Title: SOLVENT EXTRACTION PROCESS TO STABILIZE, DESULPHURIZE AND DRY WIDE RANGE DIESELS, STABILIZED WIDE RANGE DIESELS OBTAINED AND THEIR USES

Abstract: A process allowing the removal of contaminants from an unstable oil such as those produced by thermal or catalytic cracking, wherein, in at least one step of the process, mixing of the unstable oil with a pure or impure solvent having a dipole moment greater than 2 is performed. The stabilized diesels thereby obtained exhibit interesting properties among which significant stability features and are useful in numerous applications, some of these stabilized wide range diesels are new as well as their uses.
SOLVENT EXTRACTION PROCESS TO STABILIZE, DESULPHURIZE AND DRY WIDE RANGE DIESELS, STABILIZED WIDE RANGE DIESELS OBTAINED AND THEIR USES

TECHNICAL FIELD

The invention relates to an extraction process using a polarized solvent having a dipole moment greater than 2, to stabilize wide range diesels, containing or not free radicals, such as those produced by the thermal or catalytic cracking of used oils, heavy oils, vacuum gasoils or bunkers. The new process markedly improves colour, odour and storage stability of thermally cracked gasoils so they can meet market specifications. The extraction process also removes water, sulphurous compounds and chlorides when present from the wide range diesels, reduces their total acid number and increases their cetane index.

The invention also relates to a new family of wide range diesels, including those wide range diesels obtained by the processes of the invention, as well as to numerous uses of the wide range diesels of the invention, and more particularly to lucrative uses and/or to some applications beneficial to the environment.

BACKGROUND

Gasoils or diesels produced from thermal or catalytic cracking processes are known to be unstable. While in storage, they form gums and polymers that can plug burner tips in furnaces or filters in engines. Further, new environmental constraints demand that these fuels reduce their sulphur, nitrogen, water and chlorides contents. Hydrotreating is commonly used in refineries to stabilize gasoils and to remove some of their contaminants. However, hydrotreating processes require high pressures and/or temperatures and the reactors must either be made of, or clad with,
high alloy steels to resist hydrogen permeation in the metal walls. There must also be a hydrogen plant or pipeline close by. Because of the high costs of such units, they are only viable as part of refineries or large plants. Also, the hydrotreated oils must be dried to meet water content and appearance specifications.

5 Used lubricating oils are classified as hazardous products in many countries, mostly because of the additives that they contain. Of all the by-products from the oil industry, used oils pose the greatest danger to the fresh water supply. The Environmental Protection Agency (EPA) states that: "One gallon of used oil can pollute one million gallons of water". Among the processes to treat used oils for their reuse as fuel, thermal cracking is a viable option for smaller facilities.

10 More precisely, the additives in the used oil must be destroyed and removed. The main product is a wide range diesel or heating fuel. It tends to darken as soon as it comes into contact with air: it is unstable. Also, the wide range diesel has a high sulphur content, 3 or 4 times the 0.1% wt sulphur specification for heating oils in Europe, and has a bad odour.

Processes to stabilize and/or desulphurize diesel fuels produced by cracking heavier oils are well known. In refineries, hydrocracking and hydrotreating processes use hydrogen in catalytic reactors at high temperatures and pressures to achieve clear, stable diesel fuels with good burning characteristics and with sulphur contents as low as 15 ppm that meet ultra-low sulphur specifications. These processes not only require large, heavy reactors made of metals that resist hydrogen permeation, and corrosion, but also require hydrogen production plants or pipelines near-by. They are not suited for small or isolated refineries or used oil applications.
In used oil applications, the UOP Hylube process (U.S. Patent No. 5,904,838) uses hydrogen at high temperatures and pressures to recycle the feed oil into lubricating oils. Others hydrotreat only the lube oil products, obtained by successive distillations of used oils.

Canadian Patent No. 2,245,025 (Ikura et al.) mentions that gasoil produced by thermal cracking of used oils can be stabilized using methanol extraction.

There are also processes to remove sulphur and/or water from naphtha and other light oils but these are not applicable to diesel fuels. In the solutizer process, Canadian Patents Nos. 456,448 (Border) and 456,599 (Bell et al.) mention that mercaptans and other weak acids contained in sour hydrocarbon distillates, and more particularly in gasoline distillates, would be extracted with solutizer solution, i.e. aqueous solutions of alkali metal hydroxides containing solutizers.

Hassan et al. (Journal of Applied Sciences Research, 5(5); pp. 515-521, 2009) mention that sulphur could be removed from straight a in diesel fuel with a mixture of NMP (normal methyl pyridine), ethylene glycol, DMF (dimethyl formamide) and furfural.

Toteva, Topalova, and Manolova (Journal of the University of Chemical Technology and Metallurgy, 42, 1, 2007, pp. 17-20) mention that two-stage extraction of diesel fuel with DMF could reduce the aromatics and sulphur (from 2% wt to 0.33% wt) in a non-hydrotreated diesel fuel. This is not enough to meet heating fuel specifications for sulphur of less than 0.1% wt.

U.S. Patent No. 6,320,090 (Sherman et al.) mentions that DMF could be used as a solvent to remove mostly poly aromatic hydrocarbons (PAH) as well as sulphur and nitrogen compounds from used oils that have been subjected to successive vacuum distillations.

Others have tried solvent extraction processes to remove sulphur compounds from fuel oils.
U.S. Patent No. 5,753,102 (Funakoshi et al.) uses a mixture of acetone, water and iodine as the preferred solvent to remove sulphur from various straight amin oils. They also tested more polarized solvents including DMF, acetonitrile, trimethyl phosphate, nitromethane, methanol, hexamethyl phosphoramide, acetic acid, pyridine, and N-methylperolidinone with less success.

U.S. Patent No. 5,494,572 (Horii et al.) completes the sulphur removal from oil that has been hydrotreated using organic solvent containing nitrogen, specifically pyridinium salts, with another solvent containing hydroxyl groups, specifically one or more of water, methanol, ethanol, propanol, butanol, ethylene glycol, and glycerol. Hydrotreating is the more costly process.

In the process described by U.S. Patent No. 5,059,303 (Taylor et al.), oils produced via cracking processes, ranging from cracked naphtha, gasoil and vacuum residue, are contacted with an extraction solvent to reduce their sulphur and nitrogen content prior to hydrotreating. The solvents used are polarized and in an aqueous solution. They include N-methyl pyrrolidone, furfural, DMF, and phenol.

