

PROCESS FOR REMOVAL OF CONTAMINANTS IN OIL**Technical Field**

The present invention generally relates to a process
5 for removing contaminants in oil, such as a used motor
oil.

Background

Many industrial processes including those in the
10 marine, mining, steel mill, mechanical, petrochemical,
power, automobile, construction and airlines industries
generate large quantities of used oil. Some examples of
used oil include synthetic oil, engine oil, turbine oil,
transmission fluid, thermal oil, refrigeration oil,
15 compressor oil, metalworking fluids and oil, laminating
oil, industrial hydraulic fluids, etc.

During use and handling, contaminants such as water,
chemicals, dirt and metal scrapings and oxidized organic
compounds get into the oil such that they affect the
20 proper working of the oil. Such oil is currently
considered to be a toxic industrial material due to the
presence of heavy metals and aromatic compounds such as
benzene, lead, zinc, chromium and cadmium.

Burning and dumping of used oil can contribute to
25 pollution and have a serious impact on the environment. As
used oil typically contains toxic chemicals, their
presence in waterways and soil can contaminate the water
and food supply. This will affect the health of human
beings who come into contact with such contaminants.
30 Therefore, it is desirable to re-refine or recycle used
oil so that it can be reused.

From an economic perspective, used oil may contain over 90% of base oil. The efficient recovery of the base oil is highly desirable.

Used oil can be refined by a variety of methods. Traditionally, acid treatment such as adding sulphuric acid to separate or dissolve metal salts and particles, aromatics, organic acids, polar compounds and dirt from the useful hydrocarbon components of used oil had been used. However, this results in the generation of a highly toxic acid sludge that must be disposed of in landfills, leading to serious disposal and environmental problems. Furthermore, used oil generated by this method had to go through an additional step of clay addition to remove any remaining colour contaminants.

Used oil can be re-refined through an evaporation/distillation process using thin-film evaporators. However, such an evaporator is susceptible to coking effects that can foul the mechanisms and process units of the evaporator. Coking is caused by cracking of the hydrocarbons as a result of contaminants in used oil and usually occurs when the temperature of used oil in the feed stream rises above 300°C. However, such an evaporator has to be cleaned regularly and this can result in substantial downtime.

Used oil can undergo hydrotreatment processes to improve color, color stability and to reduce reactivity of lubricating oil. During hydrotreatment, a number of reactions occur such as sulphur removal, nitrogen removal and hydrogenation of colour bodies, olefins and aromatics. These reactions remove undesirable components and result in improved quality of treated oil. However, excessive contact time or temperature will cause coking and the coked catalyst will have to undergo additional treatment

steps before removal. Furthermore, there may be the possibility that gaseous by-products such as hydrogen sulphide and ammonia gases may be released into the environment if a leak or accidental release occurs.

5 Moreover, the process units used to treat used oil may be corroded due to the acidic nature of the chemical by-products.

Another method to re-refine used oil is a two-step process involving a membrane step to remove ash and an
10 adsorption step to remove colour and odour. This method suffers from the disadvantage of having to rely on a two-step unit operation to remove both color contaminants and non-color contaminants.

There is a need to provide a used oil recovery
15 process that overcomes, or at least ameliorates, one or more of the disadvantages described above.

It would be an advantage if embodiments disclosed herein provide a process for removing both color
contaminants and non-color contaminants in a single unit
20 operation.

Summary

According to a first aspect, there is provided a process for removing color contaminants and non-color
25 contaminants from oil comprising the step of passing an oil feed through a permeable transition metal oxide membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said
30 oil feed.

Advantageously, the transition metal oxide membrane is selected to allow removal of both color contaminants

and non-color contaminants from oil in a single unit operation.

According to a second aspect, there is provided use of a permeable transition metal oxide membrane to remove
5 color and non-color contaminants from oil, the process comprising the step of passing an oil feed through a permeable transition metal oxide membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color
10 contaminants relative to said oil feed.

According to a third aspect, there is provided an oil made in a process comprising the step of passing an oil feed containing color contaminants and non-color contaminants through a permeable transition metal oxide
15 membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said oil feed.

In one embodiment, there is provided a process for
20 treating used oil comprising the steps of:

- (a) providing a permeable transition metal oxide membrane;
- (b) providing a high pressure side on one side of said permeable transition metal oxide membrane, which is
25 at a higher pressure relative to a low pressure side, opposite to said high pressure side; and
- (c) introducing used oil to said high pressure side to allow part of said used oil to pass through said transition metal oxide membrane and thereby form an
30 oil permeate on said low pressure side, wherein said oil permeate has less contaminants relative to said used oil.

