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Guth et al.

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[54] METHOD FOR REMOVING SULFUR AND NITROGEN IN PETROLEUM OILS

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[21] Appl. No.: **385,894**

[52] **U.S. Cl.** **208/236**, 208/254, 208/289, 208/207
[51] **Int. Cl.** **C10g 19/08**
[58] **Field of Search** 208/254, 236, 289, 207, 208/205, 232, 211

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UNITED STATES PATENTS

3,244,618	4/1966	Dimond et al.	208/236
3,267,027	8/1966	Fierce et al.	208/228
2,556,836	6/1951	Browder et al.	208/205
1,968,842	8/1934	Malisoff	208/236
3,135,680	6/1964	Fierce et al.	208/015
3,164,546	1/1965	Millikan et al.	208/236
2,976,229	3/1961	Brown et al.	208/2
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3,135,078	6/1964	Fierce et al.	53/23
2,925,442	2/1960	Goheen et al.	260/607
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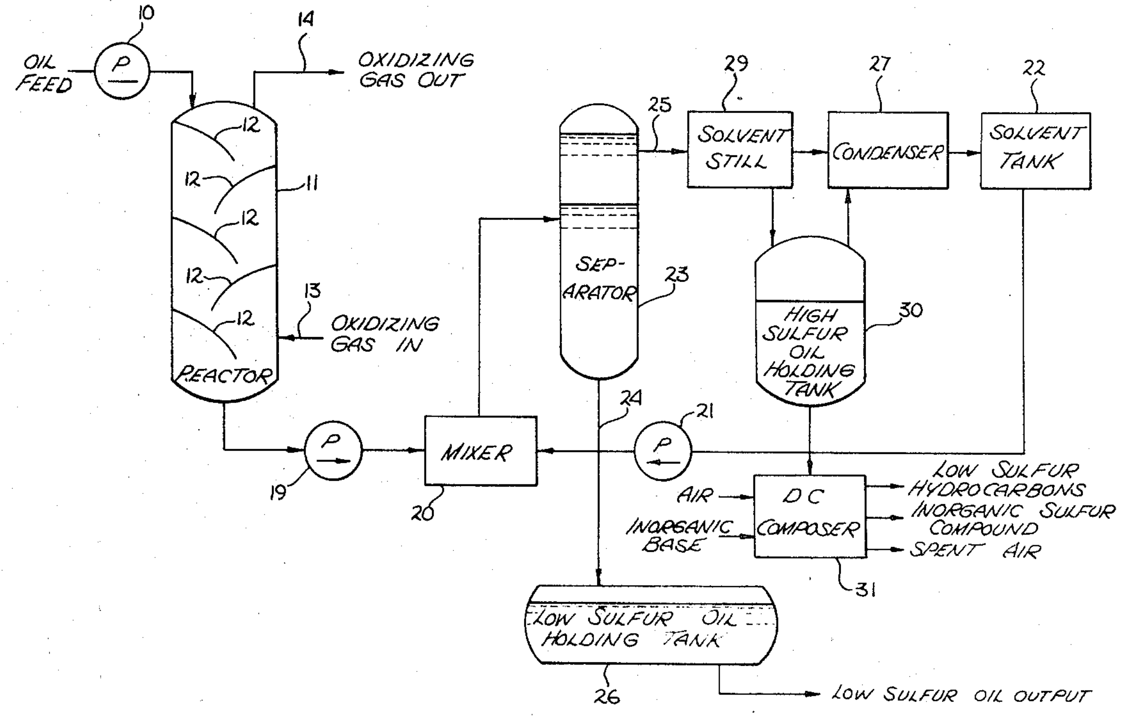
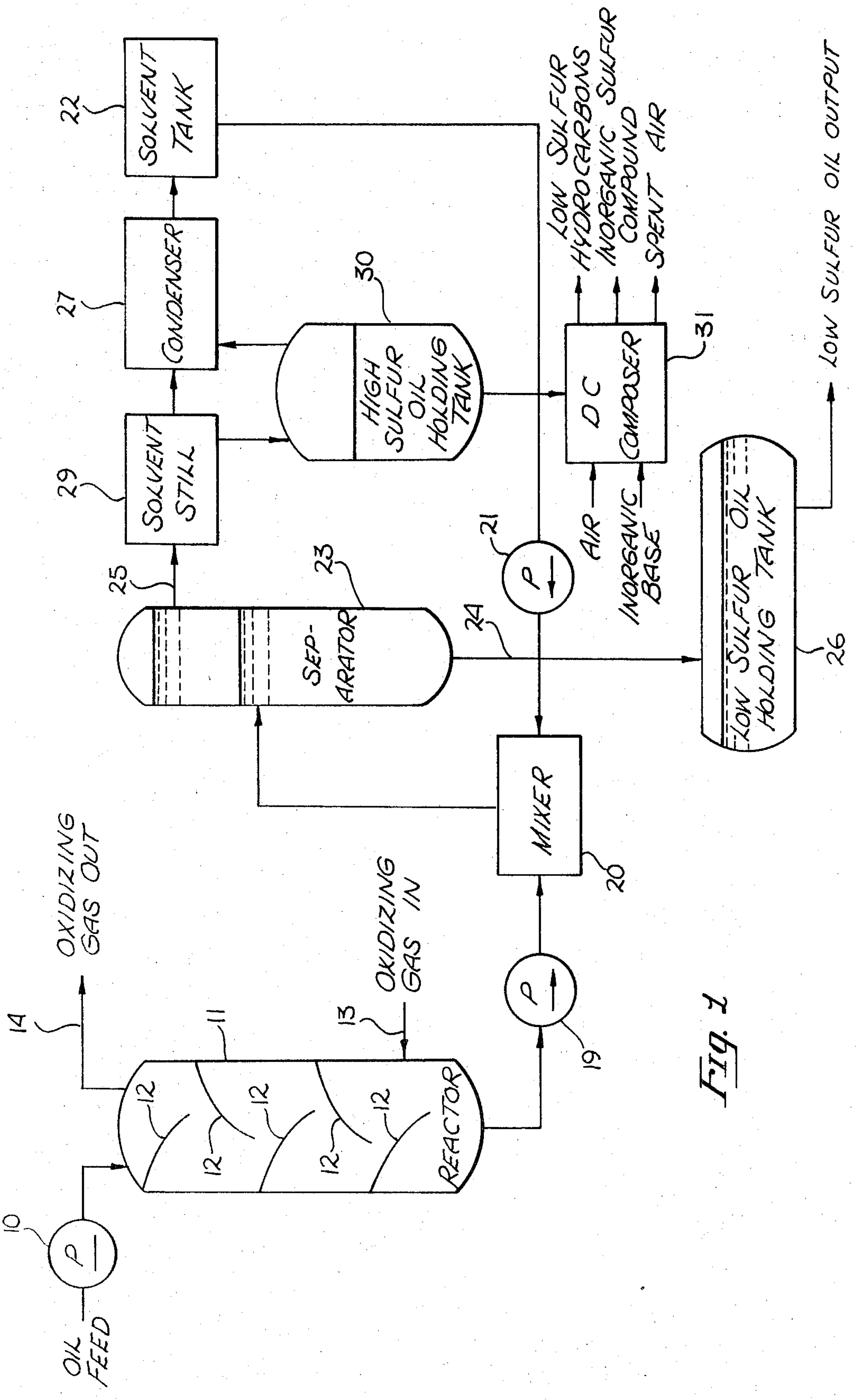
[57] ABSTRACT

