but they are actually and theoretically related (note, for example, H. J. Hibshman, Ind. Eng. Chem. 41, 1366 (1949)).

In general, the extraction operations of the present invention are conducted at temperatures between about -20° C. and about 180° C., the particular extraction temperature depending upon the specific amine sulfonate 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 neutral, oxygenated organic compound content of the feed stock, the temperature of operation, and desired efficiency, but will generally fall within a range of about 0.1 to about 10 volumes of amine sulfonate per volume of charging stock. In liquid-liquid extraction, sufficient pressure is maintained upon the system to keep the feed stock in the liquid phase. 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 be determined readily. When the feed stock is to be employed in the vapor phase, suitable pressures at which the feed stock will be a vapor at the extraction temperature can be determined readily.

Certain hydrocarbon oil fractions derived from petroleum, coal, shale, etc., are known to contain neutral, oxygenated organic compounds. It is desired in numerous instances to remove these compounds in order to produce refined hydrocarbon oils. Such oils may boil within the boiling range of gasoline, naphtha, kerosene, gas oil, heater oil, or lubricating oil stocks. The process of the present invention is particularly applicable to the refining of gasoline boiling range hydrocarbon oils containing neutral, oxygenated organic compounds, and to such oils containing a substantial proportion of mono-olefinic hydrocarbons, as in the case of synthetic gasoline or

naphtha boiling range fractions derived from the Hydrocarbon Synthesis (HCS) process, especially when alkalized iron catalysts are employed in said process.

In the HCS process, carbon monoxide is reduced by hydrogen to produce a variety of gaseous, liquid and solid hydrocarbons in the presence of eighth group metal catalysts, particularly iron, cobalt and nickel catalysts. The synthetic gas, consisting essentially of a mixture of carbon monoxide and hydrogen, is produced by partial oxidation of natural gas or other hydrocarbon gas, suitable operating conditions being, for example, a temperature of about 2500° F. and a pressure of about 250 p. s. i. g. Synthesis gas may also be produced by conventional processes of reforming natural gas with steam in the presence of a catalyst; when desired, both the oxidation and reforming processes may be employed to generate synthesis gas. The H<sub>2</sub>:CO ratio in the synthesis gas may be adjusted as desired, usually to a ratio between about 2:1 and about 5:1 in the reactor. A variety of iron-containing catalysts may be employed. The catalysts may be prepared by the reduction of fused iron oxides, mill scale, or pyrites-ash, and may be sintered before or after reduction to obtain improved activity and life. The iron catalysts are suitably promoted by small amounts of alkali metal components such as KOH, K<sub>2</sub>CO<sub>3</sub>, KF or the corresponding sodium compounds. A suitable catalyst, for example, is the commercial ammonia synthesis catalyst frequently employed in the United States, known as the C. C. C. catalyst; essentially this catalyst is iron promoted by small amounts of alkali. Synthesis can be effected in reactors utilizing a fluidized iron catalyst bed at temperatures between about 450 and about 700° F. and pressures between about 200 and about 500 p. s. i. g.

Among the hydrocarbon products produced in the above-described synthesis operation are olefinic hydrocarbon fractions which contain paraffin hydrocarbons of approximately the same carbon number and boiling range and, in addition, a substantial amount of preferentially oil-soluble, neutral oxygen-containing organic compounds such as aldehydes, ketones, esters, lactones, acetals, ethers, alcohols, and the like, having at least 4 carbon atoms in the molecule. The oxygenated compounds present in the above-mentioned HCS olefin hydrocarbon fractions cannot be removed to any satisfactory degree by simple washing with water, alkalies, or specific group reagents, for example, aqueous sodium bisulfite for the removal of carbonyl compounds.

The proportion, and possibly to some extent the nature of the oxygenated compounds produced in the iron-catalyzed HCS process, will naturally depend upon and vary with the specific catalyst, catalyst age and operating conditions employed.

The olefinic hydrocarbon content of the normally liquid HCS olefin fractions often ranges between about 50 and about 75 percent by weight and the concentration of oxy compounds ranges from about 5 to about 30 weight percent.

A range of representative compositions of alkali washed HCS fractions, obtained by the treatment of water gas with an alkalized iron catalyst at a temperature of about 600-660° F. and a pressure of about 250 p. s. i. g. in a fluidized bed reactor employing a space velocity of 5 standard cubic feet per hour of CO in fresh feed per pound of iron is shown in Figure 1.