In one embodiment, there is provided a process for treating used oil comprising the steps of:

- (a) providing a permeable transition metal oxide membrane;
- 5 (b) providing a high pressure side on one side of said permeable transition metal oxide membrane, which is at a higher pressure relative to a low pressure side, opposite to said high pressure side;
- 10 (c) introducing used oil feed stream to said high pressure side to allow part of said used oil to pass through said transition metal oxide membrane and thereby form an oil permeate on said low pressure side, wherein said oil permeate has less contaminants relative to said used oil;
- 15 (d) removing used oil that has not passed through said transition metal oxide membrane from said high pressure side in an oil retentate;
- (e) returning part of said oil retentate back to said used oil feed stream at said high pressure side;
- 20 and
- (f) repeating said steps (d) and (e) until a selected recovery rate of said oil permeate from said used oil feed stream is achieved.

25 Definitions

The following words and terms used herein shall have the meaning indicated:

The term "oil" as used herein is meant to include all kinds of chemical or biological synthetic and mineral oil
30 including crude oil, lubricating oil and fuel oil for a combustion engine, turbine engine, generator and heater, hydraulic transfer oil, edible oil and the like.

The term "used oil" is to be interpreted broadly to include any oil that contains color contaminants and non-color contaminants which can be at least partly removed to regenerate the oil and permit its re-use. Color
5 contaminants are those that cause or promote discoloration of the oil and include, but are not limited to, carbon residue that is a by-product of the combustion process, metal oxides such as iron oxide (ie rust) and degraded or oxidized organic additives present in the oil. Non-color
10 contaminants are to be interpreted broadly to include any non-oil components, such as components which may be present in the oil as by-products of its use, and which do not affect the color of the oil. For example, where the use of the oil is in a combustion engine, the products may
15 be ash, solid particulates, debris, metal particles, water and compounds that can also cause odor. Exemplary contaminants include metal particles due to wear or corrosion of engines, anti-wear additives, water from engines and storage vessels, dissolved gasoline and gas-
20 oil, solvents, aromatics and cleaning fluids, external dust, sediments consisting of carbonaceous particles resulting from combustion of motor fuels, polymeric additives for viscosity improvement or sludge dispersion, lead from gasoline and anti-knock additives, anti-oxidant
25 and detergent-dispersing additives. In one embodiment, the main non-color contaminants are ash. In some embodiments, the used oil is an uneven product of oil collected from several sources.

The terms "retentate" and "oil retentate" as used
30 herein, refer to oil that has not passed through a transition metal oxide membrane in a transition metal oxide membrane module. For example, in a process having multiple transition metal oxide membranes in series fluid flow, the oil retentate may be oil that never passed

through a transition metal oxide membrane of any transition metal oxide membrane module or it may include oil that has passed through a transition metal oxide membrane of an upstream transition metal oxide membrane module but not a transition metal oxide membrane module in which it is located.

The term "regenerated oil" includes any oil in which contaminants have been removed to such a level that the oil is capable of being re-used, such as oil for use as a lubricant in a combustion engine.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc.,

as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

5 **Disclosure of Optional Embodiments**

Exemplary, non-limiting embodiments of a process for removing color contaminants and non-color contaminants will now be disclosed. The process comprises the step of:

10 (a) passing an oil feed through a permeable transition metal oxide membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said oil feed.

15 In one embodiment, the process comprises the steps of:

 (a) providing a permeable transition metal oxide membrane;

 (d) providing a high pressure side on one side of said permeable transition metal oxide membrane, which is at a higher pressure relative to a low pressure side, opposite to said high pressure side; and

20 (b) introducing used oil to said high pressure side to allow part of said used oil to pass through said transition metal oxide membrane and thereby form an oil permeate on said low pressure side, wherein

25 said oil permeate has less contaminants relative to said used oil.

Advantageously, the process does not require the use of an adsorbent to remove color contaminants.

30 Accordingly, the process may exclude the step of contacting the oil permeate with an adsorbent.

The transition metal oxide membrane may be comprised of a porous metal substrate with a transition metal oxide coating.

5 The transition metal of said transition metal oxide membrane may be selected from the group consisting of group IIIB, group IVB, group VB, group VIB. In one embodiment, the transition metal may be titanium (Ti), Zirconium (Zr) or Hafnium (Hf).

