**EUROPEAN PATENT SPECIFICATION**

**Improved process for the production of base stock oils from used oil**

Verbessertes Verfahren zur Produktion von Grundölen aus Altöl

Procédé amélioré pour la production d'huiles de base à partir d'huile usée

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The present invention provides for an improved process of producing base stock oil from spent or used lube oils. Disposal of spent lube oils has been an environmental problem. Historically, methods of disposal of spent lube oils have included burning of such oils. Due to air quality regulations and concerns, disposal by burning is becoming impractical as well as environmentally unsound. Disposal of spent lube oils in landfills and/or city sewers is even more disastrous, since those methods contaminate soil and waterways. It has been estimated that the amount of used lube oil winding up in sewers, garbage dumps and spread on the land each year in the U.S.A. is equal to 40 times the oil spilled by the Exxon Valdez tanker in Alaska.

Lube base oils are among the most valuable constituents in crude oil. Virgin lube oils are recovered from so-called lube-crudes by solvent extraction followed by wax (i.e. paraffin) removal. To enhance color and stability, the raw lube oil is catalytically hydrotreated. Average crude oils contain 3-8% lube base oils, whereas lube crudes have typically 12-16% lube base oils. This compares with 60 to 65% of lube base oils contained in spent automotive oils. Thus, it is quite evident that mere disposal of lube oil destroys a valuable natural resource that should be reclaimed.

Total worldwide lube oil sales amounted to about 17 million tons in 1987. Automotive engine oils amounted to about eight million tons, whereas about 6.5 million tons of industrial oils were sold. It has been estimated that 42% of new lubricants sold would be available for recycling. However, actual reclaiming of lube base oils from spent lubricants is less than 5% of that available.

Recovery of lubricating base oils from used oil has been plagued by a myriad of problems, most of them associated with inordinate corrosion and fouling due to decomposition of the additives in formulated oils. It should be noted that typical automotive lube oils consist of about 75% base oil and about 25% additives. These additives include: viscosity index (VI) improvers, anti-oxidants, anti-wear improvers, pour-point depressants, detergents, etc. While the base lube stock components deteriorate only slightly, the additives undergo severe changes which make re-refining a difficult endeavor.

Oil used typically consists of about 66% base oil, about 10% water, about 12% additives and about 12% fuel. In addition, these spent oils frequently contain glycols, chlorinated solvents, gasoline, carbon, solid particles and metals. Metals in a typical used oil include the following: lead about 100 ppm, calcium about 875 ppm, phosphorous about 730 ppm, magnesium about 230 ppm, zinc about 710 ppm, sodium about 130 ppm, cadmium about 2 ppm and chromium about 3 ppm. These metals are primarily present in the form of metallo-organic compounds and are present to a minor extent as metal oxides or sulfides. Decomposition of certain metal-sulfur additives may generate sulfuric acid and, thus, may lead to problems with fouling and corrosion in subsequent steps in the re-refining process.

Decomposition of base lube oil components may result in production of lower boiling hydrocarbons which comprise materials boiling in the gasoline, kerosene and light gasoil boiling ranges respectively. These materials can be separated by distillation.

Various processes for recovering lube base oil from spent (used) oils have been developed and used. These processes have ranged from a simple filtration process to remove solids only to quite elaborate chemical processing schemes which require sophisticated thin film evaporation equipment and catalytic hydroprocessing operations. However, with all of these processing schemes, there have been recurring problems with fouling and corrosion of equipment. These problems have been so severe as to result in plugging of piping and associated equipment, particularly with the use of processes which incorporated heat treatment and/or exposure to temperatures in the range of 400° to 650°F. This plugging necessitated frequent shutdowns of the equipment for cleaning, thereby negatively affecting the economics of the recovery operation.

One of the older processes practiced widely and on a commercial scale involved contacting used oil with sulfuric acid to give an acid sludge in which objectionable used oil decomposition products and additive decomposition products were captured and then removed. An improvement to this process comprised following the acid treatment step with a clay treatment step in which the used oil was further purified by absorbing and removing impurities which remained after acid treatment. A serious disadvantage in the processes using acid and/or clay treatment was the creation of wastes, acid sludge and spent clay, which presented disposal problems. These disposal problems have led to the abandonment of these processes in industrial countries. Also in less developed countries, efforts are underway to switch to less polluting processes.

Recently, the "Association of Petroleum Re-Refiners" has organized several "International Conferences on Waste Oil Recovery and Reuse" as a forum to discuss and summarize technological developments in re-refining used oil. The last three of these conferences were: (a) Third International Conference: Houston Oaks Hotel, Houston, Texas, October 16 to 18, 1978; (b) Fourth International Conference: Caesar's Palace, Las Vegas, Nevada, September 28 to October 1, 1981; and (c) Sixth International Conference: Hilton, San Francisco, California, May 28 to 31, 1991 (the Fifth International Conference was not held).

The following is a summary of some processes which have been described for cleaning up used oil.
Another process, proposed to re-refine used lubricating oils using an extraction process. The used lube oil was contacted with a light hydrocarbon solvent, for example propane, in a first extraction zone to give a first extract and a raffinate. Removal of solvent from the first extract gave the desired lube oil base stock. The first raffinate was then solvent extracted using the same solvent to produce a second extract and a second raffinate. Removal of solvent from the second extract yielded an oil which could be further refined. Other processes which involve solvent extraction have been proposed; however, these solvent extraction processes are economically disadvantageous (i.e., expensive) due to the high energy requirements for solvent evaporation which has limited their acceptance.

Processes which employ traditional unit separation steps such as flashing, evaporation, and distillation to remove lower boiling hydrocarbons, water and decomposition products from additives have been used. In order to enhance lube oil base stock recovery and the quality of the stock so recovered, vacuum thin film evaporation equipment has been used to reduce the exposure time of the lube oil base stock to high temperatures. To obtain a lube oil base stock having quality approximately equal to virgin lube oil, catalytic hydrotreatment has been employed in increasingly sophisticated ways. Since hydrotreating catalyst life was found to be very short (about two to four weeks), use of a guard bed with absorber materials such as activated alumina, Fuller's earth or similar materials was recommended to remove polar compounds comprising nitrogen, sulfur and/or oxygen (see U.S. Patent No. 3,930,988).