In typical operations with an alkalized iron catalyst derived by reduction of pyrites, oxygenated compounds were found to total between 5 and 8 percent by weight of the oil stream and to comprise about 65% of carbonyl compounds, 30% of alcohols and 5% of carboxylic acids, mostly in the C<sub>5</sub>-C<sub>12</sub> range. The C<sub>6</sub>-7-8 alcohols and carbonyl compounds were present in largest quantities.

The selective extraction process of the present invention is not limited in its application to HCS product fractions containing neutral, oxygenated organic compounds. Thus, the process of the present invention may be applied to products derived from the so-called Synol process (B. H. Weil and J. C. Lane, "Synthetic Petroleum from the Synthine Process," Chemical Publishing Co., 1948, pages 154 and 273). The Synol process is a modified HCS process employing a highly active iron catalyst, a typical catalyst comprising iron, 3.5% alumina based on the weight of iron and 0.15 to 0.5% of K<sub>2</sub>O. A water gas charging stock is converted in the presence of this type of catalyst to straight chain terminal alcohols having molecular weights as high as C<sub>20</sub> and to olefinic hydrocarbons. The concentration of alcohol and olefins in the Synol product may reach 70 to 80% in which as much as 60% may be alcohols, together with small proportions of esters, aldehydes and ketones. Operations are usually effected at 180 to 200° C. and 18 to 30 atmospheres, employing 2,000 to 3,000 volumes per hour of water gas per volume of catalyst in recycle fixed bed operation. The application of the selective extraction process of the present invention to Synol process reaction products makes possible the segregation of oxygenated compounds, particularly the alcohols on the one hand, and olefins, on the other hand. This type of separation is very difficult to achieve by the employment of solvents other than the amine sulfonates, because conventional solvents extract both olefins and oxygenated compounds and, furthermore, acidic solvents such as phosphoric acid and sulfuric acid enter into reaction with the olefins causing the formation of alkyl sulfates and/or olefin polymers.

The selective extraction process of the present invention may also be applied to hydrocarbon oil fractions containing neutral, oxygenated organic compounds derived by thermal or catalytic oxidation of hydrocarbon charging stocks such as naphtha, kerosene, gas oil and other hydrocarbon oil fractions. These processes are well known and some are in actual operation. The separation of neutral, oxygenated organic compounds from fractions produced by the oxidation of hydrocarbons presents a difficult problem to which considerable research has been addressed (note for example J. A. Camelford, U. S. Patent 2,348,191, patented May 9, 1944).

Reference is made to the following examples, which are intended to illustrate, but not necessarily to limit, the process of the present invention.

#### EXAMPLE 1

A mixture of isomeric nonyl alcohols was prepared by subjecting an isobutylene-n-butylene codimer to the OXO process, i. e. to treatment in the liquid phase with a cobalt catalyst and an equimolar mixture of carbon monoxide and hydrogen at a temperature of about 175° C. and a pressure of about 3000 p. s. i., followed by treatment of the intermediate C<sub>9</sub> aldehyde product

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with hydrogen in the presence of a cobalt hydrogenation catalyst at a temperature of about 250° C. and a pressure of about 800 p. s. i. g. A mixture was prepared containing 0.5 volume of the isomeric nonyl alcohols thus prepared and 0.5 volume of n-dodecane. This mixture was mechanically agitated with an equal volume of the triethylamine salt of a mixture of C<sub>1</sub>-C<sub>4</sub> alkanesulfonic acids at 25° C. for a period of 15 minutes, following which agitation was discontinued and the mixture allowed to separate by gravity into a lower extract layer and a supernatant raffinate layer. The two liquid layers were separated by decantation and the extract layer was then diluted with about an equal volume of water at room temperature, following which the aqueous extract was subjected to steam distillation. The extract amounted to 1.60 volumes and the raffinate or hydrocarbon phase to 0.40 volume. The following data were obtained.

TABLE IV

*Extraction of nonyl alcohols-n-dodecane mixture with triethylamine alkanesulfonates*

	$n_D^{20}$	Volume percent	Percent Alcohol
Nonyl Alcohol.....	1.4334		
n-Dodecane.....	1.4218		
50/50 Feed mixture.....	1.4268	100	50
Raffinate.....	1.4220	40	10
Extract.....	1.4297	60	77

Percent of alcohol extracted from 50% soln.=84.  
Percent of dodecane extracted from 50% soln.=28.