10 In one embodiment, the transition metal oxide is titanium oxide. As titanium can exist in more than one valence state, titanium oxide may be titanium (II) oxide, titanium (III) oxide or titanium (IV) oxide. In one embodiment, the transition metal oxide is titanium (IV) oxide selected from the group consisting of anatase
15 titanium (IV) oxide, rutile titanium (IV) oxide, brookite titanium (IV) oxide and mixtures thereof.

The transition metal oxides used may advantageously be of ultrapure quality and allow for sintering at a temperature below the melting point of the porous metal
20 substrate used to form the membrane which may have a very narrow pore size distribution. This narrow pore size distribution may ensure that certain particles in the treated stream do not pass through the membrane.

The porous metal substrate may be comprised of
25 stainless steel. The stainless steel used may be selected from the 300 series as graded by the AISI. In one embodiment, the stainless steel used is of type 316L.

The membrane may be made by impregnating dry porous metal substrate with transition metal oxide particles and
30 sintering the transition metal oxide particles together by heating. The temperature used for sintering should be high enough for the transition metal oxide particles to form an integral structure within the pores of the metal substrate.

For titanium (IV) oxide, the sintering temperature may be from about 900°C to about 1200°C. In one embodiment, the temperature may be from about 1050°C to about 1200°C. The sintering time may be from about 5 to about 50
5 minutes. In one embodiment, the sintering time may be from about 10 to about 20 minutes. Exemplary methods of creating a membrane module are disclosed in US Patent No. 6,309,546 US Patent No. 4,888,114 and US Patent No. 6,432,308, which are incorporated herein by way of
10 reference.

The resultant membrane may have nano-sized or micro-sized pores. In one embodiment, the size of the pores of said membrane may be in the range of selected from the group consisting of about 0.001 μm to about 0.1 μm , about
15 0.005 μm to about 0.1 μm , about 0.01 μm to about 0.1 μm , about 0.05 μm to about 0.1 μm , about 0.001 μm to about 0.05 μm , about 0.001 μm to about 0.01 μm and about 0.001 μm to about 0.005 μm . In one embodiment, the pore size of said membrane is in the range of about 0.002 μm to about
20 0.01 μm .

The water contact angle of said membrane may be between about 30° and about 44°, indicating a highly hydrophilic surface. The highly hydrophilic surface may aid in substantially preventing fouling that may be caused
25 by non-polarity matters. Therefore, this may result in substantial removal of colour.

In one embodiment, the membrane module may have a tubular structure. The tube diameter of said transition metal oxide membrane module may be in the range selected
30 from the group consisting of about 0.01 inch to about 1.0 inch, about 0.2 inch to about 1.0 inch, about 0.4 inch to about 1.0 inch, about 0.6 inch to about 1.0 inch, about 0.8 inch to about 1.0 inch, about 0.01 inch to about 0.8

inch, about 0.01 inch to about 0.6 inch, about 0.01 inch to about 0.4 inch and about 0.01 inch to about 0.2 inch. In one embodiment, the tube diameter may be in the range of about 0.25 to about 0.75 inch.

5 At the high pressure side of the permeable transition metal oxide membrane, the pressure to be applied may be in the range of selected from the group consisting of about 3 bars to about 25 bars, about 5 bars to about 25 bars, about 10 bars to about 25 bars, about 15 bars to about 25
10 bars, about 20 bars to about 25 bars, about 3 bars to about 20 bars, about 3 bars to about 15 bars, about 3 bars to about 10 bars and about 3 bars to about 5 bars. In one embodiment, the pressure at the high pressure side of the permeable transition metal oxide membrane may be in the
15 range of about 4 bars to about 15 bars.

When passing used oil through the membrane, color-contaminants that are present in the used oil may come from two types of sources that may be removed by the membrane. The first colour source may be from carbon
20 residues that may be present as very fine particles and the second color source may be from degraded organic additives and metal oxides. Without being bound by theory, carbon particles may not pass through the membrane as they may be bigger than the cut-off pore size of the
25 membrane and this may ensure their removal from the used oil. Degraded organic additives and metal oxides may be adsorbed on the fine non-polar particles, such as fine gum, wax droplets, copolymerized degraded additives, that may be present in the used oil stream and may come out
30 with the oil retentate such that they may not be present in the oil permeate.