A method for the removal of sulfur and nitrogen components from petroleum oils is disclosed. The unwanted sulfur and nitrogen is oxidized to the extent that the resultant compounds exhibit preferential solubility characteristics in some solvent with respect to the oil. The oxidation step involves reacting the sulfur and nitrogen compounds present with an oxide of nitrogen. In particular instances, pretreatment of the oil to remove active groups which cause undesirable side reactions or removal of low sulfur fractions prior to the oxidation step will increase the efficiency of the process. The oil containing the oxidized forms of sulfur and nitrogen is then mixed with a selective solvent, which is immiscible in the oil and in which the sulfur and nitrogen compounds will dissolve. Methanol is the presently preferred solvent. Separation of the oil from the methanol-oxidized compound solution may be effected in a gravity separator. The oxidant gas may be regenerated by the addition of oxygen and recirculated. The oxidized sulfur and nitrogen compounds may be decomposed in a hydrolysis reaction with a dilute base to separate inorganic sulfate and sulfite, and nitrate and nitrite compounds from the hydrocarbon parts of the compounds.

31 Claims, 4 Drawing Figures

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SEP-ARATOR
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29
SOLVENT STILL
27
CONDENSER
22
SOLVENT TANK
30
HIGH SULFUR OIL HOLDING TANK
31
DC COMPOSER
AIR
INORGANIC BASE
LOW SULFUR HYDROCARBONS
INORGANIC SULFUR COMPOUND
SPENT AIR
26
LOW SULFUR OIL HOLDING TANK
LOW SULFUR OIL OUTPUT