U.S. Patent No. 4,405,448 (Googin et al.) mention a polar solvent, specifically DMF and water, intended to remove polychlorinated biphenyls (PCB) from transformer oil. A second extraction using a non-polar solvent, chosen from normal pentane to normal octane, is intended to remove the PCB from the polar solvent.

For the past ten years, several oil desulphurization processes use an oxidizing agent and a catalyst to oxidize mercaptans and thiols in the oil. In a second step, polarized solvents are used to extract the sulphur oxides from the oil.

U.S. Patent No. 6,274,785 (Gore) uses dimethylsulfoxide as the extraction solvent.
Canadian Patent No. 1,287,007 (Kittrel et al.) suggests using solvents having a dipole moment greater than 2, mixed with water, to extract the sulphur and nitrogen oxides from the oil.

U.S. Patent No. 5,154,817 (Reid) mentions that cracked oils can be stabilized with additive injection. However, additives do not remove mercaptans and thiols from the oil.

The complete solvent regeneration is difficult because the solvents and the oils to treat have similar boiling points and gravities. Solvent losses render these processes impractical.

There was therefore a need for a new process able to stabilize, desulphurize, neutralize and dry wide range diesel, which process being free of at least one of the drawbacks of the prior processes.

There was therefore also a need for a process able to stabilize, desulphurize, neutralize and dry the heating oil to meet the heating oil specifications, which process being free of at least one of the drawbacks of the prior processes.

There was a further need for a process that would also be effective in reducing the sulphur in diesel cuts produced by catalytic or thermal cracking of heavy oils in refineries.

There was particularly a need for a low cost process to stabilize and remove contaminants from wide range diesels or gasoils that can be used in smaller plants, such as used oil cracking units.

There was a further need for new stabilized wide range diesel obtained from an unstable oil.

There was also a need for uses of a stabilized and/or desulphurized wide range of diesel.
SUMMARY

A first object of the present invention is the process to stabilize and to remove contaminants from an unstable oil, said process comprising at least one step of mixing said unstable oil with an impure solvent having a dipole moment greater than 2.

According to a preferred embodiment, the processes allow to stabilize and to remove contaminants from an unstable oil, wherein the unstable oil is selected among the family of: mixtures made for at least 50% weight of hydrocarbons which may include free radicals, oils produced by thermal cracking, oils obtained by catalytic cracking, oils obtained by decomposition, oils obtained by degradation, and the mixtures of at least two of the latter oils.

Advantageously, in order to stabilize and to remove contaminants from an unstable oil, said process includes at least one step of contacting a stream of the unstable oil with a solvent having a dipole moment greater than 2 and, thus, obtaining two mixtures, the first mixture being of an oil-solvent type and containing impurities, and the second mixture being of a solvent-oil type and containing residues and impurities, the impurities in the solvent-oil mixture being identical to, or different from, the impurities in the oil-solvent mixture.

According to another preferred embodiment of the invention, in the processes at least a fraction of the solvent having a dipole moment greater than 2 that is present in at least one of the two mixtures is extracted from the mixture(s) and is at least partially regenerated before being recycled to said process.

According to a further preferred embodiment of the invention, the processes comprise the following steps of:
a) intimately contacting a stream of the unstable oil with a solvent having a dipole moment greater than 2 and, thus, obtaining two mixtures, the first mixture being of an oil-solvent type and containing impurities, and the second mixture being of a solvent-oil type and containing residues and impurities, the impurities in the solvent-oil mixture being identical or different from the impurities in the oil-solvent mixture;

b) separating the treated oil, present in the oil-solvent mixture obtained in step a), from the solvent, leaving most of the impurities in the solvent phase;

c) separating the solvent and the oil, present in the solvent-oil mixture obtained in step a), from the residues, leaving preferably at least 90% wt. of the contaminants in the residues;

d) optionally separating the solvent and the light oil present in the oil-solvent mixture obtained in step b);

e) optionally separating the solvent and the oil obtained in step c); and

f) recycling at least one of the solvents obtained in steps b), c), d) or e), wherein each of said solvent is at least partially regenerated.

The processes of the invention are particularly suited to stabilize and to remove contaminants from an unstable oil, wherein, in step b), at least 80% weight, preferably at least 90% weight, of the impurities remain in the solvent phase.

Advantageously, in step f), at least one of each of said solvent is regenerated for at least 50% weight but for less or equal to 99% weight, and preferably for at least 55% weight but for less or equal to 98% weight, before recycling.
Preferably, in step f), at least one of each of said solvent is regenerated by physical means such as distillation, vacuum distillation, including thin film or wiped film evaporation, azeotropic distillation, and or centrifuging.

Advantageously, in step f), at least one of each of said solvent is regenerated by using vacuum distillation and/or centrifuging.

The processes of the invention are of a particular interest wherein the boiling range of the unstable oil, as measured by the method ASTM D86, ranges from 125°C to 500°C and preferably when the boiling range ranges from 175°C to 450°C.

Advantageously, the boiling range of the treated oil in step a), as measured by the method ASTM D86, ranges from 125°C to 500°C and more preferably ranges from 175°C to 450°C.

The processes of the invention are of a particular interest when applied to unstable oils produced by cracking used oil, heavy oil, bitumen, vacuum gasoil, vacuum residue, tar, synthetic caide oil, bunker or is produced by cracking a mixture of at least two of these solvents.

Advantageous results are obtained when the initial solvent is chosen among N-methyl pyrrolidone, furfural, dimethyl formamide, phenol, pyridine, dimethyl acetamide, dimethyl sulfoxide and propylene carbonate, and among mixtures of at least 2 of these.

According to a further embodiment of the invention, the process, to stabilize and to remove contaminants from an unstable oil, wherein the regenerated solvent, obtained in steps b), c), d) and/or f), still contains some impurities or reaction products.
The processes of the invention are of a particular interest, when the contaminants present in the treated unstable oil include: water, sulphur compounds such as mercaptans and thiols, organic chlorides, organic and inorganic acids, free radicals, resins, gums, sediments, reaction products and mixtures of at least two of these.

The solvent concentration in the regenerated solvent stream obtained, in step f), advantageously ranges from 50% wt. to 99% wt.