Processes did not solve the principal problems of fouling and corrosion of equipment. Furthermore, an additional problem, deactivation of the hydrotreatment catalyst, was found. In hydrotreating virgin base stocks, a catalyst life of several years is typical. However, in the case of these re-refined raw lube oil distillates, observed catalyst life was only on the order of about two to four weeks which appeared to indicate the presence of catalyst poisons and/or catalyst degradation promoters.

A process involving a heat soak step (at a temperature of about 300°C) prior to distillation was proposed. The used oil was then passed first over a guard bed containing adsorbents and then over the hydrotreating catalyst to yield a high quality base lube stock. Phosphorus content of the material was said to be responsible for short catalyst life. Phosphorus levels in the lube distillate were reduced from the range of about 50 to 350 ppm to less than 6 ppm by heat soaking the de-watered and de-gasoiled raw waste oil and then separating the bottoms (asphalt) from the raw lube distillate by thin filter evaporation (see U.S. Patent No. 4,512,878).

A peculiar and particularly difficult problem is encountered in certain more modern re-refining processes that employ catalytic hydrotreating as a finishing step. Phosphorous poisons the outer surface layer of a hydroprocessing bed with absorber materials such as activated alumina, Fuller's earth or similar materials was recommended to remove polar compounds comprising nitrogen, sulfur and/or oxygen (see U.S. Patent No. 3,930,988).

Use of the above processes did not solve the principal problems of fouling and corrosion of equipment. Furthermore, an additional problem, deactivation of the hydrotreating catalyst, was found. In hydrotreating virgin base stocks, a catalyst life of several years is typical. However, in the case of these re-refined raw lube oil distillates, observed catalyst life was only on the order of about two to four weeks which appeared to indicate the presence of catalyst poisons and/or catalyst degradation promoters.

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Summary of the Invention

The present invention is directed to an improved process of re-refining used oil to produce a base stock oil which is suitable for use in automobile lubricating oil and which is substantially equivalent to a base stock oil produced from virgin crude oil.

According to the present invention, as it is disclosed in claim 1, a process is provided which comprises (a) pretreating used oil to remove hydrofinishing catalyst fouling materials to give a pretreated mixture; (b) distilling the pretreated mixture from step (a) to separate lower boiling materials (less than 150°C), gasoil and lube oil distillate from asphalt; and (c) hydrofinishing the lube oil distillate from step (b) wherein said pretreating of step (a) includes adding a sufficient amount of an alkali compound, to the used oil under vigorous mixing conditions to give a pH of at least 5 in the gas phase of all the distillates produced in step (b), the amount of alkali compound being insufficient to cause gelling of the asphalt fraction, and wherein said pretreated mixture comprises at least 3% water. Phosphorus content of the material was said to be responsible for short catalyst life. Phosphorus levels in the lube distillate were reduced from the range of about 50 to 350 ppm to less than 6 ppm by heat soaking the de-watered and de-gasoiled raw waste oil and then separating the bottoms (asphalt) from the raw lube distillate by thin filter evaporation (see U.S. Patent No. 4,512,878).

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Processes which employ traditional unit separation steps such as flashing, evaporation, and distillation to remove lower boiling hydrocarbons, water and decomposition products from additives have been used. In order to enhance lube oil base stock recovery and the quality of the stock so recovered, vacuum thin film evaporation equipment has been used to reduce the exposure time of the lube oil base stock to high temperatures. To obtain a lube oil base stock having quality approximately equal to virgin lube oil, catalytic hydrotreatment has been employed in increasingly sophisticated ways. Since hydrotreating catalyst life was found to be very short (about two to four weeks), use of a guard bed with absorber materials such as activated alumina, Fuller's earth or similar materials was recommended to remove polar compounds comprising nitrogen, sulfur and/or oxygen (see U.S. Patent No. 3,930,988).

Processes did not solve the principal problems of fouling and corrosion of equipment. Furthermore, an additional problem, deactivation of the hydrotreating catalyst, was found. In hydrotreating virgin base stocks, a catalyst life of several years is typical. However, in the case of these re-refined raw lube oil distillates, observed catalyst life was only on the order of about two to four weeks which appeared to indicate the presence of catalyst poisons and/or catalyst degradation promoters.
combination thereof. At least about 3% water is present in the pretreated mixture. Preferably, the pretreated mixture comprises 3% to 20% water, more preferably 5% to 15% water.

According to the present invention, catalyst life was typically about 3 to 6 months which represents a significant extension in catalyst life.

Operations that are conducted to improve a variety of important quality/stability parameters of the lube oil base stock.

Component in lube distillates, since its presence deactivates hydrotreating catalyst in subsequent hydroprocessing operations.

Salts of weak acids and include sodium carbonates, bicarbonates, sulfites and bisulfites. Phosphorus is an undesirable component in lube distillates, oil, oxide, aluminate, carbonate, bicarbonate, sulfite, or bisulfite or a combination thereof.

Especially preferred alkali compounds include sodium hydroxide, sodium aluminate and combinations of the two. Preferably pretreating step (a) is conducted at a temperature of 80°C to 170°C under well-mixed conditions. More preferably pretreating step (a) is conducted at 90°C to 150°C, an especially preferred temperature range is from 100°C to 130°C. According to an especially preferred aspect, distilling step (b) includes holding the pretreated mixture at a temperature of about 300°C with mixing for 30 minutes to 2 hours, more preferably for 45 to 75 minutes.