## EXAMPLE II

One volume of a mixture containing 0.5 volume of n-heptane and 0.5 volume of diethyl ketone was mechanically agitated with an equal volume of the triethylamine salt of ethanesulfonic acid at 25° C. for 15 minutes, following which the mixture was allowed to separate by gravity into extract and raffinate layers which, in turn, were separated from each other by decantation. The volume of the extract layer was 1.27 and of the hydrocarbon or raffinate phase was 0.73. The following data were obtained:

TABLE V

*Extraction of diethyl ketone-n-heptane mixture with triethylamine ethanesulfonate*

	$n_D^{20}$	$d_4^{20}$	Volume percent	Percent Ketone
Diethyl Ketone.....	1.3948	0.814		
n-Heptane.....	1.3882	0.682		
50/50 Feed Mixture.....	1.3901	0.748	100	50
Raffinate.....	1.3886	0.727	73	34
Extract.....	1.3933	0.793	27	89

Percent of ketone extracted from 50% soln.=45.0.  
Percent of heptane extracted from 50% soln.=8.0.

## EXAMPLE 3

An HCS operation was effected by treating an equimolar mixture of carbon monoxide and hydrogen with an alkalinized iron catalyst at 600-660° F. and 250 p. s. i. g. and the hydrocarbon product was washed with alkali and then fractionated to separate a fraction boiling in the range of 126 to 151° C. consisting essentially of hydrocarbons containing, on the average, 9 carbon atoms per molecule and neutral, oxygenated organic compounds containing, on the average, 7 carbon atoms per molecule. This fraction contained 40 to 50 weight percent of olefins and 15

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to 20 weight percent of neutral, oxygenated organic compounds, comprising principally alcohols and carbonyl compounds. One volume of said HCS liquid hydrocarbon fraction was mechanically agitated at 25° C. for 15 minutes with one volume of the triethylamine salt of a mixture of C<sub>1</sub>-C<sub>4</sub> alkanesulfonic acids, following which the mixture was allowed to separate by gravity into extract and raffinate layers. The extract layer amounted to 1.16 volumes and the hydrocarbon or raffinate layer amounted to 0.84 volume. The liquid layers were separated by decantation and the solute in the extract layer was recovered by dilution with about an equal weight of water followed by steam distillation and separation of distilled oxygenated compounds by condensation and settling from water passing overhead from the steam still. Ultimate analyses were made of the charging stock, the extract and the raffinate layers, the results being given in the following table. On the basis of this data, 62.5 weight percent of the oxygen compounds in the charging stock were extracted from the HCS liquid fractions, which originally contained 11.1 weight percent of neutral, oxygenated organic compounds. The concentration of oxygenated compounds in the extract layer was 40.2 weight percent and in the raffinate layer was 4.8 weight percent.

TABLE VI

	Analyses and Material Balance for Process					
	Charge—75.63 g.		Raffinate—63.03 g.		Extract—12.67 g.	
	Weight, Percent	Weight, g.	Weight, Percent	Weight, g.	Weight, Percent	Weight, g.
Carbon....	84.85	64.15	85.65	53.96	81.48	10.33
Hydrogen....	13.65	10.32	13.89	8.75	12.82	1.64
Oxygen....	1.54	1.16	0.67	0.42	5.55	0.70
Total....	100.04	75.63	100.21	63.03	99.85	12.67

- (1) 75.63 g. material charged—75.70 g. material recovered.
- (2) 64.15 g. carbon charged—64.29 g. carbon recovered.
- (3) 10.32 g. hydrogen charged—10.39 g. hydrogen recovered.
- (4) 1.16 g. oxygen charged—1.12 g. oxygen recovered.

An illustrative process flow and suitable operating equipment are schematically depicted in Figure 2, from which various valves, pumps, heat exchangers, etc. have been eliminated in the interests of simplicity. Referring now to Figure 2, a charging stock for example an HCS liquid fraction boiling in the gasoline or naphtha range and containing carboxylic acids as well as neutral, oxygenated organic compounds, monoolefinic hydrocarbons, paraffinic hydrocarbons and small proportions of aromatic hydrocarbons, is passed through valved line 10 into the lower portion of a washing tower 11 wherein it flows countercurrently to a stream of water introduced by line 12 into the upper portion of tower 11. The tower may be provided with suitable packing or spacing materials as is conventional in the liquid-liquid extraction art. The water extraction operation may be conducted at room temperature or slightly elevated temperatures up to about 75° C., in order to remove preferentially water-soluble oxygenated compounds from the charging stock. The aqueous extract is removed from tower 11 through line 13, whence all or a portion thereof may be recycled to line 12 for reuse as the absorption medium. Alternatively, part of all of the aqueous extract may be treated, for example by distillation, solvent extraction, etc.,

to separate the solute from the aqueous extract phase.