Advantageously, the solvent concentration in the regenerated solvent stream obtained, in step f), ranges from 70% wt. to 90% wt. and is more preferably about 83% wt.

According to a preferred embodiment of the invention, the regenerated solvent is produced, in step f), by a physical process such as distillation and/or centrifugation. The distillation is thus advantageously performed at pressures ranging from 0.5 psia to 15 psia, preferably the distillation pressures ranging from 0.6 psia to 12 psia, advantageously from 0.7 psia to 4 psia and more preferably the distillation is performed at pressures about 1.5 psia.

Advantageously, the regenerated solvent is produced, in steps b), c), d), and f), by distillation conducted at temperatures ranging from 50°C to 350°C, more preferably distillations are thus conducted at temperatures ranging from 100°C to 175°C, and more preferably at a temperature of about 130°C.

The processes of the invention are of a particular interest when the impurities, present in the regenerated and/or recycled solvent, have a boiling temperature ranging from 120°C to 250°C, and more preferably in the case wherein the impurities, present in the regenerated and/or recycled solvent, have a boiling temperature ranging from 130°C to 200°C.
The processes are very efficient when the impurities, present in the regenerated and/or recycled solvent, have catalytic and/or solution enhancing and/or bridging properties.

The processes are very efficient when in step a) the solvent extraction is carried out at temperatures not exceeding the decomposition temperature of the solvent. In the case of DMF, the temperature is advantageously 10% above the boiling point of the solvent and not exceeding 400°C. Preferably, in the particular case of DMF, the solvent extraction is carried out at temperatures ranging from 8°C to 175°C, more preferably at temperatures ranging from 15°C to 155°C, advantageously at temperatures ranging from 10°C to 40°C, and more advantageously at a temperature of about 25°C.

Advantageously, the solvent extraction in step b) is carried out as soon as possible after the unstable oil is produced, preferably after less than 1 day, and more preferably after less than 5 minutes after the cracked oil is produced.

According to a preferred embodiment, the initial solvent to oil volume ratio ranges from between 5/1 and 1/5, preferably this ratio is between 2/1 and 1/2; more preferably about 1/1.

Advantageously, step a) of the processes is performed in a continuously stirred extraction column.

Advantageously, step b) of the processes is performed by using at least one of the following techniques: in a thin film evaporator, in a wiped film evaporator, azeotropic distillation and/or in a centrifuge.
According to another preferred embodiment of the invention, step c) of the processes is advantageously performed in a vacuum flasher such as in a thin film evaporator, in a wiped film evaporator and/or in other separation equipment such as a centrifuge.

Advantageously, step d) of the processes is performed by phase accumulation, or in a wiped film evaporator or in a centrifuge or by combination of at least two of these methods.

The processes of the invention are of a particular interest for treating contaminated wide range diesel fuel, the initial solvent is thus advantageously a nearly pure solvent having a dipole moment greater than 2.

The stable operation of the processing unit, wherein the operating conditions remain unchanged, may be reached, depending upon the size of the unit and/or upon the type of the unit and/or upon the solvent, in between 5 and 120 minutes, and preferably in about 45 minutes.

The processes of the invention are also of a particular interest for treating thermally cracked oils or thermally cracked used oil, and the initial solvent, having a dipole moment greater than 2, is thus advantageously DMF.

In the processes of the invention, the initial temperature in step a) is between 15°C and 110°C, preferably between 20°C and 30°C, and the initial temperatures in steps b), c) and d) are between 10°C and 175°C and more preferably is about 25°C.

In the processes of the invention, the initial pressures in steps b), c) and d) are between 0.5 psia and atmospheric pressure.
According to a preferred embodiment, the temperatures in the various steps of the processes are determined by the vacuum distillation obtained, but kept below the thermal decomposition temperature of the solvent and/or the cracking or polymerization initiation temperatures of the oil.

Advantageously, the equilibrium temperature in step a) is between 15°C and 100°C, and most preferably about 25°C.

The solvent content in the recycled solvent stream is preferably between 50% weight and 99% weight, more preferably between 60% weight and 95% weight, and most advantageously about 83% weight.

According to further preferred embodiments of the invention:

- the temperatures in steps b), c) and d) are between 10°C and 175°C; and/or
- the pressures in steps b), c) and d) are between 0.5 psia and atmospheric pressure; and/or
- the residual water content in the stabilized diesel obtained is less than 1% weight, preferably less than 0.25% weight; and/or
- the residual water content in the stabilized diesel, obtained in step a), is less than 1% weight, preferably less than 0.25% weight.

A second objet of the present invention is constituted by the family of the stabilized diesels obtained by any one of the processes defined in the first objet of the present invention.

These stabilized diesels are, according to ASTM method D6468, stable for at least a day, or until it is used, and most preferably they are stable for about 6 months or more.
Among the stabilized diesels obtained by the processes of the invention, these having at least one of the following properties:

- a sulphur content, according to ISO 8754, that is less than 0.2% weight, preferably less than 0.1% wt, and more preferably about 0.08% weight, are of a particular interest;

- a boiling temperature, according to ASTM D-86, that is comprised between 150°C and 500°C, preferably between 175°C and 450°C;

- an abnormal peak in the ATM D-86 curb in the in the area of the peak of recycled solvent, i.e. of the solvent that passes at least once through the process, preferably in the 0 to 10% area of distilled volume, and more advantageously in the area of 5% of distilled volume, appears to be new and are of a particular interest;

- a total acid number, according to ASTM 996, that is lower than 4, preferably lower than 1; and

- a cetane index over 40.

A third object of the present invention is constituted by the family of new stabilized diesels showing:

- according to ASTM method D6468, a stability for at least a day, or until it is used;

- according to ASTM method D1500, a colour index that is lower than 3; and

- an abnormal peak, in the ATM D-86 curb, in the 0 to 10% area of distilled volume.

Preferably, new stabilized diesel of the invention has a boiling temperatures range that is, according to ASTM D-86, comprised between 150°C and 450°C.
A fourth objet of the present invention is made by the uses of a stabilized fuel obtained by one of the process defined in the first object of the present invention, or as defined in the second and third object of the present invention, as:

- a fuel, or a component in a blended fuel, such as a home heating oil, a low sulphur marine fuel, a diesel engine fuel, a static diesel engine fuel, power generation fuel, farm machinery fuel, off road and on road diesel fuel; and/or
- a cetane index enhancer; and/or
- a drilling mud base oil or component, in the same way as currently produced wide range diesels are used; and/or
- a solvent or component of a solvent; and/or
- a diluent for heavy fuels, bunker or bitumen; and/or
- a light lubricant or component of a lubricating oil; and/or
- a cleaner or a component in oil base cleaners; and/or
- a flotation oil component; and/or
- a wide range diesel; and/or
- a clarified oil; and/or
- a component in asphalt blends.