Used oil may be introduced to said high pressure side of permeable transition metal oxide membrane at a temperature in the range of selected from the group

consisting of about 30°C to about 300°C, about 50°C to about 300°C, about 100°C to about 300°C, about 150°C to about 300°C, about 200°C to about 300°C, about 250°C to about 300°C, about 30°C to about 250°C, about 30°C to about 200°C, about 30°C to about 150°C, about 30°C to about 100°C and about 30°C to about 50°C. In one embodiment, the temperature of the used oil may be in the range of about 80°C to about 150°C.

The feed flow rate of used oil introduced to said high pressure side of permeable transition metal oxide membrane may be in the range of selected from the group consisting of about 1 m/s to about 10 m/s, about 2 m/s to about 10 m/s, about 4 m/s to about 10 m/s, about 6 m/s to about 10 m/s, about 8 m/s to about 10 m/s, about 1 m/s to about 8 m/s, about 1 m/s to about 6 m/s, about 1 m/s to about 4 m/s and about 1 m/s to about 2 m/s. In one embodiment, the feed flow rate may be in the range of about 2 m/s to about 6 m/s.

Under such conditions, due to the relatively high linear velocity of the used oil feed stream that may be introduced into the membrane module, a turbulent flow may be created in the feed stream and may result in the prevention, or at least the inhibition, of fouling. Due to the high linear velocity, high flux may be generated such that it is in the range of selected from the group consisting of about 5 L/m²/h to about 25 L/m²/h, about 10 L/m²/h to about 25 L/m²/h, about 15 L/m²/h to about 25 L/m²/h, about 20 L/m²/h to about 25 L/m²/h, about 5 L/m²/h to about 20 L/m²/h, about 5 L/m²/h to about 15 L/m²/h, and about 5 L/m²/h to about 10 L/m²/h. In one embodiment, the feed oil flux may be in the range of about 12 L/m²/h to about 20 L/m²/h.

Moreover, the feed oil viscosity, at 40°C, may be in the range of selected from the group consisting of about

20 cSt to about 200 cSt, about 40 cSt to about 200 cSt, about 60 cSt to about 200 cSt, about 80 cSt to about 200 cSt, about 100 cSt to about 200 cSt, about 120 cSt to about 200 cSt, about 140 cSt to about 200 cSt, about 160 cSt to about 200 cSt, about 180 cSt to about 200 cSt, about 20 cSt to about 40 cSt, about 20 cSt to about 60 cSt, about 20 cSt to about 80 cSt, about 20 cSt to about 100 cSt, about 20 cSt to about 120 cSt, about 20 cSt to about 140 cSt, about 20 cSt to about 160 cSt and about 20 cSt to about 180 cSt. In one embodiment, the feed oil viscosity may be in the range of about 40 cSt to about 150 cSt at 40°C.

The percentage of contaminants removed from used oil may be in the range selected from the group consisting of about 70% to about 99%, about 75% to about 99%, about 80% to about 99%, about 85% to about 99%, about 90% to about 99%, about 95% to about 99%, about 70% to about 95%, about 70% to about 90%, about 70% to about 85%, about 70% to about 80% and about 70% to about 75%. In one embodiment, the percentage of contaminants removed from used oil may be greater than about 85%.

In one embodiment, the amount of carbon residue in the product oil may be reduced by about 90% as compared to that in the feed oil.

In another embodiment, the amount of heavy metals in the product oil may be reduced by about 90% as compared to that in the used oil.

In a further embodiment, the ASTM color grade of the product oil may be less than 5 as compared to that of the feed oil, wherein the color may be at least 8.

The membrane module may be made by welding the parts of the module together such that no sealing material is present in the module. By welding the membrane module together, the module may be able to handle high vibrations

that may be caused by high flow rates described above. Moreover, as the membrane housing may be made from the same material as the membranes, this may ensure that the membrane module may be able to withstand high thermal
5 shock.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the
10 disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 is a schematic flow diagram of a first process
15 for removing contaminants from used oil using transition metal oxide membrane modules;

Fig. 1A is a schematic cross-sectional view of a tubular membrane used in the transition metal oxide membrane modules of Fig. 1; and

20 Fig. 2 is a schematic flow diagram of a second process for removing contaminants from used oil.

Disclosure of Detailed Embodiment

Fig. 1 shows an overall process 100 which consists of
25 four transition metal oxide membrane modules (9,10,11,12) which each comprise a tubular-shaped membrane 200 as shown in Fig. 1A.