Among other factors, the present invention is based on the surprising finding that the present process results not only in distillates (produced in the distillation step) having an advantageous basic pH which are less corrosive to refinery equipment, but also produces an asphalt fraction which does not gel and, thus, foul and block piping and associated equipment. In particular, use of the process of the present invention removes metallo-sulfur compounds which are present in the lubricating oil additives and/or result from the decomposition of lubricating oil additives and which in later processing steps may cause serious fouling and corrosion due to acid-catalyzed polymerization reactions.

Pretreatment of used oil with a sodium (or potassium) salt of a weak acid, such as sodium hydroxide or sodium carbonate, removes certain of the products from decomposition of lubricating oil additives, but overtreatment is disadvantageous and has been hard to avoid. For example, overtreatment with these compounds, particularly when using sodium hydroxide, leads to serious plant operational problems in addition to being expensive. Fats and fatty oils present in the used oils may be hydrolyzed, producing soaps which cause gelling of the oil. Excess sodium hydroxide may also increase the viscosity of the distillation residue, resulting in associated problems in pumps and mechanical equipment. Certain processing problems are also associated with overtreatment and include an apparent lack of performance of heat transfer equipment which may be caused by changes in chemical and physical properties of the oil in the liquid phase, due to ion exchange and/or hydrolysis reactions during treatment. Also, the radical increase in viscosity of the distillation residue may lead to difficulties in extracting the material from the process equipment, which must be avoided, particularly in view of vacuum operating conditions which may be employed for certain processing steps.

The improved process described herein substantially avoids overtreatment in the pretreating of step (a).

Furthermore, it has been found that pretreatment with alkali metal hydroxide results in a reduced phosphorus content in lube distillate. In addition, it has been found that use of sodium aluminate in the pre-treating step is particularly effective in reducing phosphorus content in the lube oil distillate fraction (see Table VI). This reduction in phosphorus content is believed to occur by formation of aluminum phosphates and/or aluminum phospho esters. In place of sodium aluminate other suitable alkali compounds which form low-solubility phosphorus products may be used. Such suitable alkali compounds include magnesium aluminate, calcium oxide, calcium hydroxide, magnesium oxide, calcium aluminate, and magnesium hydroxide and other compounds which form insoluble phosphorus compounds that end up in the bottom (asphalt) fraction upon evaporation (or distillation). Other suitable alkali compounds include the sodium salts of weak acids and include sodium carbonates, bicarbonates, sulfites and bisulfites. Phosphorus is an undesirable component in lube distillates, since its presence deactivates hydrotreating catalyst in subsequent hydrosprocessing operations that are conducted to improve a variety of important quality/stability parameters of the lube oil base stock.

Before using the pretreatment according to the present invention, the catalyst life of the hydrosprocessing catalyst was typically about 3 to 4 weeks. After application of the process according to a preferred embodiment of the present invention, catalyst life was typically about 3 to 6 months which represents a significant extension in catalyst life.

**Brief Description of the Drawings**

**FIGURE 1** depicts a flow chart of the overall re-refining process.
Detailed Description of the Invention

General Process

[0031] A simplified block flow diagram of the overall re-refining process is depicted in Figure 1. This process comprises high-efficiency re-refining technology. Key steps include the pretreatment and subsequent base lube oil recovery via thin-film vacuum distillation that produces base lube oils in the overhead product and asphalt in the bottoms. Deleterious metals wind up encapsulated in the asphalt fraction. The asphalt fraction meets the leaching test criteria. The asphalt produced in this manner is suitable for use as a blending component for road paving asphalt or for production of roofing shingles.

[0032] The raw lube base distillates are catalytically hydrotreated to improve color and stability. The resulting finished lube base oils are of equal or better quality than virgin oil produced via extraction from lube crudes.

[0033] The pretreatment steps assure low maintenance and continuous, trouble-free operation, by minimizing fouling and corrosion.

[0034] An analysis of a typical used oil used in re-refining is set forth in Table I.
An important aspect of the processes of this invention comprises the pretreatment of the used oil to reduce fouling of catalyst and equipment and corrosion of equipment and to reduce the phosphorous content of the lube distillate that results from such pretreatment.

A major obstacle in the re-refining of used automotive oils is the presence of a wide variety of additives, including organo-metallic compounds, that have been added to lube base oils to impart desirable properties in a lubricating oil. These additives involve a considerable spectrum of compounds and include, but are not limited to, the following: antiwear compounds, corrosion inhibitors, pour point depressants, oxidation inhibitors, antifoam agents, etc. Modern automotive lubricants may contain up to about 25 percent additives. Such additives decompose much more rapidly than the base oils. The decomposition of these additives dictates the frequency of lube oil changes, since base oils are reported to be considerably more stable than additives. See, e.g., P.C. Keith, Jr., J.T. Ward and L.C. Rubin, API Proceedings, 3rd Mid-Year Meeting, Tulsa, Oklahoma, May 7-19, 1933; and W.L. Nelson, Petroleum Refinery Engineering, 628-679 (1959) (reporting virtually no thermal degradation (cracking) of saturated hydrocarbons below 650°F).

In contrast to the reported stability of base oils, lubricating oil additives have been reported to break down and decompose at significantly lower temperatures. This was reported a number of years ago by researchers who tried to minimize exposure of used oil to high temperatures by using vacuum (1-10mm Hg), indirect heating and thin film or wiped film evaporation equipment (see Third International Conference on Waste Oil Recovery and Reuse (1978)).

### Table I

<table>
<thead>
<tr>
<th>Analysis of Typical Used Oil for Re-Refining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity centistokes @ 100 deg Fahrenheit (≈37.7°C)</td>
</tr>
<tr>
<td>API Gravity - degrees</td>
</tr>
<tr>
<td>Composition - Volume Percentages</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Light Ends</td>
</tr>
<tr>
<td>Gas Oil Fraction</td>
</tr>
<tr>
<td>Lube Oil Fraction</td>
</tr>
<tr>
<td>Asphalt Flux</td>
</tr>
<tr>
<td>Sulphur - weight percentage</td>
</tr>
<tr>
<td>Nitrogen - weight percentage</td>
</tr>
<tr>
<td>Chlorine - ppm</td>
</tr>
<tr>
<td>Sulphated Ash - weight percentage</td>
</tr>
<tr>
<td>Flash Point (degrees Fahrenheit)</td>
</tr>
<tr>
<td>Metals - ppm</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td>Phosphorus</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Sodium</td>
</tr>
<tr>
<td>Cadmium</td>
</tr>
<tr>
<td>Chromium</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
</tbody>
</table>
Nevertheless, despite use of these techniques fouling and corrosion have remained significant problems.