As an illustrative and non limitative example of use as a cetane index enhancer, if a refinery has 10,000 barrels of diesel fuel with a cetane index of 38, adding 1,000 barrels of a new stabilized oil of the invention, with a 60 cetane index, will bring the combined 11,000 barrels to the specified 40 cetane index for road diesel in North America.

As an illustrative and non limitative example of use as flotation component, when mixed with a product such as a refinery's catalytic cracker fractionators bottom oil (CCFB). The ratio of
stabilized oil to CCFB can vary between 1/0.5 and 1/5 depending on the type of ore entering the floatation cell, its concentration, particle size, density and temperature.

In a preferred embodiment of the invention, the stabilized diesel, are used in a mixture in combination with:

- conventional diesel fuels, low sulphur diesels or wide range diesel oils; and/or
- bitumen, light or heavy vacuum gasoil, heavy fuels, bunker, tar or asphalt products; and/or
- refinery intermediate streams such as catalytic cracker fractionators bottoms; and/or
- organic solvents; and/or
- water and/or additives to make specialty products such as drilling muds or fractionating oils; and/or
- lubricating base oils, greases and additives to make lube oils or greases.

**BRIEF DESCRIPTION OF THE FIGURES**

FIG. 1 is a simplified flow sheet that illustrates an example of an embodiment of a process according to the invention.

FIG. 2 is a block diagram illustrating the steps performed, and the streams produced while operating in the preferred embodiment described herein.
FIG. 3 is a distillation curve of raw and treated gasoil, along with the distillation curves of pure and recycled solvent; of the wide range diesel obtained by the process according to the invention, as further specified in example 3 thereafter.

FIG. 4 is another distillation curve of raw and treated gasoil, along with the distillation curves of pure and recycled solvent, of the wide range diesel obtained by a process according to the invention, as further specified in example 4 thereafter.

DETAILED DESCRIPTION

Preliminary definitions

Unstable oils: are mixtures mainly made of hydrocarbons that may degrade, for example by aging and/or heating and/or under oxidizing conditions such as air exposition, oxygen exposition, high temperatures and/or in the presence of catalysts. This expression more particularly covers any mixtures of hydrocarbons containing free radicals (and more specifically those mixtures containing at least 50% wt. of hydrocarbons), any oil which colour deteriorates when exposed to heat or/and oxygen and/or other oils; any oils produced by thermal cracking and/or oils obtained by catalytic cracking and/or oils obtained by decomposition and/or unstable oils obtained by degradation, and the mixtures of at least two of the latter unstable oils; the processes of the invention are suited for stabilizing any such unstable oils in the broader sense

Wide range diesel: are oils mainly based on mixtures of hydrocarbons with boiling points between 100°C and 500°C,

Impurities: one or more chemical compounds that may be unwanted in a mixture but that may finally assist the extraction process.
Residues: contaminant and by-products obtained by reaction and/or extraction, that are unwanted and to be eliminated.

GO: gasoil (wide range diesels) in different steps of the process of the invention, n is a numerical index, an integral number, each of these integers corresponding to step of the process and represent changes in composition.

Initial solvent: solvent introduced at the beginning of the process and before its contamination by the solubilizing component.

FIG. 1 is a simplified flow sheet that illustrates an example of an embodiment of a process according to the invention. As shown, pure DMF (dimethyl formamide) and/or recycled DMF is introduced at the top of a continuously stirred contactor (1), while the cracked oil to be treated is introduced at the bottom of the column. A decanter (7) at the top of the column separates the raffinate (16) from the DMF. A decanter (8) at the bottom of the column separates the extract (17) from the oil to be treated. The column has up to 30 compartments (2), separated from each other by a disc with a hole in the middle (5). A stirrer shaft (3) equipped with paddles (4) ensures good mixing of the solvent with the oil at each level. The stirrer motor (6) is mounted at the top of the top decanter (7). The oil level in the contacting column is held with a level controller or simply with a column of liquid (9) using the principle of communicating of vases. A jacket (13) surrounding the extraction column maintains a constant temperature in the column with steam or cooling water as required.

The raffinate (16) is routed to a vacuum distillation column (10). The solvent and some light diesel exit through the top of the column (18). They are cooled and condensed in a condenser (11), and allowed to separate in an accumulator (12). The treated diesel (19) exits from the
bottom of the column, cooled, mixed with the oil recovered from the solvent (23) and the light oil phase from the accumulator (20) and sent to storage.

Another method to recover the solvent in the raffinate is to centrifuge the raffinate. However, the separation between the solvent and the oil is not as good as in the vacuum distillation recovery method. The solvent losses increase.

The extract (17), drawn from the bottom of the bottom decanter (8), is routed to another vacuum distillation column (14) to recover the solvent and oil, exiting from the top of the column (22), from the residue, exiting from the bottom of the column. After passing through a separator (15), the solvent (24) is recycled to the extraction column, along with the solvent (21) from the oil recovery column. The oil (23) is routed to storage, along with streams (19) and (20). The portion of the recycled solvent boiling between 150°C and 250°C contains the solutizing components.

EXAMPLES

The invention will now be further illustrated by mean of the following non limiting examples 1 to 4. All four examples were performed using the purification unit illustrated in FIG. 1 and the reactive solvent extraction according to block diagram in FIG. 2. Except for Example 1, wherein the methanol was introduced at the bottom of the extraction column and the unstable oil at the top of the extraction column. In FIG. 2, "S" refers to the solvent, "GO" refers to the gasoil (or wide range diesel), "I" refers to the impurities, "R" refers to the residue, and indicia "1, 2, 3, 4" indicate varying concentrations and stages in the process.