Referring to Fig. 1A, the tubular-shaped membrane 200 consists of a tubular-shaped permeable membrane inner wall
30 202 made of titanium (IV) oxide particles surrounding a porous 316L stainless steel tubular substrate. The tubular-shaped permeable membrane inner wall 202 is

surrounded by an outer tubular casing 204. A high pressure is maintained in the permeable membrane inner wall 202 with a relatively low pressure maintained at the outer tubular casing 204. During use, used oil 1 passes
5 into the high pressure side of the tubular-shaped membrane 200 as shown by arrow 210. As the used oil passes through the length of the permeable membrane inner wall 202, oil and particles that are smaller than the cut-off point of the membrane passes through the outer tubular casing 204
10 to form an oil permeate stream as shown by arrow 212. Oil and particles that did not pass through the outer tubular casing 204 will be ejected from the other side, forming an oil retentate stream as shown by arrow 214.

Referring again to Fig. 1, a used motor oil feed
15 stream 1 is fed via pump 2 to a pre-filter 3 to remove bulky contaminants (ie more than 0.1 μ m) before entering into holding tank 4 where it is heated to improve the flowability of the oil by making less viscous. The heated oil then passes through gate valve 5 and is pumped via
20 pump 6 to either of two parallel streams (50,52) that respectively have transition metal oxide membrane module pair (11,12) and (9,10), respectively via valves 8 and 7. Hence, valve 7 controls the used oil flow to membrane module pair (9,10) while valve 8 controls the used oil
25 flow to membrane module pair (11,12).

The two parallel streams (50,52) allow for one stream to be used while the other stream is being cleaned (see below) or is shut-down for maintenance. Hence the parallel streams (50,52) minimize disruption and down-time to the
30 used oil recovery process 100.

The heated oil enters into the high pressure side of the transition metal membranes 200 of each of the membrane modules (9,11). The high pressure side is about 4 bars to 15 bars to force oil through the pores of the permeable

membrane inner wall 202. Due to the pore size of the permeable membrane inner wall 202 (ie 0.002 to 0.01 μm) and the non-polarity of the titanium (iv) oxide particles, both color contaminants and non-color contaminants are prevented, or at least inhibited, from passing through the permeable membrane inner wall 202. Hence, an oil permeate stream 212 forms on the low pressure side disposed between permeable membrane inner wall 202 and outer tubular casing 204. The oil in the region enclosed by the permeable membrane inner wall 202 that has not passed through the permeable membrane inner wall 202 forms an oil retentate stream 214, which contains the color contaminants and the non-color contaminants which have not passed through the permeable membrane inner wall 202. Hence, the oil retentate stream 214 contains a higher amount of color contaminants and the non-color contaminants relative to the permeate stream 212 and the feed stream 210.

Part of the oil retentate stream 214 from the first stage membrane modules (9,11) enters into the high pressure side of the second stage membrane modules (10,12) while the remaining oil retentate is recycled to the used oil feed stream via valve 13.

Part of the oil retentate from the first stage membrane module (9,11) that enters the high pressure side of the second stage membrane module (10,12) forms the feed stream of the second stage membrane module (10,12). Part of the resultant oil retentate from the second stage membrane module (10,12) is recycled back to the feed stream via respective pumps (18,17) to the second stage membrane modules (10,12) while the rest of the oil retentate is rejected as stream 20 or 19, respectively. Hence, by operating a first stage membrane module (9,11) and then a second stage membrane module (10,12) operating in series fluid flow with respect to the oil retentate, it

is possible to increase the yield of oil recovered from the used oil feed stream 1. It will be appreciated that in other embodiments, multiple permeable membrane modules may be operated in series fluid flow to increase the capacity of the process 100. Importantly, it is not necessary to have a separate adsorption unit operation in the process 100 to remove color contaminants and non-color contaminants from the used oil.

Oil permeate from membrane modules (9,10) enters collection tank 16 via valve 14 while oil permeate from membrane modules (11,12) enters collection tank 16 via valve 15.

A second exemplary embodiment will now be disclosed with reference to Fig. 2. Fig. 2 shows an overall process 100' which consists of four transition metal oxide membrane modules (9',10',11',12'), first stage membrane modules (9',11') and second stage membrane modules (10',12'). The membrane modules (9',10',11',12') used are the same as those as described above for the process 100 shown in Fig. 1 above and they are described here using the same reference numerals but with a prime (') symbol.