Fig. 1

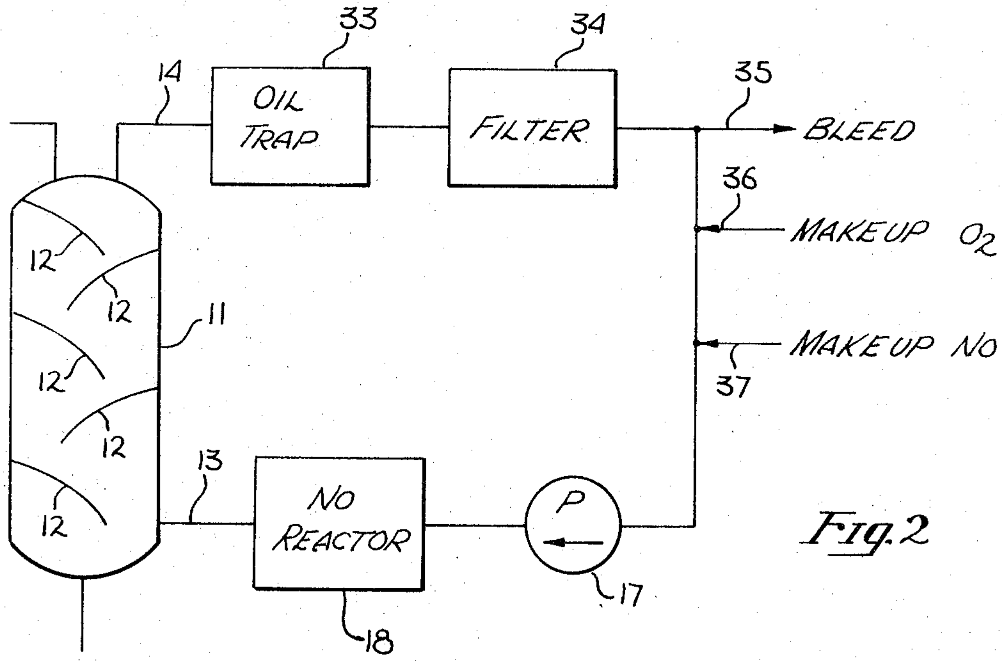


Fig. 2

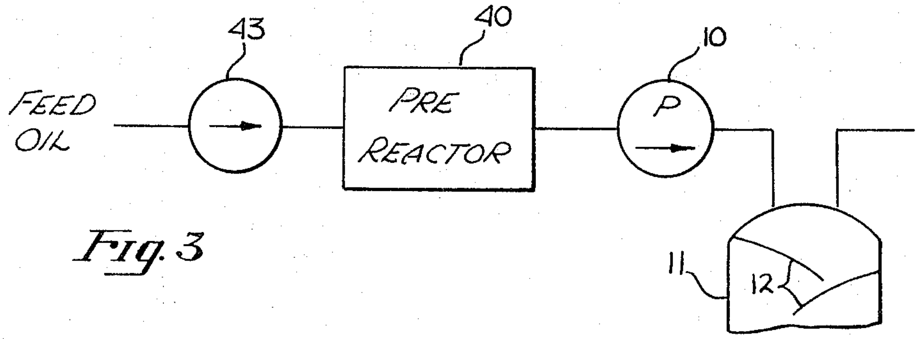


Fig. 3

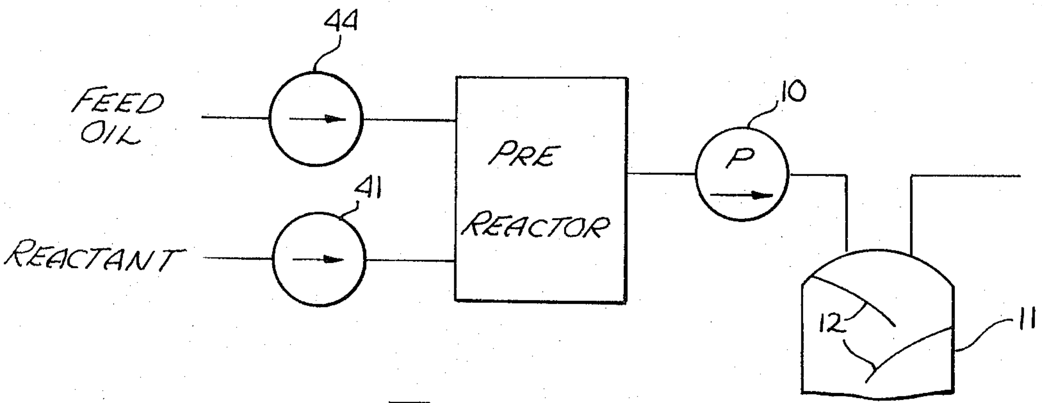


Fig. 4

METHOD FOR REMOVING SULFUR AND NITROGEN IN PETROLEUM OILS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of removing unwanted sulfur and nitrogen compounds from petroleum oils.

2. Prior Art

The presently used method for performing the function of the present invention involves the use of a high temperature-high pressure process to desulfurize hydrocarbon fuels using hydrogen, and an acid extraction process for the removal of basic nitrogen compounds. The old methods have major disadvantages. Hydrogen is a valuable material, made in refineries by pyrolyzing (heating to decompose) hydrocarbon materials or through combustion to form carbon monoxide which is subsequently reacted catalytically with water at high temperature. In any case, it is costly to use hydrogen to remove sulfur (as hydrogen sulfide) from fuels. The reaction of hydrogen is nonselective in that some of the hydrogen will react with the oil to saturate hydrocarbon molecules (aromatics, olefins) in addition to the desired reaction forming hydrogen sulfide. This means that a large quantity of hydrogen is required to desulfurize hydrocarbon fuels.

The second disadvantage of the present method for sulfur removal is that it requires a heterogeneous catalyst. The surface of the solid catalyst tends to become fouled, particularly when residual oils are desulfurized, and this makes the old method inefficient or inoperable with some residual fuels.

The third disadvantage of the present method for sulfur removal is that it requires high temperatures and high pressures for desulfurizing fuels. The reaction conditions make it necessary to use expensive equipment for the old process.

Several other methods of removing sulfur from hydrocarbons have been proposed and are known to the applicant but these have not become commercially popular.

U.S. Pat. No. 1,968,842 issued to Malisoff proposes to treat the sulfur containing oil with a solution of an alkali in an organic solvent. The alkali reacts with mercaptans in the oil forming sulfur compounds which are more soluble in the solvent than in the oil.

The Malisoff patent is directed specifically to sulfur in the form of mercaptans in the oil and does not deal in any way with the broad range of sulfur and nitrogen compounds susceptible to the method of the present invention.

U.S. Pat. No. 3,267,027 issued to Fierce discloses reacting light petroleum distillates with NO_2 followed by washing with an aqueous caustic and finally a water wash. The temperature of the reaction is limited to 35°C. This process also is directed primarily to the removal of mercaptans and thus also has limited applicability.

"Sweetening" of petroleum oils has also been known to applicant as having been proposed by several people, and is a related process. While not considered directly applicable, the most pertinent of these is U.S. Pat. No. 3,224,618 issued to Dimond. Again, the process considers only mercaptans and proposes to convert any mercaptans present in hydrocarbons to disulfides by reacting the mercaptans with oxygen in the presence of an oxide of nitrogen. The resulting disulfides are not as odorous as the mercaptans and thus the treated oil is considered sweet.

The major disadvantage of the old method for nitrogen removal is that it achieves only partial nitrogen removal. Specifically, it removes only some of the basic nitrogen compounds.

While in concept the old methods can be used to desulfurize and partially denitrogenate fuels they lead to large economic penalties. In some cases the cost of desulfurizing may exceed the cost of the fuel.