It has now been discovered that neutralizing the acidic groups and/or acids that are contained in the additive compounds associated with magnesium, calcium and/or zinc leads to a more stable used oil mixture that exhibits a greatly reduced tendency for fouling and corrosion under all conditions. Moreover, it has been theorized that aryl sulfonates are hydrolyzed in the presence of alkali metal and/or alkali earth metal oxide/hydroxide whereby the sulfonate group is converted into sulfuric acid which then is neutralized and rendered harmless. This neutralization with an alkali compound involves all organo-metallic compounds containing magnesium, calcium and zinc. However, it also has been discovered that appropriate dosing of the alkali compound is crucial, since an excess of alkali compound will result in gelling of the asphalt produced which in turn requires addition of lube base stock to allow pumping of this material. Thus, over-dosing of alkali will result in yield loss of desirable lube base oil.

It has also been discovered that the reaction will not proceed under "dry" conditions, that is a minimum of 3% water is required to effect hydrolysis. Figure 2 depicts a proposed reaction scheme. The reaction is not instantaneous. Depending on conditions, the reaction takes about 15 to 20 minutes and in some instances up to 60 minutes, to go to completion. Mixing is important to assure thorough contacting of the aqueous phase with the hydrocarbon phase.

Some release of ammonia is triggered, if the alkali compound is dosed properly, due to decomposition of amines, amides and similar nitrogen containing compounds which keep the vapor space alkaline and allow use of carbon steel equipment without corrosion protection measures being required. If the alkali compound is improperly dosed, acidic gasoil fractions will be obtained that cause fouling and corrosion of equipment.

Gelling of asphalt due to over-treatment with sodium hydroxide is principally due to formation of soaps from fats and fatty oils. This gelling is also believed to be due to formation of sodium alcoholates and, in general, sodium oxygenates, all of which may cause gelling.

According to principles of chemical equilibrium, formation of insoluble sulfates helps to shift the reaction to the right, i.e. to complete sulfonate conversion. Thus, presence of Ca, and to a lesser extent Mg, shifts the sulfonate hydrolysis reaction to the right. This observation applies, but is not limited, to this type of reaction, it is only noted here as an example. Similar considerations apply to other hydrolysis reactions in used oil processing of the present invention that are shifted to completion in the presence of certain metal ions such as Ca and Al, notably conversion of phosphorous compounds such as phosphorous esters, thiophosphates, dithiophosphates and the like.

It has been discovered that phosphorous content in the lube distillate produced can be decreased by addition of an alkali compound and/or materials that promote hydrolysis of the phosphorous-bearing compounds. Particularly useful is sodium aluminate per se or in combination with another alkali compound.

The following stoichiometric relationship has been developed between phosphorous, Ca and Mg content of waste oil and maximum phosphorous content of the raw lube distillate:

\[ P_{RL} = P_{WO} - 0.52 \text{Ca} - 0.86 \text{Mg} \]

wherein

\[ P_{RL} = \text{Maximum phosphorous content in raw lube distillate, ppm.} \]
\[ P_{WO} = \text{Phosphorous content in waste oil, ppm.} \]
\[ \text{Ca} = \text{Calcium content in waste oil, ppm.} \]
\[ \text{Mg} = \text{Magnesium content in waste oil, ppm.} \]

It has been discovered that proper processing that promotes hydrolysis of the phosphonates together with appropriate reaction conditions for formation of insoluble metal-phosphates (and/or intermediate hydrolyzed phosphonates) results in a significant decrease of phosphorous in the resulting raw lube distillate. Note that the other metal, Zn, does not enter the picture since under hydrolysis conditions more than sufficient sulfides are produced that react to yield insoluble ZnS. Since the solubility product for ZnS is lower than that for zinc phosphate or zinc hydroxide, zinc will be present in the form of zinc sulfide and not in the form of either zinc phosphate or zinc hydroxide.

According to a preferred embodiment of the present invention for reduction of phosphorus content in lube oil distillates, the alkali compound used in the pretreating of step (a) comprises a combination of an alkali metal or alkaline earth hydroxide and an alkali metal or alkaline earth aluminate. According to an especially preferred aspect of the process of the present invention, we have found the use of a combination of sodium hydroxide and sodium aluminate to be particularly advantageous. Also advantageous is the use of sodium aluminate alone.

Catalytic Hydrotreatment

To improve color and enhance stability, hydrogenation is employed as indicated in the schematic process flow diagram, Figure 1. During catalytic hydrotreatment, a number of other important reactions occur simultaneously. These
include: a) heteroatom removal, and b) olefin and aromatics hydrogenation. Typical hydrotreating results are displayed in Table II where feed and product properties are compared. Nitrogen and sulfur are reduced from 390 ppm to 90 ppm and 1900 ppm to 700 ppm, respectively. Similarly, the bromine number is reduced from a feed value of 2.0 to 0.5 in the product, and dienes from 1.2 mg/g maleic anhydride for the feed to 0.2 mg/g maleic anhydride in the product. It should be noted, though, that a value of 0.5 for the product bromine number and 0.2 for dienes indicates basically zero olefins and diolefins, respectively. The fact that some value for total olefins and diolefins, respectively, is observed is due to reaction of other materials, principally aromatics, with bromine and maleic anhydride, respectively.