In this process 100', the oil permeate stream 212' from the first stage membrane modules (9',11') enters into the high pressure side of the respective second stage membrane modules (10', 12'), forming the feed stream to the second stage membrane modules (10', 12').

Part of the oil retentate stream 214' from the first stage membrane modules (9',11') is recycled back via valve 13' to stream 54' to be pumped into the first stage membrane modules (9',11') via pump 6' while the remaining oil retentate stream 214' is rejected as respective streams 20' and 19'.

Part of the oil retentate stream 214' from the second stage membrane modules (10',12') is recycled back to the high pressure side of the second stage membrane modules (10',12') while the remaining oil retentate stream 214' is recycled back to stream 54' via valve 21'.

The oil permeate stream 212' from second stage membrane module 12' enters into the collection tank 16' via valve 15' (9',11') while the oil permeate stream 212' from the second stage membrane module 10' enters into the collection tank 16' via valve 14'.

The number of stages to be chosen for the used oil recovery process depends on the conditions of the used oil stream. In one embodiment, if the viscosity of the used oil stream is in the range from 40 cSt to 150 cSt at 40°C, a two-stage system is used. In another embodiment, if the used oil stream viscosity is higher than 150 cSt at 40°C, three or more stages are used. This ensures that the system performance is optimized leading to savings in energy consumption.

For continuous operation, a cleaning system (not shown in Figs.) will be implemented to remove any build-up of residues that can occur during membrane fouling. As discussed above, while one stream (controlled by, for example, valve 7) is used during the recovery process, the second stream (controlled by, for example, valve 8) can be cleaned. In one embodiment, an inert gas can be used in a back flush cleaning in place (CIP) mechanism to clean the stream. Once flux declines to about 40% to 70% of the original flux rate, the CIP system will start. The decline in the flux rate depends on the feed properties. The pressure of the stream undergoing cleaning will be reduced and recirculation rate of the retentate stream will be maintained. An inert gas will be supplied to the

low pressure side of the membrane module. The inert gas will be maintained at a high pressure such that the low pressure side of the module in the normal operation will now become the high pressure side during CIP. As the
5 inert gas passes through the membrane wall, it will peel off any fouling residues on the membrane surface. The CIP process will continue for about 20 minutes to about 120 minutes depending on feed properties and operation conditions to ensure that all of the fouling residues on
10 the membrane surface are removed. The fouling residues will be carried off to the CIP tank by the high flow rate circulation stream.

Examples

15 Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

20 Example 1

The used oil feed used in this experiment was mixed used motor oil obtained from a used oil collector located in Singapore. Hence, the used motor oil was a blend of used motor oils and its composition is given in Table 1
25 below.

The transition metal oxide membrane used was made by impregnating dry porous stainless steel 316L type substrate with titanium oxide (TiO_2) particles and sintering the TiO_2 particles together by heating to form a
30 TiO_2 coating. The resultant pore size of the membrane was $0.02 \mu\text{m}$. One membrane module was used in this experiment.

The used oil was heated to 100°C to 130°C and introduced into the high pressure side of the membrane

module maintained at between 8 bars to 11 bars. The recirculation flow rate of the used oil is between 2 m/s to 5 m/s resulting in a flux rate of 9 L/m²/h to 15 L/m²/h.

The properties of the used oil and product oil are shown in Table 1 below. It can be seen that the appearance, colour and quantities of contaminants in the product oil were significantly improved as compared to those in the used oil. For example, the colour of the product oil improved by three grades (from >8 to <5) as compared to the colour of used oil. In addition, water, micro carbon residues and sulfated ashes are removed with high efficiency with at least 88% reduction.