A low cost simple method of removing sulfur and nitrogen from petroleum fuels is mandatory if current and projected air pollution regulations are to be met. Accordingly, the general purpose of the present invention is to provide such a low cost process. The process is low cost since it is carried out at low pressures and temperatures, that is, the process equipment is inexpensive compared to the equipment required for high pressure, high temperature processes. Further, the process uses only low cost chemicals (i.e., oxygen, nitrogen oxides an methanol, the latter two being recycled) to remove substantially all of the sulfur and nitrogen from the fuels. The process has broad applicability since it can be used to treat liquid petroleum distillates (diesel oil, jet fuel) as well as residual oils. The process makes it possible to upgrade hydrocarbon fractions from initially low value-high sulfur and nitrogen materials to produce high value-low sulfur and nitrogen materials for use particularly as fuels. The process significantly increases the quantity of fossil fuels available to use within the current air pollution regulations and makes possible a large future reduction in the oxides of sulfur and oxides of nitrogen emissions by fuel users.

SUMMARY OF THE INVENTION

The present invention is a process based on the selective oxidation of the sulfur and nitrogen compounds in liquid petroleum oil. Petroleum oil is used herein to signify diesel oil, jet fuel, furnace oil, residual oil, crude oil, topped crude oil, and similar hydrocarbon mixtures. Oxygen is used to regenerate the gas phase oxidizers (oxides of nitrogen containing two or more oxygen atoms, e.g., NO_2) which are recycled. The process can be carried out batch-wise or continuously as desired. A batch of oil can be placed in a vessel and treated with the gas phase oxidizer to oxidize the sulfur and nitrogen compounds or the oil can be continuously pumped through a reactor in which the oxidation is accomplished. For example, the oxidizing gas may be passed upward through a vessel while the oil passes downward. The vessel may be packed with a material (like Berl saddles) which permits the two flows to occur without interference or a large pressure drop. The reacted oil is extracted with a suitable solvent to separate the oxidized sulfur and nitrogen compounds. The extraction can also be carried out continuously or batch-wise. At this point, a major fraction of the oil has low sulfur and nitrogen content and is solvent stripped and removed from the process for use.

One difficulty which may occur in this process is that some oils may tend to react non selectively during the oxidation step and form undesirable polymers and coke. This problem may be obviated by preheating the feed oil to 300° to 600° F for some time, typically 2 to 20 hours to permit the reactive groups in the oil to combine with parts of the other hydrocarbon molecules and thus become less active. An alternate pretreatment procedure is to react the oil with a reactant such as water, hydrogen, or ammonia to remove the active groups in the oil.

The solvent containing dissolved sulfur and nitrogen compound and a fraction of dissolved oil can be separated from its solute either by evaporating the solvent or cooling the mixture to a temperature where the oxidized sulfur and nitrogen compounds have low solubility. The solvent is then recycled through the process. Finally, the sulfur and nitrogen may be separated from the solute, for example, by hydrolysis or pyrolysis.

The process consumes oxygen and energy and produces a low sulfur, low nitrogen oil having physical properties similar to the feed, a lighter oil fraction (from the solute) and inorganic sulfur as sulfite or sulfate ions and inorganic nitrogen as nitrate and nitrite ions or nitrogen. The process steps are all carried out at near ambient pressure and temperatures below about 300° F so the equipment, tanks, piping, etc., are all inexpensive compared to those needed for a high temperature, high pressure process.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a block diagram of the process of the present invention.

FIG. 2 is a block diagram of the oxidizing gas recirculating system.

FIG. 3 is a block diagram of a first pretreatment step.

FIG. 4 is a block diagram of an alternative pretreatment step.

DETAILED DESCRIPTION

The general functions to be accomplished in the removal of sulfur and nitrogen compounds from petroleum oils are:

1. Oxidation. Sulfur and nitrogen exist in petroleum oils in various forms as mercaptans, disulfides, sulfides, amines, and other organic nitrogen compounds having one or more carbon bonds. By exposing feed oil containing such compounds to a gas which includes one or more oxides of nitrogen, these compounds are oxidized into sulfoxides aminoxides or similar compounds which can easily be removed from the oil. The useful oxides of nitrogen for this process are those containing two or more oxygen atoms, e.g., NO_2, N_2O_3, N_2O_4, N_2O_5. The prior art (e.g., U.S. Pat. No. 3,244,618) discusses the oxidation or mercaptans in petroleum oils into disulfides for the purpose of "sweetening" the oils. Disulfides, while not having the objectionable odor of mercaptans, are, unfortunately, not easily separated from the oil and thus the oxidation step contemplated by the method of this invention is intended to oxidize the sulfur compounds into a higher state which exhibits low solubility in oil, but relatively good solubility in some other solvent so that the compounds can be subsequently removed by the process of preferential solubility.

2. Mixing. The oxidized oil is mised with a suitable solvent, such as methanol, which is immiscible with the oil, but in which the oxidized sulfur and nitrogen compounds readily dissolve. Methanol is not the only possible solvent, but is presently preferred since it embodies the characteristics desired in a suitable solvent. The desired characteristics are as follows:

a. Immiscibility in oil;
b. A solvent for oxidized sulfur and nitrogen compounds;
c. Low boiling point to simplify separation from sulfoxides, aminoxides, etc. and oil.
d. does not readily form an emulsion with the oil;
e. density substantially different from the oil for ease in separation;
f. Low-cost-comparable to oil;
g. Does not degrade fuel properties of the oil.

The significance of items (f) and (g) is that small amounts of solvent which cannot economically be separated from the final oil stream will not either increase the cost of the product or render it less desirable as a fuel.

3. Separation. The different densities of the oil and the solvent allow separation of the oil (with reduced sulfur and nitrogen content) from the solvent (in which the sulfur and nitrogen compounds are dissolved) by gravitational settling or contrifuging. The resulting oil has a low sulfur and nitrogen content as is necessary to meet the present stringent requirements for fuels.