Recycled DMF from the process, or from another source, along with make-up DMF, is measured and introduced at the top of a continuously stirred extraction column (a), 6 cm in diameter and
250 cm high. Wide range diesel produced from used oil in a thermal cracker is measured and introduced at the bottom of the same column. The column's 111 cm stirred section is divided into three parts, each part containing ten cells. The cells are divided from one another by a horizontal, doughnut-shape baffle. The stirrer's shaft, in the middle of the column, is equipped with two paddles per cell. The variable speed stirrer can turn at between 50 rpm and 150 rpm.

The envelope around the contactor maintains stable temperatures in the contactor with circulating water or steam. The contactor operates at atmospheric pressure and 25°C. The stirrer turns at around 100 rpm. The decanter at the top of the contactor column separates the raffinate from the solvent and the decanter at the bottom of the column separates the extract from the feed diesel.

The level in the contactor is maintained with a container, attached by a tube to the contactor, and placed at variable heights. The extract and raffinate are weighted and sent off plot for solvent recovery by vacuum distillation or centrifuging at 10,000 rpm of both the extract and the raffinate.

**Example 1 - Use of methanol in the process**

Table I, Experiment 1, illustrates the best results obtained using methanol as solvent. For this experiment, the column was heated to 50°C (122°F).

Although the oil is stabilized, its sulphur content is unchanged by the extraction process, and its flash point is reduced below the 55°C (131°F) specified for heating oil in Europe.
It is to be noted that the methanol extraction does not reduce the sulphur content in the treated diesel.

**Example 2 - Use of DMF - pure (99.9% weight)**

Table II illustrates the results of three experiments using the polarized solvent: dimethyl formamide (DMF).

In all experiments, the oil is stabilized and keeps its light yellow colour for at least 6 months.

The flash point is unchanged in the extraction process. The net heating value is also unchanged.
The sulphur content is reduced in all three tests. There is a 63% reduction in sulphur content when pure solvent is used. When a solvent that is not completely regenerated is used, the sulphur removal is improved to meet the new European sulphur specifications for heating oil of less than 0.1%wt. The water content of the oil is also reduced to below the 250 ppni specification.

### Table II

| EXPERIMENT No 2: Solvent at 99.9% wt DMF, Feed diesel/solvent ratio = 1/1 |
|-----------------|----------|--------|----------|
| Method          | Units    | Feed Diesel | Product Diesel |
| Density         | ISO 3675 | Kg/l     | 0.844     | 0.828     |
| Sulphur         | ISO 8754 | % m/m    | 0.322     | 0.119     |
| Water           | ISO 10336 | mg/kg   | 0.077     | 0.009     |
| Total Acid Number | mg KOH/g | 4.37     | 1.13      |
| Flash Point     | ASTM D92 | C        | 69        | 66        |
| Micro Carbon Residue | ISO 10370 | % m/m   | 0.53      | 0.047     |
| Cetane Index    | EPCN 322 |          | 54.8      | 60.7      |
| Colour after 1 day exposed to air | ASTM | 1500 | 6        | 1          |
| Colour after 5 months exposed to air | ASTM | 1500 | 7        | 1.5        |

### Example 3 - Contaminated DMF - at 83.4% weight in the solvent feed stream

The same experiment as in example 1 and 2 is performed, except that the solvent is at 83.4% wt DMF, Feed diesel/solvent ratio = 1/1.
## Table III

### EXPERIMENT No 3: Solvent at 83.4% wt DMF, Feed diesel/solvent ratio = 1/1

<table>
<thead>
<tr>
<th></th>
<th>Method</th>
<th>Units</th>
<th>Feed Diesel</th>
<th>Product Diesel</th>
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<tr>
<td>Density</td>
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Note the abnormality in the 0 to 10% cut of the treated gasoil, and the corresponding heads and tails in the recycled solvent curve. The distillation curves in FIGS. 2 and 3 demonstrate that the "solutizers" in this process have boiling points between 125°C and 200°C. With another solvent, the "solutizers" may have a different boiling point range.

### Example 4 - Contaminated DMF: 77.25% weight in the solvent feed stream

The same experiment as in example 1 and 2 is performed, except that the solvent contains 77.25% wt DMF, Feed diesel/solvent ratio = 1/1.
These experiments show that the impurities in the incompletely regenerated solvent facilitate the mass transfer of sulphur compounds from the gasoils to the solvent, as did the solutizers for light oils in older patents.

The incompletely regenerated solvent was obtained by heating the extract to 170°C in a thin film evaporator operating at 120 mBar.

**Example 5 - Use as cetane index enhancer**

In the case of a refinery having 10,000 barrels of diesel fuel with a cetane index at 38, adding 1,000 barrels of the new stabilized oil, with a 60 cetane index, obtained in previous example 4,
will bring the combined 11,000 barrels to the specified 40 cetane index for road diesel in North America.

**Example 6 - Use in a drilling mud base oil or component**

The new stabilized oil obtained in previous example 3 is mechanically incorporated in a drilling fluid according to the protocol described in U.S. Patent No. 2,994,660, where diesel oil is mixed with an aqueous phase containing a variety of chemicals. The ratio of oil phase to water phase ranges from 80/20 to 35/65 preferably about 50/50 resulting in a new invert emulsion drilling fluid.

**Example 7 - Use in as flotation oil component**

In order to get the floatation oil a refinery's catalytic cracker fractionators bottom oil (CCFB) is mixed with the new stabilized oil obtained in previous example 4. The ratio of stabilized oil to CCFB can vary between 1/0.5 and 1/5 depending on the type of ore entering the floatation cell. In the present example the ratio of stabilized oil to CCFB is of 1/5 and the ore is of the potash type. The temperature in the floatation cell is about 15°C.

The resulting floatation composition is advantageously used in Canada.

**ADVANTAGES OF THE INVENTION**

The extraction process described in this patent stabilizes, dries and neutralizes wide range diesel, while removing most of the sulphur, chlorine, and water. As in other extraction processes researched, complete regeneration of the solvent is difficult because DMF or other solvents having a dipole moment greater than 2 disintegrate around 350°C (or at other temperatures
depending upon the selected solvent). Usually azeotropic distillation is used, with water as the third component. However, in this case, complete regeneration of the DMF is not necessary, or even desirable, since the extraction process is more effective when reaction products from previous passes are present in the solvent.