Table 1: Characteristics of used oil and product oil

Test	Method	Unit	Raw Used Oil	Product Oil	Reduction (%)
Appearance			Black	Red Brown	
Kinematic Viscosity @ 40°C		cSt	99.58	67.05	
Water Content (%)	ASTM D95-99	wt%	8.1	< 0.1	99%
Total Chloride	ASTM D4929-99	wt.ppm	343	50	85%
Micro Carbon Residue	ASTM D4530-03	wt%	1.8	0.03	98%
Sulfated Ash	ASTM D874-00	wt%	0.99	0.12	88%
ASTM Color	ASTM D1500-98		>8.0	<5.0	-3
Specific Gravity (20°C)			0.83	0.85	
Flash Point, PMCC	ASTM D93-02	°C	90	182	
Inorganic Elements	ASTM 5185-02	mg/kg			
Ag			<1	<1	
Al			12	<1	96%
B			52	2	96%
Ba			5	<1	90%
Ca			1162	34	97%
Cd			<1	<1	
Co			3	<1	83%
Cr			2	<1	75%
Cu			21	9	57%
Fe			74	2	97%
K			20	<1	98%
Mg			236	13	94%
Mn			1	<1	
Mo			19	<1	97%
Na			86	<1	99%
Ni			5	<1	90%
P			541	124	77%
Si			22	3	86%
Sn			<1	<1	
Ti			<1	<1	
Zn			621	74	88%
V			<1	<1	

Example 2

The used oil feed used in this experiment was mixed used motor oil obtained from a used oil collector located in Indonesia. Hence, the used motor oil was a blend of used motor oils and its composition is given in Table 1 below.

The same membrane module was used as for experiment 1, except in this experiment, the membrane module was used continuously for 95 hours. CIP treatment was carried out as needed using nitrogen as the inert gas.

The used oil was heated to 90°C to 120°C and introduced into the high pressure side of the membrane module maintained at between 6 bars to 10 bars. The recirculation flow rate of the used oil was between 2 m/s to 5 m/s resulting in a flux rate of 5 L/m²/h to 10 L/m²/h.

The properties of the used oil and recovered oil are shown in Table 2. It can be seen that the appearance, colour and quantities of contaminants in the recovered oil are significantly improved as compared to those in the used oil. For example, the colour of the product oil improved by at least 3 grades (from >8 to <4.5) as compared to the colour of used oil. In addition, water, micro carbon residues and sulfated ashes are removed with high efficiency with at least 86% reduction (based on calculated percentage reduction in water content).

Table 2: Characteristics of used oil and recovered oil

Properties	Method	Used Oil	Recovered Oil
Appearance		Black with solid	Bright & Clear
Color		Black	Light orange
Kinematic Viscosity @40 (cSt)	ASTM D445	86.5	70.2
Water content (%)	ASTM D95	0.7	<0.1
Chlorine Content (ppm)	XRF/D4929	310	59
Sulphur content (%)	XRF/D4294	0.61	0.438
Micro Carbon Residue (wt%)	ASTM D4530	1.1	0.11
Sulfate ash (wt%)	ASTM D847	0.8	0.03
ASTM Color	ASTM D1500	>8	<4.5
Specific Gravity (20 °C)	ASTM D287	0.885	0.893
Inorganic elements (PPM)	XRF/ICP/D5185		
Ag		<1	<1
Al		17	<1
B		17	<1
Ba		2	<1
Ca		1501	2
Cd		<1	<1
Co		<1	<1
Cr		2	<1
Cu		13	2
Fe		80	<1
K		3	2
Mg		77	<1
Mn		1	<1
Mo		11	<1
Na		18	<1
Ni		2	1
P		840	242
Sn		<1	<1
Tl		1	<1
Zn		859	34

Applications

Advantageously, the disclosed transition metal oxide membrane module permits both color contaminants removal (ie such as carbon residues, metal oxides etc) and non-
5 color contaminants removal (ie ash, sulphur and inorganic elements) from the used oil in a single unit operation. Hence it is not necessary to use a separate color polishing unit operation (ie such as a clay adsorption unit) to obtain a good color grade and reduced contaminant
10 levels for an oil product recovered from used oil.

The disclosed process can be used to remove contaminants from used oils from various industries such as marine, petrochemical, mining, steel mill, mechanical, power, automobile, construction and airlines.

15 The disclosed process provides an efficient process to remove contaminants from an oil. Hence the disclosed process assists in reducing the incidence of used oil burning and dumping, thereby reducing pollution issues associated with used oil disposal.

20 The disclosed process does not require the use of any chemical reagents such as acids to remove contaminants from the oil. Hence, the disclosed process may overcome problems associated with known acid treatment processes for oil contaminant removal and thereby avoids the
25 generation of a highly toxic acid sludge.

The disclosed process does not require the use of an evaporation/distillation process using thin-film evaporators. Hence, the disclosed process avoids problems associated with coking effects that tend foul the
30 evaporators used in such known processes.