While the solvent is generally immiscible with the oil, a small part of the oil will inevitably dissolve in the solvent along with the oxidized sulfur and nitrogen compounds. This oil may be recovered by distilling off the solvent (which is then reused), and removing the sulfur and nitrogen compounds by decomposition in a hydrolysis or pyrolysis reaction, as further described below.

It will be appreciated that the three basic steps outlined above may be supplemented by other steps, such as pretreatment of the oil, in some circumstances. For example, one difficulty which may occur in the process is that some oils may tend to react non selectively during the oxidation step and form undesirable polymers and coke. This problem is obviated by preheating the feed oil to 300° to 600° F for some time, typically 2 to 20 hours to permit the reactive groups in the oil to combine with parts of the other hydrocarbon molecules and thus become less active. An alternate pretreatment procedure is to react the oil with a reactant such as water, hydrogen, or ammonia to remove the active groups in the oil.

In order to improve the efficiency of the process, oils which have a high volatility portion (such as an untopped crude oil) can be topped at temperatures up to 800°F, at atmospheric pressure, or 1,000°F., in vacuum, before processing. In general, the high volatility portion of the oil is low in sulfur. Also, oils having a methanol soluble portion can be treated with methanol first to separate the methanol soluble portion.

Referring now to FIG. 1 where a block diagram of one preferred embodiment of the process of this invention is shown in the form of a continuous process. It will be understood that the steps of this process leading to the removal of unwanted sulfur and nitrogen compounds from oil can be accomplished by batch processing as well as by the continuous process described. The process can also be a combination of batch and continuous, for example, the pretreatment steps, if utilized, can be done batch-wise while the remainder of the process is continuous. Other combinations of batch and continuous processing are also possible and practical within the spirit of the present invention. The process, as illustrated in FIG. 1, does not include any pretreatment steps, it being assumed that such steps are either unnecessary or already performed on the particular oil being processed.

Pump **10** pumps the oil from its previous location, not shown, into the top of reactor **11.** The reactor preferably operates at near atmospheric pressure since this results in simple and relatively inexpensive processing equipment. No particular advantage is to be gained by increasing the pressure of the system, but to some extent a somewhat higher than room temperature can be of advantage. A higher temperature will tend to cause the reaction in which mercaptans become disulfides to proceed further converting the disulfides into sulfoxides. Typical temperatures which are desirable range from about 50° to 350° F. As the temperature increases some undesirable side reactions such as polymerization and coke formation begin to occur. The process temperature should not be so high nor the time of application so long that these side reactions become a problem.

The reactor is the vessel which provides contact between the feed oil and the oxidizing gas allowing the reaction to take place. It can take many forms, but in the particular embodiment being described, is a relatively tall cylindrical vessel in which the oil is introduced at the top and the oxidizing gas at the bottom. The oil flows downward due to gravity, flowing over baffles, or other packing which provide a large surface over which the oil can flow. The oil flows in thin layers so that a large surface of oil is presented to the oxidizing gas. A typical reactor **11** may be packed with Berl saddles **12,** which occupy about 50 percent of the reactor volume, leaving open spaces through which the oxidizing gas can pass in contact with the oil on the surface of the saddles. Other forms of reactor to obtain intimate contact between the oil and oxidizing gas may, of course, be used, for example, agitated vessels. The volume of the reactor is a function of the volumetric flow rate of the oil and usually ranges from about 10 to 100 times the hourly oil flow rate.

The flow of oil is such that the flowing oil remains in the reactor for up to about 20 minutes at temperatures up to about 350° F., the time and temperature being enough to allow the sulfur and nitrogen compounds in the oil to oxidize as needed to form the compounds which will preferentially dissolve in the solvent used, but not so hot or so long as to cause polymerization or side reactions. The use of too high a temperature tends to cause polymerization of the oil and is thus not desirable, while overlong exposure to the oxidant allows other unwanted side reactions to occur which are also undesirable.

The oxidizing gas is comprised of oxides of nitrogen. It can be a single oxide, or a mixture of nitrogen oxides. The oxides which have been found to be useful are NO_2, N_2O_3, N_2O_4, and N_2O_5, A potential problem exists if the oxidizing gas is used undiluted in that a possible explosive mixture with the petroleum vapors may be formed within the reactor. To prevent this, it is preferable to dilute the oxidizing agent with some relatively inert gas such as nitrogen. Typically the gas used is 1 to 20 percent oxidizer, the balance being inert or, as will be discussed below, partly oxygen and partly inert, the oxygen being utilized in a regenerating cycle for the oxidizer. Presently, a preferred composition of oxidizing gas is 1 to 9 percent by volume $NO + NO_2$, 1 to 19 percent by volume O_2 with the balance N_2. The function of the NO in the system will be discussed below.

Since the unwanted sulfur and nitrogen compounds appear in the oil in various forms, no single reaction can be presented which describes the process whereby these compounds are oxidized, however the following reactions, among others, are probably involved.

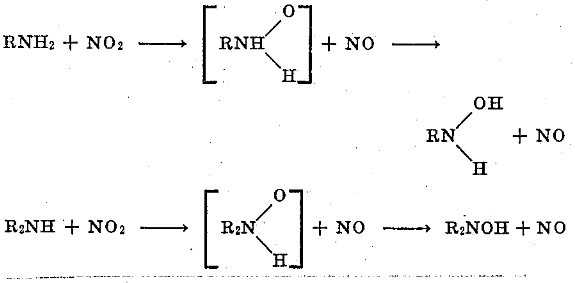
$R_2S + NO_2 \rightarrow R_2SO + NO$

$R_2S + NO_2 \rightarrow R_2SO_2 + NO$

$RSH + 2NO_2 \rightarrow RSOOH + 2NO$

The oxidizing gas is introduced at inlet **13** located near the bottom of the reactor and flows upward through the reactor contacting the oil which is flowing over the surfaces of the Berl saddles **12.** The oxidizer flows out through outlet **14.** It will be found to be most economical to reconstitute the oxidizer and continuously recycle the gas through the reactor. The procedure for accomplishing this will be discussed below.