<table>
<thead>
<tr>
<th>Table II</th>
<th>Hydrotreatment Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
</tr>
<tr>
<td>Degrees API</td>
<td>30.5</td>
</tr>
<tr>
<td>Nitrogen - ppm</td>
<td>390</td>
</tr>
<tr>
<td>Sulfur - ppm</td>
<td>1900</td>
</tr>
<tr>
<td>Bromine Number</td>
<td>2.0</td>
</tr>
<tr>
<td>Dienes mg MA/g</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The influence of hydrotreating on bulk hydrocarbon composition is demonstrated in Table III where feed and product values are listed. These data indicate that paraffins increase slightly, whereas naphthenes decrease, presumably as a result of ring opening reactions. The total aromatics content stays roughly the same, however, monoaromatics increase at the expense of the more condensed (triaromatics, tetraaromatics and higher) aromatics.

<table>
<thead>
<tr>
<th>Table III</th>
<th>Hydrocarbon Content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed (% Volume)</td>
</tr>
<tr>
<td>Paraffins</td>
<td>20.7</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>66</td>
</tr>
<tr>
<td>Aromatics</td>
<td>13.3</td>
</tr>
<tr>
<td>Mono</td>
<td>5.8</td>
</tr>
<tr>
<td>Di</td>
<td>2.7</td>
</tr>
<tr>
<td>Tri</td>
<td>1.5</td>
</tr>
<tr>
<td>Tetra and higher</td>
<td>3.3</td>
</tr>
</tbody>
</table>

To assist in understanding the present invention, the following Examples are included which describe the results of a series of experiments. The following examples relating to this invention should not, of course, be construed as specifically limiting the invention and such variations of the invention, now known or later developed, which would be within the purview of one skilled in the art are considered to fall within the scope of the invention as described herein and hereinafter claimed.

Examples

Example 1

200 g waste oil were placed in a 1000 ml three neck flask provided with: a) reflux condenser, b) motor-driven half-moon paddle stirrer, and c) thermometer. After placing the noted amount of sodium hydroxide and/or other chemicals into the flask, the flask was heated with an electrical heating pad up to refluxing at 105-110°C while stirring at 30-60 rpm. After refluxing for a set time, the reflux condenser was replaced with a water-cooled distillation arm and the
temperature was raised within a set period of time up to 300°C while collecting distillate fractions of:

1. 120-150°C
2. 150-200°C
3. 200-250°C
4. 250-300°C

The reaction mixture was then cooled to room temperature and the content of the reaction flash was subjected to a D-1160 vacuum distillation with a distillate end point corresponding to 975°F (=524°C) at 760mm Hg. The lube oil distillate fraction comes over at a temperature range of 650°F to 950°F or 350°C to 520°C.

[0051] An attempt was made to measure the kinetics of the neuralisation/decomposition/hydrolysis reaction when heating/treating waste oil with varying amounts of sodium hydroxide. The results for the feed composition listed in Table IV are presented in Table V and indicate that there was a significant effect of the amount of sodium hydroxide on the pH in the gas phase during refluxing.

[0052] With no NaOH added, the pH in the gas phase was about 8.0, whereas with 0.51 ml NaOH 30% added, it was about 9.0, and with addition of 2.1 ml NaOH 30%, it was about 10.0. Note that there was only a slight effect of kinetics, i.e., discernible pH change as a function of reaction time, for series #2. 0.51 ml NaOH 30% and series #1. For the maximum amount NaOH added, there was no effect of reaction time on pH.

[0053] A number of tests have been conducted with the feed whose properties are listed in Table IV when using sodium aluminate and/or sodium hydroxide as additives. The results are listed in Table VI. Note that the test using 2.88 ml of an aqueous sodium aluminate solution (NaAlO₂, 1.5 H₂O, 14%) corresponds to five fold excess of aluminum over that needed to convert all remaining phosphorous to aluminum phosphate. The amounts of sodium aluminate added for run 7 and 9, respectively, corresponded to a 50 fold excess over that amount needed to convert all free phosphorous to aluminum phosphate.

[0054] Runs 1 and 2 clearly showed the beneficial effect of NaAlO₂ in that phosphorous was reduced to 0.3 ppm with NaAlO₂ whereas NaOH added alone resulted in a phosphorous content of 1.9 ppm. Elimination of the 60 minute holding time increased the phosphorous contents of the respective distillates to 28 ppm for NaOH and to 18 ppm for the NaAlO₂. Thus, there was a 30% improvement in phosphorous reduction when using NaAlO₂. In the experiments 5 and 6, the heat up from 12°C-300°C was changed as well as the holding time at 300°C. Again, there was an advantage for NaAlO₂. In experiments 7 and 8, as well as in experiments 9 and 10, a substantial 50 fold amount of NaAlO₂ was added over that required to convert all free phosphorous to AlPO₄, and in each case the result was compared with the stoichiometric amount of NaOH added. In both cases, an advantage for NaAlO₂ was observed. However, there was no advantage by increasing the amount of NaAlO₂ from a five-fold excess to a fifty-fold excess.

[0055] A set of interesting results is displayed in Table VII. There was a significant effect on the pH's of the gasoil boiling range fractions as a function of sodium hydroxide added to the waste oil. The pH of each of the heaviest three fractions was measured in the mixture obtained after adding the same amount of deionized water as the weight of the fraction, followed by vigorous shaking for one minute. The pH of the 150°C minus fraction was measured directly. When no sodium hydroxide was added, the pH's of the 150-200°C, 200-250°C and 250-300°C fractions were extremely acidic, pH 2.2 to 5.1. When NaOH was added, the respective pH's are in the 7.4 to 8.3 range, i.e., clearly above 7 and hence non-corrosive. Also, phosphorous content was reduced to 23 ppm in the distillate vs. 39 ppm when no NaOH was added.