This invention is a simple and low cost process to stabilize, desulphurize, neutralize and dry unstable oils, containing free radicals, such as those oils produced by thermal or catalytic cracking of heavier oils. It can be used as a product oil finishing process in a used oil plant, to debottleneck a hydrotreating unit in a refinery or as a diesel oil finishing step in a refinery. The extraction is performed at ambient temperatures and pressures. The solvent can be regenerated with a simple vacuum distillation or centrifuge. It does not require an azeotropic distillation to achieve near complete regeneration, since complete regeneration is not desired. Oxidation of the mercaptans, thiols, and nitrogen compounds prior to their extraction from the oil is not required. In the case of used oil plants, a gasoil meeting all European heating oil specifications can be produced without hydrotreating.

Although the present invention has been described with the aid of specific embodiments, it should be understood that several variations and modifications may be grafted onto said embodiments and that the present invention encompasses such modifications, usages or adaptations of the present invention that will become known or conventional within the field of activity to which the present invention pertains, and which may be applied to the essential elements mentioned above.
CLAIMS:

1. A process to stabilize and to remove contaminants from an unstable oil, said process comprising:
   - at least one step of mixing said unstable oil with an impure solvent having a dipole moment greater than 2; and/or
   - at least one step of mixing said unstable oil with a pure solvent having a dipole moment greater than 2, provided that said pure solvent, after its contamination with impurities produced during the first contact between the unstable oil and the pure solvent, is at least partially recycled in said process after being partially purified or without any purification.

2. The process according to claim 1, to stabilize and to remove contaminants from an unstable oil, wherein the unstable oil is selected among the family of: mixtures made of at least 50% of hydrocarbons which may include free radicals, unstable oils containing free radicals, any oil which colour deteriorates over time and/or when exposed to heat or/and oxygen and/or oxidizing chemicals and/or other oils, oils produced by thermal cracking, unstable oils obtained by catalytic cracking, unstable oils obtained by decomposition, unstable oils obtained by degradation, and/or the mixtures of at least two of the latter unstable oils.

3. The process according to claim 1 or 2, to stabilize and to remove contaminants from an unstable oil, said process including at least one step of contacting a stream of the unstable oil with a solvent having a dipole moment greater than 2 and, thus, obtaining two mixtures, the first mixture being of an oil-solvent type and containing impurities, and the second
mixture being of a solvent-oil type and containing residues and impurities, the impurities in the solvent-oil mixture being identical or different from the impurities in the oil-solvent mixture.

4. The process according to any one of claims 1 to 3, to stabilize and to remove contaminants from a unstable oil, wherein at least a fraction of the solvent having a dipole moment greater than 2 that is present in at least one of the two mixtures is extracted from the mixture(s) and is at least partially regenerated before being recycled to said process.

5. The process according to any one of claims 1 to 4, to stabilize and to remove contaminants from an unstable oil, said process including the following steps of:
   a) intimately contacting a stream of the unstable oil with a solvent having a dipole moment greater than 2 and, thus, obtaining two mixtures, the first mixture being of an oil-solvent type and containing impurities, and the second mixture being of a solvent-oil type and containing residues and impurities, the impurities in the solvent-oil mixture being identical or different from the impurities in the oil-solvent mixture;
   b) separating the treated oil, present in the oil-solvent mixture obtained in step a), from the solvent, leaving most of the impurities in the solvent phase;
   c) separating the solvent and the oil, present in the solvent-oil mixture obtained in step a), from the residues, leaving preferably at least 60% weight, preferably 75% weight and more preferably more than 90% weight of the contaminants in the residues;
   d) optionally separating the solvent and the light oil present in the oil-solvent mixture obtained in step b);
   e) optionally separating the solvent and the oil obtained in step c); and
f) recycling at least one of the solvents obtained in steps b), c), d) or e), wherein each of
said solvent is at least partially regenerated.

6. The process according to claim 5, to stabilize and to remove contaminants from an
unstable oil, wherein, in step b), at least 80% weight, preferably at least 90% weight, of the
impurities remain in the solvent phase.

7. The process according to claim 5 or 6, to stabilize and to remove contaminants from an
unstable oil, wherein in step f), at least one of each of said solvent is regenerated for at
least 50% weight but for less or equal to 99% weight, and preferably for at least 55% weight
but for less or equal to 98%, before recycling.

8. The process according to any one of claims 5 to 7, to stabilize and to remove contaminants
from an unstable oil, wherein in step f), at least one of each of said solvent is regenerated
by using at least one of the following means: distillation, vacuum distillation, azeotropic
distillation and/or centrifugation.

9. The process according to claim 8, to stabilize and to remove contaminants from an
unstable oil, wherein in step f), at least one of each of said solvent is regenerated by using
distillation and/or vacuum distillation and/or centrifugation.

10. The process according to any one of claims 1 to 9, to stabilize and to remove contaminants
from an unstable oil, wherein the boiling range of the unstable oil, as measured by the
method ASTM D86, ranges from 125°C to 500°C.
11. The process according to claim 10, to stabilize and to remove contaminants from an unstable oil, wherein the boiling range of the unstable oil, as measured by the method ASTM D86, ranges from 75°C to 450°C.

12. The process according to any one of claims 1 to 11, to stabilize and to remove contaminants from an unstable oil, wherein the boiling range of the treated oil in step a), as measured by the method ASTM D86, ranges from 125°C to 500°C.

13. The process according to claim 12, to stabilize and to remove contaminants from an unstable oil, wherein the boiling range of the treated oil in step a), as measured by the method ASTM D86, ranges from 175°C to 450°C.

14. The process according to any one of claims 1 to 13, to stabilize and to remove contaminants from an unstable oil, wherein the unstable oil is produced by cracking used oil, heavy oil, bitumen, vacuum gasoil, vacuum residue, tar, synthetic caide oil, bunker or is produced by cracking a mixture of at least two of the latter.

15. The process according to any one of claims 1 to 14, to stabilize and to remove contaminants from an unstable oil, wherein the solvent is chosen among N-methyl pyrrolidone, furfural, dimethyl formamide, phenol, pyridine, dimethyl acetamide, dimethyl sulfoxide and propylene carbonate, and among mixtures of at least two of the latter.

16. The process according to any one of claims 1 to 15, to stabilize and to remove contaminants from an unstable oil, wherein the regenerated solvent, obtained in steps b), c), d) and/or f), may still contains some impurities or reaction products.
17. The process according to claim 16, to stabilize and to remove contaminants from an unstable oil, wherein contaminants include: water, sulphur compounds such as mercaptans and thiols, organic chlorides, organic and inorganic acids, free radicals, resins, gums, sediments, reaction products and mixtures of at least two of these.