The water-washed charging stock passes overhead from tower 11 through line 14, thence through a heat exchanger 15, to provide suitable temperature adjustment, in the lower portion of washing tower 16, in which it flows countercurrently to an aqueous alkali stream introduced by line 17 into the upper portion of tower 16. Tower 16 may be provided with suitable spacing or packing materials, as is well known in the art. We may employ various alkalis dissolved or dispersed in water or other solvents or carrying media, e. g., methanol or ethanol. Suitable alkalis comprise NaOH, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, the corresponding potassium-based alkalis, etc. The alkali washing may be effected at ambient temperatures, e. g., between about 10 and about 50° C. The purpose of the alkali extraction operation is to remove acidic constituents, particularly carboxylic acids, which may be contained in the charging stock. The alkaline extract phase is withdrawn from tower 16 through line 18, whence all or a portion may be recycled to the upper end of tower 16. Preferably, however, at least an aliquot portion of the alkaline extract is treated to liberate the solute contained therein, for example by acidification with dilute mineral acids such as sulfuric acid, followed by steam distillation.

It should be remarked that the alkali extraction operation which is effected in tower 16 results in the production of alkali metal carboxylates which solubilize normally insoluble alcohols and carbonyl compounds in the aqueous alkali, thereby reducing not only the carboxylic acid content of the feed stock passing into tower 16, but also reducing the concentration of alcohols and carbonyl compounds in the feed stock.

The alkali-treated feed stock passes overhead from tower 16 through line 19, thence through heat exchanger 20 wherein its temperature is suitably adjusted, into contacting zone 21. If desired, this alkali-treated feed stock may be water-washed and dried before passing to heat exchanger 20. Zone 21 may take the form of conventional contacting 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 amine sulfonate solvent. Suitable materials of construction for the contacting zone are aluminum and stainless steel, which have proven strongly resistant to corrosion by alkyl ammonium sulfonates, 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, McMahan 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 21 against a counterflow of an amine sulfonate, for

example, triethylammonium ethanesulfonate, which is introduced into the upper portion of tower 21 through lines 22 and 23. Diluents, e. g. pentane or hexane, or modifying solvents, e. g., methanol, may be introduced with the feed stock, the amine sulfonate solvent or separately, through a line not shown, into zone 21.

The contacting of the amine sulfonate and charging stock results in the production of raffinate and extract phases whose common boundary or interface is indicated at 24. The countercurrent extraction zone may be operated with either the charging stock or solvent as the continuous phase. In the mode of operation illustrated in Figure 2 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 24 in zone 21, whence it is discharged through line 25. The raffinate phase contains a substantially reduced content of neutral, oxygenated organic compounds, as well as any aromatic hydrocarbons or sulfur compounds contained in the feed stock, as compared with the feed stock. It should be understood, however, that the raffinate phase may be further treated to reduce its content of neutral, oxygenated organic compounds, sulfur compounds and aromatic hydrocarbons, if it is so desired. For this purpose, a portion at least of the raffinate phase may be recycled from line 25 by a line not shown to re-enter zone 21 with fresh feed stock. Alternatively, or in addition, the raffinate in line 25 may be sent to another contacting zone, identical in all substantial respects with zone 21, for treatment in a second stage with fresh solvent, which may be the same amine sulfonate or a different amine sulfonate from that passing into line 22, or may be an entirely different type of solvent, e. g., liquid hydrogen fluoride, HF—BF<sub>3</sub>, liquid SO<sub>2</sub>, phenol, furfural, this-(beta-chloroethyl) ether, etc. It should be noted that further extraction of the raffinate passing through line 25 with solvents different from the amine sulfonate passing through line 22 is greatly facilitated by the fact that the amine sulfonate is substantially insoluble in said raffinate, averting the necessity of special procedures for the removal of said amine sulfonate from said raffinate. The inappreciable solubility of the amine sulfonate of this invention in the raffinate phases is noteworthy and substantially different from the behavior heretofore observed in extraction processes employing conventional solvents, such as phenol, furfural, nitromethane, etc.

The extract phase is withdrawn from the lower end of tower 21 through line 26, whence it is passed into separation zone 27. If desired, a part of the extract in line 26 may be recycled to feed line 23 by means of a line not shown in the drawing. Zone 27 may be a separating vessel into which water or aqueous solvents are introduced by line 28 in suitable amounts, e. g., between about 0.5 and about 3.0 volumes per volume of extract, to effect the resolution of the extract into an aqueous amine sulfonate layer and a layer comprising essentially neutral, oxygenated organic compounds. Alternatively, the separation zone 27 may take the form of a distillation vessel, preferably a steam distillation vessel, in which the neutral, oxygenated organic compounds are vaporized, with steam introduced through line 28, and pass overhead through line 29 and heat exchanger 30 into a settling vessel 31, whence the water layer is withdrawn through valved line 32

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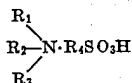
and neutral, oxygenated organic compounds are withdrawn through valved line 33. Salts, e. g., NaCl, Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> or the like, may be introduced into drum 31 to salt out the oxy compounds.