[0056] In accordance with earlier observations recorded in Table V, the pH of the lightest fraction (boiling at 150°C or less) is above 7.0 even with no alkali compound added. This observation was again confirmed in Table VII, experiment #11, where a pH of 7.3 is indicated for the fraction boiling below 150°C. This result is somewhat unexpected and surprising, yet decisive. It indicates that in a commercial process the dewatering (removal of materials boiling at 150°C or less, i.e., water and light ends) is not crucial with respect to corrosion and fouling, since pH's of 7 and higher are prevalent.

[0057] To better define the effect of sodium hydroxide on the pH of the various boiling range fractions, as well as its effect on the phosphorous content of the resulting lube distillate, a number of additional experiments were conducted and are listed in Table VII. The data in Table VII clearly indicate that the pH of the gasoil fraction increases as the amount of sodium hydroxide is increased. The pH of the two lower boiling fractions, i.e., 150°C minus and 150°C-200°C fraction, were always lower than the respective pH's of the fractions boiling at 200°C-250°C and 250°C-300°C.

[0058] A graphic representation of the results in Table VII is depicted in Figure 3, where the phosphorous content of the lube distillate and the pH of the 150°C-200°C gasoil boiling range fraction are plotted as a function of sodium

\[ \text{In some experiments, pH measurements were made of the aqueous gas phase during refluxing. This was done by using a "cold finger" to trap the condensed vapors from the reflux condenser. Under the prevailing operating conditions, it took typically ten minutes to fill the cold finger volume of about 13 ml.} \]
hydroxide added. Figure 3 clearly indicates that the phosphorous content of the lube distillate decreases as a function of sodium hydroxide added.

[0059] On the other hand, the pH of the gasoil fraction, 150°C-200°C boiling range, is observed to increase with increasing amounts of sodium hydroxide added, whereby a steep increase is observed between 1.1 ml and 2.0 ml aqueous sodium hydroxide solution (30% NaOH). This steep slope of the curve occurs between pH 3 and 7, and it is similar to a titration curve. Thus, this behavior suggests the concept of neutralisation stoichiometry involving sodium hydroxide on one hand and waste oil content of the predominant metals magnesium, calcium and zinc on the other hand. Moreover, the values of the pH's for all gasoil fractions are above 6.5 at a point where about 1.7 ml sodium hydroxide solution (30% NaOH) had been added.

[0060] The results of the above experiments indicate that phosphorous reduction can be accomplished by decomposing phosphorous containing additives with NaOH and converting the resulting phosphates into non-volatile metal (aluminum) phosphates. There was quantitative evidence that NaOH aided in reducing the pH of gasoils. Furthermore, addition of alkali compound also aided in phosphorous reduction, possibly by increasing the rate of hydrolysis of phosphorous esters.

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<th>Component</th>
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<td>Mg</td>
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<tr>
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<td>845</td>
</tr>
<tr>
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<tr>
<td>H₂O, % by weight</td>
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Table V

<table>
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<th>Reaction Time Before Cold Finger</th>
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<th>pH 2</th>
<th>pH 3</th>
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<td>50</td>
<td>8.4</td>
<td>9.2</td>
<td>9.9</td>
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</table>

1 Waste Oil only.
2. 0.5 ml NaOH 30% added.
3. 2.1 ml NaOH 30% added.
### Table VI

**PHOSPHOROUS REDUCTION WITH SODIUM ALUMINATE/SODIUM HYDROXIDE**

<table>
<thead>
<tr>
<th>EX#</th>
<th>NaAlO₂, 14% (ml)</th>
<th>NaOH, 30% (ml)</th>
<th>Heat Up (min)</th>
<th>Reflux (min)</th>
<th>120-300°C (min)</th>
<th>120-250°C (min)</th>
<th>250-300°C (min)</th>
<th>300°C (min)</th>
<th>ppm Dist.</th>
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### Table VII

**EFFECT OF NaOH ON PH OF GASOIL FRACTIONS, PHOSPHORUS CONTENT OF DISTILLATE AND CONDITION OF RESIDUE**

<table>
<thead>
<tr>
<th>EX#</th>
<th>NaOH, 30% (ml)</th>
<th>Heat Up (min)</th>
<th>reflux (min)</th>
<th>105-115°C (min)</th>
<th>120-300°C (min)</th>
<th>150°C/150-200°C</th>
<th>200-250°C</th>
<th>250-300°C</th>
<th>P Dist. (ppm)</th>
<th>Residue</th>
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Table VII Cont’d

EFFECT OF NaOH ON PH OF GAS OIL FRACTIONS, PHOSPHORUS CONTENT OF DISTILLATE AND CONDITION OF RESIDUE

<table>
<thead>
<tr>
<th>EX#</th>
<th>NaOH, 30% (ml)</th>
<th>Heat Up (min)</th>
<th>Reflux (min)</th>
<th>120-300°C (min)</th>
<th>150°C/105-115°C (min)</th>
<th>150-200°C</th>
<th>200-250°C</th>
<th>250-300°C</th>
<th>P Dist. (ppm)</th>
<th>Residue</th>
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</table>

Note: W = Weight of fractions, g.
P = Phosphorous content of fraction, ppm.
pH = pH of fraction.
Claims

1. A process of re-refining used oil to produce a base stock oil which is substantially equivalent to a base stock oil produced from virgin crude oil which comprises:
   (a) pretreating used oil to remove hydrofinishing catalyst fouling materials to give a pretreated mixture;
   (b) distilling the pretreated mixture from step (a) to separate a lower boiling distillate fraction which boils at less than 150°C, a gasoil distillate fraction; and a lube oil distillate fraction from an asphalt fraction; and
   (c) hydrofinishing the lube oil distillate fraction from step (b);
   wherein the pretreating of step (a) includes adding to said used oil under vigorous mixing conditions a sufficient amount of an alkali compound to give a pH of at least 5 in the gas phase of all the distillates produced in step (b), the amount of alkali compound being insufficient to cause gelling of the asphalt fraction, and wherein said pretreated mixture comprises at least 3% water.