At the same time that sulfur compounds in the oil are being oxidized, organic nitrogen compounds present in the oil having one or more carbon bonds (e.g., amines, saturated aliphatic compounds or parts of an aromatic ring) also react with the oxygen present to form an oxidized form of the compound. Typical reactions could be as follows:



$R_3N + NO_2 \longrightarrow R_3NO + NO$

The oxidized compounds formed are soluble in methanol and are thus susceptible to removal from the oil in the process as described below.

The oil containing the oxidized sulfur and nitrogen compounds flows out of the bottom of reactor **11** and is pumped by pump **19** to mixer **20** where it is mixed with a solvent, which is preferably methanol, pumped into mixer **20** by pump **21** from solvent storage tank **22.** A quantity of solvent about 1 to 5 times the volume of oil insures that substantially all of the soluble components in the oil dissolve in the solvent. The solvent must be selective, that is, one in which the oxidized sulfur and nitrogen compounds are soluble but in which the oil itself is not soluble. Methanol is the presently preferred solvent but other solvents such as methanol-water mixtures, methanol-ethanol-water mixtures, and methanol-inorganic salt (e.g., sodium chloride, potassium chloride and calcium chloride) solutions can be used.

The mixer may be a stirred vessel or simply a static mixer in which the flow streamlines are broken up by the shape of the vessel or by obtructions therein. Again the mixing may be done at atmospheric pressure and the temperature is not critical but is preferably between 80° and 150° F, the upper temperature limit being the boiling point of solvent.

After the oxidized compounds are dissolved in the solvent, the mixture flows to separator **23** where the fluid is brought essentially to rest and the lighter liquid, which in the case of a methanol-diesel oil system is the methanol, rises to the top and the oil sinks to the bottom.

The desulfurized and denitrogenated oil flows out of a bottom tap **24** of separator **23** while the solvent carrying the oxidized sulfur and nitrogen compounds in solution is decanted from tap **25** at the top of separator **23.** The separator is preferably maintained at 1 atmosphere pressure and between 80° and 150° F., neither condition being critical. Separation of the fluids occurs in about 10 to 30 minutes and a separator vessel with sufficient volume to hold 10 to 30 minutes of flow would be satisfactory. A continuous flow from taps **24** and **25,** keeping the line of demarcation between the oil and the methanol solution about in the middle of the vessel allows the separation to take place and prevents contamination of the separator output streams.

Any residual solvent remaining in the oil leaving tap **24** is removed in holding tank **26** which is maintained at a relatively high temperature, for example, 160° F which causes the solvent to vaporize. The vaporized solvent flows to condenser **27** where it is condensed and is then added to the solvent in solvent tank **22.**

The solvent stream, including the dissolved sulfur and nitrogen compounds, as well as a small fraction of oil (generally 2 to 5 percent of the initial oil volume), flows from separator **23** through outlet **25** to the solvent still **29,** which is maintained at a high enough temperature to evaporate the solvent. The solvent vapor is condensed in condenser **27** and the distilled liquid solvent then flows to tank **22** for recycling.

The residue of the solvent distillation, containing sulfur and nitrogen compounds, oil, and some amount of solvent is passed through a holding tank **30,** maintained at over the boiling point of the solvent, where the last vestiges of solvent are stripped from the liquid and recovered in condenser **27.**

The high sulfur, high nitrogen oil remaining as the residue can either be used as is, for applications where the high sulfur and nitrogen content is unimportant, or the oil can be further processed in decomposer **31** which subjects the oil to a pressure of 1 to 5 atmospheres at 150° to 300° F for 5 to 30 minutes in the presence of air and a dilute inorganic base such as sodium hydroxide. The ensuing hydrolysis reaction decomposes the oxidized sulfur and nitrogen compounds forming hydrocarbons and sulfite or sulfate compounds and nitrite or nitrate compounds.

As previously mentioned, it is desirable to recirculate the oxidizer gas continuously for reasons of economy. FIG. **2** shows how this may be accomplished.

Assuming that the oxidizing gas being used is the presently preferred mixture previously referred to (NO_2, O_2 and N_2), the reaction in the reactor reduces the NO_2 to NO while oxidizing the sulfur and nitrogen compounds in the oil. As the NO_2 is being reduced, it is replenished to a large extent by the reaction of NO and O_2 present to maintain an equilibrium of NO_2, NO, and O_2 as follows:

$$NO + \tfrac{1}{2} O_2 \rightleftarrows NO_2.$$

Thus the net reaction with the compounds in the oil results in consumption of oxygen. At the same time the oil will emit some vapors which tend to contaminate the oxidant gas, notably CO and CO_2. In order to maintain the composition, therefore, it is necessary to somehow remove the contaminants. This may be conveniently done by venting a small fraction (typically 1 to 5 percent) of the circulating gas and to replace the vented portion with makeup gas. This gas is shown in FIG. **2** as being vented at bleed **35** and makeup oxygen and NO are shown being supplied at **36** and **37.** While in the preferred embodiment described, makeup gas is NO and O_2 which are reacted as will be presently described to form NO_2, it will be clear to those skilled in the art that the oxidizing and makeup gases may be any one or more of the higher oxides of nitrogen previously mentioned and in such case it would not be necessary to provide the NO reacting means. Pump **17** circulates the oxidizer in the system. The rate of circulation is not critical, the most desirable rate depending on the temperature of the reactor, the quality of the contact of the oxidant with the oil and the length of time the oil is in contact with the gas. The order of magnitude of the circulation is 10 to 20 moles of oxygen per mole of sulfur and nitrogen removed.