18. The process according to any one of claims 1 to 17, to stabilize and to remove contaminants from an unstable oil, wherein the solvent concentration in the regenerated solvent stream obtained, in step f), ranges from 50% wt. to 99% wt.

19. The process according to claim 18, to stabilize and to remove contaminants from an unstable oil, wherein the solvent concentration in the regenerated solvent stream obtained, in step f), ranges from 70% wt. to 90% wt. and is more preferably about 83% wt.

20. The process according to claim 18 or 19, to stabilize and to remove contaminants from an unstable oil, wherein the regenerated solvent is produced, in step f), by physical processes such as distillation and/or centrifugation.

21. The process according to claim 20, to stabilize and to remove contaminants from an unstable oil, wherein the distillation is performed at pressures ranging from 0.5 psia to 15 psia, preferably ranging from 0.55 psia to 12 psia.

22. The process according to claim 21, to stabilize and to remove contaminants from an unstable oil, wherein the distillation is performed at pressures ranging, from 0.6 psia to 4 psia and preferably performed at pressures about 1.5 psia.
23. The process according to any one of claims 18 to 22, to stabilize and to remove contaminants from an unstable oil, wherein the regenerated solvent is produced, in steps b), c), d), and f), by distillation conducted at temperatures ranging from 50°C to 350°C.

24. The process according to claim 23, to stabilize and to remove contaminants from an unstable oil, wherein the regenerated solvent is produced, in steps b), c), d), and f), by distillation conducted at temperatures ranging from 100°C to 175°C, and more preferably at a temperature of about 130°C.

25. The process according to any one of claims 17 to 24, to stabilize and to remove contaminants from an unstable oil, wherein the impurities, present in the regenerated and/or recycled solvent, have a boiling temperature depending upon the selected solvent, the boiling temperature ranging in the case of DMF from 120°C to 250°C.

26. The process according to claim 25, to stabilize and to remove contaminants from an unstable oil, wherein the impurities, present in the regenerated and/or recycled solvent, have a boiling temperature ranging from 130°C to 200°C.

27. The process according to claim 25 or 26, to stabilize and to remove contaminants from an unstable oil, wherein the impurities, present in the regenerated and/or recycled solvent, have catalytic and/or solution enhancing and/or bridging properties.

28. The process according to any one of claims 1 to 15, to stabilize and to remove contaminants from an unstable oil, wherein in step a) the solvent extraction is carried out at temperatures not exceeding 10% above the boiling point of the solvent and not
exceeding 400°C, and for the DMF at temperatures ranging from 8°C to 175°C, preferably at temperatures ranging from 15°C to 150°C.

29. The process according to any one of claims 1 to 15, to stabilize and to remove contaminants from an unstable oil, wherein in step a) the solvent extraction is carried out at temperatures ranging from 10°C to 40°C, and more preferably at a temperature of about 25°C.

30. The process according to any one of claims 1 to 29, to stabilize and to remove contaminants from an unstable oil, whereby the solvent extraction in step b) is carried out as soon as possible after the unstable oil is produced.

31. The process according to claim 30, to stabilize and to remove contaminants from an unstable oil, whereby the solvent extraction in step b) is carried out, after less than 1 day, and more preferably after less than 5 minutes after the cracked oil is produced.

32. The process according to any one of claims 1 to 31, to stabilize and to remove contaminants from an unstable oil, wherein the solvent to oil volume ratio ranges from between 5/1 and 1/5.

33. The process according to claim 32, to stabilize and to remove contaminants from an unstable oil, wherein the solvent to oil volume ratio is between 2/1 and 1/2; more preferably about 1/1.

34. The process according to any one of claims 1 to 33, to stabilize and to remove contaminants from an unstable oil, wherein step a) of the process is performed in a continuously stirred extraction column.
35. The process according to claim 34, to stabilize and to remove contaminants from an unstable oil, wherein step b) of the process is performed by using physical separation such as: settling, vacuum flashing or distillation in a thin film evaporator, in a wiped film evaporator, azeotropic distillation and/or in a centrifuge or by combination of at least two of these methods.

36. The process according to claim 34 or 35, to stabilize and to remove contaminants from an unstable oil, wherein step c) of the process is performed by physical separation such as settling, vacuum flashing, distillation in a thin film evaporator, in a wiped film evaporator, azeotropic distillation, and/or in a centrifuge, or by combination of at least two of these methods.

37. The process according to any one of claims 30 to 36, to stabilize and to remove contaminants from an unstable oil, wherein step d) of the process is performed by physical separation such as: settling, vacuum flashing, distillation in a thin film evaporator, in a wiped film evaporator, azeotropic distillation, and/or in a centrifuge, or by combination of at least two of these methods.

38. The process according to any one of claims 1 to 37, to stabilize and to remove contaminants from an unstable oil, wherein the contaminated oil is a wide range diesel fuel, the initial solvent is a nearly pure solvent having a dipole moment greater than 2.

39. The process according to any one of claims 28 to 37, to stabilize and to remove contaminants from an unstable oil, wherein the stable operation of the processing unit, wherein the operating conditions remain unchanged, be reached in between 5 and 120
minutes, depending upon the size of the unit and/or upon the type of the installation and/or upon the type of solvent.

40. The process according to claim 39, to stabilize and to remove contaminants from an unstable oil, wherein the stable operating conditions are reached in about 45 minutes.

41. The process according to any one of claims 1 to 40, to stabilize and to remove contaminants from an unstable oil, wherein the oil is thermally cracked oil or is a thermally cracked used oil, and the initial solvent, having a dipole moment greater than 2, is DMF.

42. The process according to claim 41, to stabilize and to remove contaminants from an unstable oil, wherein the initial temperature in step a) is between 15°C and 110°C, preferably between 20°C and 30°C, and the initial temperatures in steps b), c) and d) are between 100°C and 175°C,

43. The process according to claim 42, to stabilize and to remove contaminants from an unstable oil, wherein the initial temperature in step a) is about 25°C.

44. The process according to any one of claims 41 to 43, to stabilize and to remove contaminants from an unstable oil, wherein the initial pressures in steps b), c) and d) are between 0.5 psia and atmospheric pressure.