2. A process according to claim 1 wherein said pretreatment mixture comprises from 3 to 20 percent water.

3. A process according to claim 1 or claim 2 wherein said alkali compound is selected from alkali metals and weak acid salts of an alkali metal or alkaline earth.

4. A process according to claim 3 wherein said alkali compound comprises an alkali metal, or a salt selected from an alkali metal or alkaline earth hydroxide, oxide, aluminate, carbonate, bicarbonate, sulfite or bisulfite, or a combination thereof.

5. A process according to claim 4 wherein said alkali compound comprises sodium hydroxide, potassium hydroxide, sodium aluminate, sodium carbonate, sodium bicarbonate, sodium sulfite, sodium bisulfite, or a combination thereof.

6. A process according to claim 5 wherein said alkali compound comprises sodium aluminate, sodium carbonate, sodium bicarbonate, sodium sulfite, sodium bisulfite or a combination thereof.

7. A process according to claim 5 wherein said alkali compound comprises sodium hydroxide in combination with sodium aluminate.

8. A process according to claim 5 wherein said alkali compound comprises sodium hydroxide added in step (a) in an amount sufficient to give a pH of 6.5 or greater for gasoil fractions boiling in a range of 150°C to 300°C.

9. A process according to any one of claims 1 to 7 wherein said alkali compound is added in step (a) in an amount sufficient to give a pH of at least 6 in the gas phase of all the distillates produced in step (b).

10. A process according to claim 9 wherein said alkali compound is added in step (a) in an amount sufficient to give a pH of at least 6.5 in the gas phase of all the distillates produced in step (b).

11. A process according to any one of claims 1 to 10 wherein the amount of an alkali compound added in the pretreating of step (a) is sufficient to convert substantially all free phosphorus to an insoluble phosphate or phosphoro compound.

12. A process according to claim 11, wherein said alkali compound comprises sodium hydroxide.

13. A process according to any one of claims 1 to 12 wherein said pretreating step (a) is conducted at a temperature of 80°C to 170°C.

14. A process according to claim 13 wherein said pretreating step (a) is conducted at a temperature of 90°C to 150°C.

15. A process according to claim 14 wherein said pretreating step (a) is conducted at a temperature of 100°C to 130°C.

16. A process according to any one of claims 1 to 15 where distilling step (b) includes holding the pretreated mixture at a temperature of about 300°C for 30 minutes to 2 hours with good mixing.
17. A process according to claim 16 wherein said holding time at about 300°C is for 45 to 75 minutes.

**Patentansprüche**

1. Verfahren zum Regenerieren von Altöl, um ein Grundöl herzustellen, welches im wesentlichen einem aus jungfräulichem Rohöl hergestellten Grundöl entspricht, umfassend:

   (a) das Vorbehandeln von Altöl, um Hydrofinishing-Katalysator-Foulingmaterialien zu entfernen unter Erhalt einer vorbehandelten Mischung;

   (b) das Destillieren der vorbehandelten Mischung von Schritt (a), um eine niedriger siedende Destillatfraktion, die bei weniger als 150°C siedet, eine Gasöl-Destillatfraktion; und eine Schmieröl-Destillatfraktion von einer Asphaltfraktion abzutrennen; und

   (c) Hydrofinishing der Schmieröl-Destillatfraktion von Schritt (b);

   wobei die Vorbehandlung von Schritt (a) die Zugabe zu dem Altöl unter kräftigen Mischbedingungen einer ausreichenden Menge einer Alkaliverbindung einschließt, wodurch ein pH-Wert von mindestens 5 in der Gasphase von allen in Schritt (b) gebildeten Destillaten erhalten wird, wobei die Menge der Alkaliverbindung nicht ausreichend ist, um ein Gelieren der Asphaltfraktion zu bewirken, und wobei die vorbehandelte Mischung mindestens 3 % Wasser umfaßt.

2. Verfahren gemäß Anspruch 1, wobei die Vorbehandlungsmischung 3 bis 20 Prozent Wasser umfaßt.

3. Verfahren gemäß Anspruch 1 oder Anspruch 2, wobei die Alkaliverbindung aus Alkalimetallen und schwachen Säuresalzen eines Alkalimetalls oder Erdalkalis gewählt ist.


5. Verfahren gemäß Anspruch 4, wobei die Alkaliverbindung Natriumhydroxid, Kaliumhydroxid, Natriumaluminat, Natriumcarbonat, Natriumbicarbonat, Natriumsulfid, Natriumbisulfid oder eine Kombination hiervon umfaßt.

6. Verfahren gemäß Anspruch 5, wobei die Alkaliverbindung Natriumaluminat, Natriumcarbonat, Natriumbicarbonat, Natriumsulfid, Natriumbisulfid oder eine Kombination hiervon umfaßt.

7. Verfahren gemäß Anspruch 5, wobei die Alkaliverbindung Natriumhydroxid in Kombination mit Natriumaluminat umfaßt.

8. Verfahren gemäß Anspruch 5, wobei die Alkaliverbindung in Schritt (a) zugesetztes Natriumhydroxid in einer Menge umfaßt, die ausreicht, um einen pH-Wert von 6,5 oder größer für Gasölfaktionen, die im Bereich von 150°C bis 300°C sieden, zu erhalten.

9. Verfahren gemäß mindestens einem der Ansprüche 1 bis 7, wobei die Alkaliverbindung in Schritt (a) in einer Menge zugesetzt wird, die ausreicht, um einen pH-Wert von mindestens 6 in der Gasphase von allen in Schritt (b) gebildeten Destillaten zu erhalten.

10. Verfahren gemäß Anspruch 9, wobei die Alkaliverbindung in Schritt (a) in einer Menge zugesetzt wird, die ausreicht, um einen pH-Wert von mindestens 6,5 in der Gasphase von allen in Schritt (b) gebildeten Destillaten zu erhalten.