NO reactor **18** is a heated vessel maintained at 200° to 450° F. in which the NO and O_2 react forming NO_2 so that the gas stream entering reactor **11** will be rich in NO_2, the primary oxidant. NO reactor **18** is preferably of a size which allows the gas to remain in it for 1 to 3 minutes in order that the desired reaction take place.

After leaving NO reactor **18,** the gas having the desired composition enters reactor **11** through inlet **13.** After exiting through outlet **14,** the gas is fed through oil trap **33** and filter **34** before any portion of the gas is vented through bleed **35.** The purpose of these units is to help clean up the circulating gas and to prevent oil vapors or solid particles from being vented to the atmosphere. It may be necessary in order to comply with anti-pollution statutes, to further treat the bleed stream **35** before allowing it to escape to the atmosphere.

As is well known to those skilled in the art, petroleum products have very complicated structures and contain varying impurities and fractions. For this reason it is not possible to describe a single inflexible process for handling all such products. The process as has been described to this point is general and it will be noted that the parameters given are subject to wide variation to accommodate a particular oil product to be processed. Even this latitude may not be enough in some cases, however, and a pretreatment of the oil may be desirable in order to fully utilize the capabilities and efficiency of the method.

Some oils may tend to react non selectively during the oxidation step and form undesirable polymers and coke. For such products, a pretreatment as illustrated in FIGS. **3** or **4** might be found advantageous.

In the embodiment shown in FIG. **3,** a pump **43** drives oil from a reservoir or other source, not shown, into prereactor **40.** The prereactor **40** is maintained at an elevated temperature of 300° to 600° F and is of sufficient size to that oil will remain in the prereactor for from 2 to 20 hours. During residence in the prereactor **40,** reactive groups in the oil combine with parts of other hydrocarbon molecules and become less active. The purpose of this step is to reduce undesirable side reactions in the oxidation step which follows. Active groups in the oil, unless disposed of in some manner, may tend to react nonselectively in the oxidation reactor to form undesirable polymers and coke. By pretreating the oil to reduce the activity of these groups, the side reactions can be held to a minimum.

An alternate pretreatment is illustrated in FIG. 4 where that portion of the apparatus used in the pretreatment step only is shown.

In addition to pump **44** pumping feed oil, a pump **41** pumps a suitable reactant, such as water, hydrogen, or ammonia, into prereactor **42.** Prereactor **42** need not be heated but agitation means, not shown, should be supplied to insure good mixing of the feed oil and the reactant. The reactant reacts with the active groups in the feed oil thereby reducing the amount of active material in the oil.

Other pretreatments which might be used to improve the efficiency of the sulfur/nitrogen reduction process include topping oils which have a high volatility portion by heating the feed oil to 800° F at atmospheric pressure or 1,000° F in vacuum. In general, the high volatility portion of oil is low in sulfur and removing such portion before processing will increase the efficiency of the process. An oil which contains a methanol soluble portion can be treated with methanol first to separate the soluble portion.

After any pretreatment process or processes, the oil is fed to reactor **11** and processed in the manner previously described.

In Tables I and II a group of test results are presented indicating the efficacy of the invented method using methanol as the solvent. As can be seen, up to 97 percent of the sulfur and 93 percent of the nitrogen present are removed.

In Table I results for diesel oil treatment show the effects of temperature of oxidation, reaction time, catalyst concentration and solvent volume on sulfur removal. It has been seen that substantial reductions in sulfur and nitrogen content can be made using the invented method under widely varying conditions. In Table II the results for a variety of residual oils show that the method removes sulfur and nitrogen from these fuels.

In treating the high sulfur oil remaining from the residue in Test **41-1** at 250°F and one atmosphere for 30 minutes using an equal volume of 10 percent sodium hydroxide in water with air passing through the oil at the rate of 4 volumes per minute per volume of oil the sulfur content of said oil was reduced 62 percent and the nitrogen was reduced 48 percent.

What has been described is a novel method for reducing the sulfur and nitrogen content of petroleum oil. Various modifications will be apparent to those skilled in the art and are considered to be within the spirit of the invention as set forth in the appended claims.

I claim:

1. The method of reducing sulfur and nitrogen compound concentrations in petroleum oil which comprises:

a. exposing petroleum oil to an oxidizing gas containing one or more oxides of nitrogen chosen from the following list: NO_2, N_2O_3, N_2O_4, N_2O_5, whereby sul-

TABLE I

DIESEL OIL TESTS
Initial Wt. % S-0.21; Initial Wt. % N-0.035

Sample	Oxidation Time	Temp. °F	Oxidizer[1] Conc. Vol. % NO	Extraction Vol. Solv/ Vol. Oil	% S[2] Removed	% N[3] Removed
Batch Reactor Tests						
17-3	21 hrs.	150	5	0	0	
17-2	21 hrs.	150	5	4	76	
17-1	17 hrs.	150	5	4	76	
16-1	6 hrs.	150	5	4	66	
19-1	6 hrs.	105	7	4	76	14
19-2	27 hrs.	105	7	4	97	
13-2	2 hrs.	205	5	5	57	
13-3	5 hrs.	205	5	3	76	
14-1	8 hrs.	205	5	1	43	
Continuous Reactor Tests						
21-1	10 min.	85	5	4	43	22
22-2	3 min.	200	2	3	29	
26-1	12 min.	200	10	3	48	
41-1	12 min.	170	10	3	72	91
41-3	12 min.	170	10	3	72	93
20-4	12 min.	170	10	3	81	

1. The treating gas was prepared by mixing air and nitrogen oxide (NO) and heating the mixture to 250°F for 30 seconds before passing the gas through the reactor.
2. Analyzed by ASTM Method D1266-70 with an acidimetric determination.
3. Analyzed by the Kjeldahl method.