45. The process according to any one of claims 41 to 44, to stabilize and to remove contaminants from an unstable oil, wherein the temperatures are determined by the vacuum obtained, but kept below the thermal decomposition temperature of the solvent and/or the cracking or polymerization initiation temperatures of the oil.
46. The process according to any one of claims 41 to 45, to stabilize and to remove contaminants from an unstable oil, wherein the equilibrium temperature in step a) is between 15°C and 100°C, and most preferably about 25°C.

47. The process according to any one of claims 41 to 46, to stabilize and to remove contaminants from an unstable oil, wherein the solvent content in the recycled solvent stream is between 50% weight and 99% weight.

48. The process according to claim 47, to stabilize and to remove contaminants from an unstable oil, wherein the solvent content in the recycled solvent stream is between 60% weight and 95% weight, and most preferably about 83% weight.

49. The process according to any one of claims 44 to 48, to stabilize and to remove contaminants from an unstable oil, wherein the temperatures in steps b), c) and d) are between 10°C and 175°C,

50. The process according to any one of claims 44 to 49, to stabilize and to remove contaminants from an unstable oil, wherein the pressures in steps b), c) and d) are between 0.5 psia and atmospheric pressure.

51. The process according to any one of claims 1 to 50, wherein the residual water content in the stabilized diesel obtained is less than 1% weight, preferably less than 0.25% weight.

52. The process according to any one of claims 1 to 51, wherein the residual water content in the stabilized diesel, obtained in step a), is less than 1% weight, preferably less than 0.25% weight.
53. Stabilized diesel obtained by any one of the processes defined in claims 1 to 52.

54. Stabilized diesel according to claim 53, stable, according to ASTM method D6468, for at least a day, or until it is used.

55. Stabilized diesel according to claim 53 or 54, stable, according to ASTM method D6468 for at least a week, and most preferably for about 6 months.

56. Stabilized diesel according to any one of claims 53 to 55, wherein the sulphur content, according to Iso 8754, is less than 0.2% weight.

57. Stabilized diesel according to claim 56, wherein the sulphur content, according to Iso 8754, is less than 0.1% weight and more preferably is about 0.08% weight.

58. Stabilized diesel according to any one of claims 53 to 57, wherein its boiling temperatures, according to ASTM D-86, ranges from 50°C to 500°C and preferably ranges from 75°C to 450°C.

59. Stabilized diesel according to any one of claim 53 to 58, having an abnormal peak in the ASTM D-86 curb in the area of the peak of the recycled solvent that has passed at least once through the process.

60. Stabilized diesel according to any one of claim 53 to 59, having an abnormal peak in the ASTM D-86 curb in the area of 0 to 10% of distilled volume, preferably in the area of 5% of distilled volume.

61. Stabilized diesel showing:
- according to ASTM method D6468, a stability for at least a day, or until it is used;
- according to ASTM method D1500, a colour index that is lower than 3; and
- an abnormal peak, in the ASTM D-86 curb, in the area of 0 to 10% of distilled volume.

62. Stabilized diesel according to claim 61, wherein its boiling temperatures range is, according to ASTM D-86, comprised between 150°C and 450°C,

63. Use of a stabilized diesel, obtained by one of the process disclosed in any one of claims 1 to 53, or as defined in any one of claims 54 to 62, as:
   • a fuel, or a component in a blended fuel, such as a home heating oil, a low sulphur marine fuel, a diesel engine fuel, a static diesel engine fuel, power generation fuel, farm machinery fuel, off road and on road diesel fuel; and/or
   • a cetane index enhancer; and/or
   • a drilling mud base oil or component; and/or
   • a solvent or component of a solvent; and/or
   • a diluent for heavy fuels, bunker or bitumen; and/or
   • a light lubricant or component of a lubricating oil; and/or
   • a cleaner or a component in oil base cleaners; and/or
   • a flotation oil component; and/or
   • a wide range diesel; and/or
   • a clarified oil; and/or
   • a component in asphalt blends.

64. Use of a stabilized diesel, obtained by one of the process disclosed in any one of claims 1 to 53, or as defined in any one of claims 54 to 63 in a mixture in combination with:
   • conventional diesel fuels, low sulphur diesels or wide range diesel oils; and/or
bitumen, light or heavy vacuum gasoil, heavy fuels, bunker, tar or asphalt products;
and/or
refinery intermediate streams such as catalytic cracker fractionators bottoms; and/or
organic solvents; and/or
water and/or additives to make specialty products such as drilling muds or
fractionating oils; and/or
lubricating base oils, greases and additives to make lube oils or greases.
## A. CLASSIFICATION OF SUBJECT MATTER

| IPC: CIOG 21/28 (2006.01) | BOW 11/04 (2006.01) | CIOG 21/12 (2006.01) |

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOG 21/28 (2006.01) | BOW 11/04 (2006.01) | CIOG 21/12 (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>CA 2200525 A1 (Olivier, C. et al.) 01 October 1997 (01-10-1997) * page 13, lines 9-10; table 2 *</td>
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[ ] Further documents are listed in the continuation of Box C. [X ] See patent family annex.

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"Y" | document other than a document of particular relevance |

"X" | document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is considered alone |

"Y" | document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |

"&" | document member of the same patent family |

Date of the actual completion of the international search | Date of mailing of the international search report |

Name and mailing address of the ISA/CA | Authorized officer |
| Canadian Intellectual Property Office | Chi Wing Hung (8 19) 994-7614 |
| Place du Portage I, C1 14 - 1st Floor, Box PCT | |
| 50 Victoria Street | |
| Gatineau, Quebec K1A 0C9 | |
| Facsimile No.: 001-819-953-2476 | |
INTERNATIONAL SEARCH REPORT

Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claim Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claim Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. [ ] Claim Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The claims are directed to a plurality of inventive concepts as follows:
Group A - Claims 1-60 and 63-64 are directed to a process to stabilize and remove contaminants from an unstable oil, a stabilized diesel obtained by said process and the use of said stabilized diesel.
Group B - Claims 61-62 are directed to a stabilized diesel showing: according to ASTM method D6468, a stability for at least a day, or until it is used; according to ASTM method D1500, a colour index that is lower than 3; and an abnormal peak, in the ASTM D-86 curb, in the area of 0 to 10% of distilled volume.

1. [X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest
[X] The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.
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