11. Verfahren gemäß mindestens einem der Ansprüche 1 bis 10, wobei die Menge einer in der Vorbehandlung von Schritt (a) zugesetzten Alkaliverbindung ausreicht, um praktisch den gesamten freien Phosphor in eine unlösliche Phosphat- oder Phosphorverbindung umzuwandeln.

12. Verfahren gemäß Anspruch 11, wobei die Alkaliverbindung Natriumhydroxid umfaßt.

13. Verfahren gemäß mindestens einem der Ansprüche 1 bis 12, wobei der Vorbehandlungsschritt (a) bei einer Tem-
Revendications

1. Procédé pour le ré-raffinage d'huiles usées pour fournir une huile de base qui est essentiellement équivalente à une huile de base obtenue à partir d'une huile de pétrole vierge qui comprend :

   (a) le prétraitement de l'huile usée pour éliminer les matières d'encrassement du catalyseur d'hydrofinition et conduire à un mélange prétraité,

   (b) la distillation du mélange prétraité de l'étape (a) pour séparer, d'une fraction d'asphalte, une fraction de distillat de faible point d'ébullition qui bout à moins de 150° C, une fraction de gasoil et une fraction d'huile lubrifiante, et

   (c) l'hydrofinition de la fraction d'huile lubrifiante de l'étape (b),

   procédé dans lequel l'étape de prétraitement comprend l'addition à la dite huile usée, dans des conditions d'agitation vigoureuses, d'une quantité suffisante d'un composé alcalin pour conduire à un pH d'au moins 5 dans la phase gazeuse de tous les distillats obtenus à l'étape (b), la quantité du composé alcalin étant insuffisante pour provoquer la gélification de la fraction d'asphalte et dans lequel le mélange prétraité contient au moins 3 % d'eau.

2. Procédé selon la revendication 1 dans lequel ledit mélange de prétraitement contient de 3 à 20 % d'eau.

3. Procédé selon la revendication 1 ou 2 dans lequel le composé alcalin est choisi parmi les métaux alcalins et les sels d'acides faibles d'un métal alcalin ou alcalino-terreux.

4. Procédé selon la revendication 3 dans lequel le composé alcalin comprend un métal alcalin ou un sel choisi parmi les hydroxydes, oxides, aluminates, carbonates bicarbonates ou bisulfites d'un métal alcalin ou alcalino-terreux ou un mélange de ceux-ci.

5. Procédé selon la revendication 4 dans lequel ledit composé alcalin comprend de l'hydroxyde de sodium, de l'hydroxyde de potassium, de l'aluminate de sodium, de l'alkalinate de sodium, du carbonate de sodium, du bicarbonate de sodium, du sulfite de sodium, du bisulfite de sodium ou un mélange de ceux-ci.

6. Procédé selon la revendication 5 dans lequel le composé alcalin comprend de l'aluminate de sodium, de l'alkalinate de sodium, du carbonate de sodium, du bicarbonate de sodium, du sulfite de sodium, du bisulfite de sodium ou un mélange de ceux-ci.

7. Procédé selon la revendication 5 dans lequel le composé alcalin comprend de l'hydroxyde de sodium en mélange avec de l'aluminate de sodium.

8. Procédé selon la revendication 5 dans lequel ledit composé alcalin comprend de l'hydroxyde de sodium additionné à l'étape (a) en une quantité suffisante pour donner un pH de 6,5 ou supérieur aux fractions de gasoils de point d'ébullition compris entre 150° C et 300° C.

9. Procédé selon l'une quelconque des revendications 1 à 7 dans lequel ledit composé alcalin est additionné à l'étape (a) en une quantité suffisante pour donner un pH d'au moins 6 dan la phase gazeuse de tous les distillats obtenus à l'étape (b).
10. Procédé selon la revendication 9 dans lequel ledit composé alcalin est additionné à l'étape (a) en une quantité suffisante pour donner un pH d’au moins 6,5 dans la phase gazeuse de tous les distillats obtenus à l'étape (b).

11. Procédé selon l'une quelconque des revendications 1 à 10 dans lequel la quantité du composé alcalin additionnée à l'étape de prétraitement (a) est suffisante pour convertir essentiellement tout le soufre libre en un composé phosphorate ou phosphoro insoluble.

12. Procédé selon la revendication 11 dans lequel ledit composé alcalin comprend de l'hydroxyde de sodium.

13. Procédé selon l'une quelconque des revendications 1 à 12 dans lequel ladite étape de prétraitement (a) est réalisée à une température de 80°C à 170°C.

14. Procédé selon la revendication 13 dans lequel ladite étape de prétraitement (a) est réalisée à une température de 90°C à 150°C.

15. Procédé selon la revendication 14 dans lequel ladite étape de prétraitement (a) est réalisée à une température de 100°C à 130°C.

16. Procédé selon l'une quelconque des revendications 1 à 15 dans lequel ladite étape de distillation (b) consiste à maintenir le mélange prétraité à une température d'environ 300°C pendant 30 minutes à 2 heures sous bonne agitation.

17. Procédé selon la revendication 16 dans lequel le temps de contact, à environ 300°C, est de 45 à 75 minutes.
USED LUBE OIL

PRETREATMENT

WATER

LT HYDROCARBON REMOVAL

LT HYDROCARBON FOR PLANT FUEL

WATER TO TREATMENT

GASOIL REMOVAL

GASOIL FOR PLANT & SALES FUEL

BASE LUBE OIL RECOVERY

ASPHALT FOR BLENDING

HYDROGEN FROM SUPPLIER

HYDROFINISHING

LUBE BASE OIL FRACTIONATION

LIGHT BASE NEUTRAL OIL

HEAVY BASE NEUTRAL OIL

HYDROFINISHED GASOIL
FIGURE 2.

\[ 2 \text{C}_n\text{H}_{2n-1} \text{SO}_3(\text{Me})_{0.5} + 2\text{H}_2\text{O} \rightleftharpoons 2 \text{C}_n\text{H}_{2n-1} + \text{MeSO}_4 + \text{H}_2\text{SO}_4 \]
FIGURE 4.