TABLE II

RESIDUAL OIL TESTS

Sample	Type of Oil	Initial Wt. % S	Initial Wt. % N	Process Conditions Oxidation Time	Temp. °F	Oxidizer Conc.[2] Vol.% NO	Extraction Vol. Solv/ Vol. Oil	Final[1] Wt. % S	Final[1] Wt. % N	Removal % S	Removal % N
Batch Reactor Tests											
7-3	High Sulfur Stock	2.2		3 hrs.	225	10	4	1.8		14	
32-2	Topped Alaskan Crude	0.36		7 hrs.	210	10	4	.13		64	
10-1	Kern County Stock	1.0		2 hrs.	200		4	.30		70	
Continuous Reactor Tests											
42-2	High Sulfur Stock	2.2	2.45	4 mins.	275	10	5	.3	1.34	86	45
37-3	Topped Alaskan Crude	.36		8 mins.	150	10	5	.16		56	

1. Sulfur determined by ASTM Method D 1266-70; Nitrogen by the Kjeldahl method.
2. The treating gas was prepared by mixing air and nitrogen oxide (NO) and heating the mixture to 250°F for 30 seconds before passing the gas through the reactor.

fur and nitrogen compounds in said petroleum oil will be oxidized:

b. mixing said petroleum oil with a solvent selected from the group consisting of methanol, methanol-water mixtures, methanol-ethanol-water mixtures and methanol-inorganic salt solutions, said solvent being substantially immiscible with said oil but being a solvent for said oxidized sulfur compounds, said oxidized sulfur compounds dissolving in said solvent; and

c. separating said oil from said solvent solution.

2. The method of claim **1** where said oxidizing gas further contains an inert gas.

3. The method of claim **1** where said oxide of nitrogen chosen is NO_2.

4. The method of claim **3** where said oxidizing gas contains about 1–20 percent NO_2 and about 70 to 98 percent N_2.

5. The method of claim **4** where said petroleum oil is exposed to said oxidizing gas at a temperature of 50° to 350° F.

6. The method of claim **5** where said exposure is for less than 20 minutes.

7. The method of claim **1** where an oxide of nitrogen in said oxidizing gas is formed by reacting NO with O_2.

8. The method of claim **7** where said oxidizing gas contains NO, NO_2 and O_2.

9. The method of claim **8** where said oxidizing gas further contains an inert gas.

10. The method of claim **9** where said oxidizing gas is comprised of:

1–9 percent by volume $NO+NO_2$, 1–19 percent by volume O_2, and the balance nitrogen.

11. The method of claim **10** where said petroleum oil is exposed to said oxidizing gas at a temperature of 50° to 350°F.

12. The method of claim **11** where said exposure is for less than 20 minutes.

13. The method of claim **1** where said solvent is methanol.

14. The method of claim **1** where said separation is performed by gravitational settling.

15. The method of claim **14** where said oxidizing gas further contains an inert gas.

16. The method of claim **14** where said oxide of nitrogen chosen is NO_2.

17. The method of claim **16** where said oxidizing gas contains about 1–20 percent NO_2 and about 70 to 98 percent N_2.

18. The method of claim **17** where said petroleum oil is exposed to said oxidizing gas at a temperature of 50° to 350°F.

19. The method of claim **18** where said exposure is for less than 20 minutes.

20. The method of claim **14** where an oxide of nitrogen in said oxidizing gas is formed by reacting NO with O_2.

21. The method of claim **20** where said oxidizing gas contains NO, NO_2 and O_2.

22. The method of claim **21** where said oxidizing gas further contains an inert gas.

23. The method of claim **22** where said oxidizing gas is comprised of:

1–9 percent by volume $NO+NO_2$, 1–19 percent by volume O_2, and the balance nitrogen.

24. The method of claim **23** where said petroleum oil is exposed to said oxidizing gas at a temperature of 50° to 350°F.

25. The method of claim **24** where said exposure is for less than 20 minutes.

26. The method of claim **1** including the steps in which said solvent stream is further treated after said separation:

a. evaporating said solvent from said solvent solution;

b. exposing the residue of said solvent solution to air and a dilute mixture of an inorganic base and water whereby said oxidized sulfur compounds will react to form inorganic sulfur compounds and a hydrocarbon fraction; and

c. separating said hydrocarbon fraction from said inorganic sulfur compounds.

27. The method of claim **1** and further including the step of heating said oil, prior to exposure to said oxidizing gas, to a temperature of from 300° to 600°F for from 2 to 20 hours.

28. The method of claim **1** and further including the step of mixing a reactant with said oil prior to exposure to said oxidizing gas, said reactant being chosen from the following: water, hydrogen, ammonia.

29. The method of claim **1** and further including the step of heating said oil, prior to exposure to said oxidizing gas, to a temperature of 800°F at atmospheric pressure.

30. The method of claim **1** and further including the steps of heating said oil, prior to exposure to said oxidizing gas, to a temperature of 1,000°F in a vacuum.

31. The method of claim **1** and further including the steps of:

a. mixing said oil with methanol;

b. allowing said oil to separate from said methanol; and

c. decanting said methanol from said oil, said steps being taken prior to exposure of said oil to said oxidizing gas.

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