A bottoms fraction containing the amine sulfonate is withdrawn from zone 27 through line 34 for recycle to line 23 and extraction zone 21. If desired, the amine sulfonate stream withdrawn from zone 27 may be purified before recycle to contacting zone 21, for example, by blowing with hot inert gases such as flue gas, nitrogen, carbon dioxide or other inert gases to effect substantial dehydration thereof, following which the treated amine sulfonate may be recycled to extraction zone 21. Alternatively, the recycle stream of amine sulfonate may be dehydrated by azeotropic distillation of water therefrom with various azeotropic agents, e. g., benzene, toluene, n-heptane, etc. At least partial dehydration of the recycled solvent is necessary when the extract is sprung by means of water or wet steam.

Although Figure 2 represents a continuous countercurrent, single stage extraction operation, it will be apparent that the process of the present invention is amenable to batch processing, multi-stage 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 our invention, what we claim is:

1. A process for the selective extraction of a neutral, oxygenated organic compound from a solution thereof in a hydrocarbon mixture comprising essentially an aliphatic hydrocarbon, which process comprises contacting said solution with a selective solvent consisting essentially of an amine salt of a sulfonic acid, said salt having the formula



where R<sub>1</sub> and R<sub>2</sub> are selected from the class consisting of hydrogen and saturated hydrocarbon radicals, R<sub>3</sub> is a saturated hydrocarbon radical, and R<sub>4</sub> is selected from the class consisting of saturated hydrocarbon radicals and aromatic hydrocarbon radicals, said amine salt containing between 4 and 20 carbon atoms, inclusive, per molecule, and separating an extract phase comprising said selective solvent and said neutral, oxygenated organic compound.

2. The process of claim 1 wherein the amine sulfonate contains between 5 and 12 carbon atoms, inclusive, per molecule.

3. The process of claim 1 wherein the hydrocarbon mixture comprises essentially a mono-olefinic hydrocarbon.

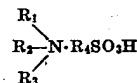
4. The process of claim 1 wherein said solution comprises essentially neutral, oxygenated organic

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compounds and mono-olefinic hydrocarbons produced by the hydrogenation of carbon monoxide in the presence of a catalyst comprising essentially iron.

5. The process of claim 4 wherein the hydrocarbon fraction boils within the boiling range of gasoline.

6. A process for the selective extraction of a neutral, oxygenated organic compound from a solution thereof in a hydrocarbon mixture comprising essentially an aliphatic hydrocarbon, which process comprises contacting said solution with between about 0.1 and about 10 volumes, per volume of said solution, of a selective solvent consisting essentially of an amine salt having the formula



wherein R<sub>1</sub> and R<sub>2</sub> are selected from the class consisting of hydrogen and saturated hydrocarbon radicals, R<sub>3</sub> is a saturated hydrocarbon radical, and R<sub>4</sub> is selected from the class consisting of saturated hydrocarbon radicals and aromatic hydrocarbon radicals, said amine salt containing between 4 and 20 carbon atoms, inclusive, per molecule, said contacting being effected at a temperature between about -20° C. and about 180° C. under pressure sufficient to maintain the liquid phase, and separating an extract phase comprising said selective solvent and said neutral, oxygenated organic compound.

7. The process of claim 6 wherein said amine salt contains between 5 and 12 carbon atoms, inclusive, per molecule.

8. The process of claim 6 wherein said solution comprises essentially neutral, oxygenated organic compounds and mono-olefinic hydrocarbons produced by the hydrogenation of carbon monoxide in the presence of a catalyst comprising essentially iron.

9. The process of claim 8 wherein the hydrocarbon fraction boils within the gasoline boiling range.

10. The process of claim 1 wherein R<sub>4</sub> is a saturated hydrocarbon radical.

11. The process of claim 1 wherein R<sub>4</sub> is an aromatic hydrocarbon radical.

12. The process of claim 1 wherein said selective solvent is a mixture of triethylamine salts of C<sub>1</sub>-C<sub>4</sub> alkanesulfonic acids.

13. The process of claim 1 wherein said selective solvent is triethylamine ethanesulfonate.

14. The process of claim 6 wherein R<sub>4</sub> is a saturated hydrocarbon radical.

15. The process of claim 6 wherein R<sub>4</sub> is an aromatic hydrocarbon radical.

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No references cited.