The disclosed process does not require the use of a hydrotreatment processes to improve color and color stability to an oil. Hence, it is not necessary to conduct

a series of reactions involving sulphur removal, nitrogen removal and hydrogenation of colour bodies, olefins and aromatics.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims. For example, although the disclosed embodiments have specifically described the treatment of a used oil, it should be realized that in other embodiments, the process could be applied to remove color contaminants and non-color contaminants from a crude oil or partially refined oil.

Claims

1. A process for removing color contaminants and non-color contaminants from oil comprising the step of
5 passing an oil feed through a permeable transition metal oxide membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said oil feed.
10
2. A process as claimed in claim 1, comprising the step of selecting a used oil for the oil feed.
3. A process as claimed in claim 1, wherein said
15 passing step comprises the step of:
 - (a) providing a high pressure side on one side of said permeable transition metal oxide membrane, which is at a higher pressure relative to a low pressure side, opposite to
20 said high pressure side; and
 - (b) introducing used oil to said high pressure side to allow part of said used oil to pass through said transition metal oxide membrane thereby form an oil permeate on said low
25 pressure side, wherein said oil permeate has less contaminants relative to said used oil.
4. A process according to claim 1, comprising the step
30 of selecting titanium oxide as said transition metal oxide.
5. A process according to claim 4, comprising the step of selecting titanium (IV) oxide as said titanium oxide.

6. A process according to claim 1, wherein said permeable transition metal oxide membrane comprises a porous metal substrate with a permeable transition metal oxide coating thereon.
7. A process according to claim 6, wherein said metal substrate comprises stainless steel.
8. A process according to claim 1, wherein the pore size of said permeable transition metal oxide is in the range of 0.001 μm to 0.1 μm or 0.002 μm to 0.01 μm .
9. A process according to claim 1, wherein the permeable transition metal oxide membrane is a tubular-shaped membrane.
10. A process according to claim 9 comprising the step of selecting the tube diameter of said tubular membrane from the range of 0.254 mm (0.01 inch) to 25.4 mm (1 inch) or 6.35 mm (0.25 inch) to 19.05 mm (0.75 inch)
11. A process according to claim 1, comprising the step of heating said oil to a temperature in the range of 30°C to 300°C before passing said oil through said permeable transition metal oxide membrane.
12. A process according to claim 11, wherein said heating is in the range of 80°C to 150°C.
13. A process according to claim 3, comprising the step of maintaining the high pressure side of said

permeable transition metal oxide membrane in the range of 3 bars to 25 bars or 4 bars to 15 bars.

- 5 14. A process according to claim 1, comprising the step of passing said oil into said permeable transition metal oxide membrane at a feed rate in the range of 1 m/s to 10 m/s or 2 m/s to 6 m/s.
- 10 15. A process according to claim 1, comprising the step of passing said oil into said permeable transition metal oxide membrane at a flux rate in the range of 5 L/m²/h to 25 L/m²/h or 12 L/m²/h to 20 L/m²/h.
- 15 16. A process according to claim 1, comprising the step of providing said oil to said permeable transition metal oxide membrane at a viscosity in the range of 20 cSt to 200 cSt at 40°C or 40 cSt to 150 cSt at 40°C.
- 20 17. A process according to claim 1, comprising, after said passing step, the step of regenerating said transition metal oxide membrane by removing contaminants adsorbed thereon.
- 25 18. A process according to claim 3, comprising the step of returning oil that has not passed through said transition metal oxide membrane to said high pressure side.
- 30 19. A process according to claim 18, comprising the step of repeating said returning step until a selected contaminant removal level has been achieved.

20. A process according to claim 1, wherein at least two transition metal oxide membranes which are in series fluid flow with respect to each other are provided.
- 5 21. A process according to claim 20, comprising the step of passing oil that has not passed through one of the transition metal oxide membranes to a subsequent upstream transition metal oxide membrane.
- 10 22. A process according to claim 20, comprising the step of passing oil that has not passed through one of the transition metal oxide membranes to a downstream transition metal oxide membrane.
- 15 23. A process according to claim 20, comprising the step of passing oil that has passed through one of the transition metal oxide membranes to a subsequent upstream transition metal oxide membrane.
- 20 24. A process according to claim 20, comprising the step of passing oil that has passed through one of the transition metal oxide membranes to a downstream transition metal oxide membrane
- 25 25. Use of a permeable transition metal oxide membrane to remove color and non-color contaminants from oil, the process comprising the step of passing an oil feed through a permeable transition metal oxide membrane, wherein said oil that has passed through
- 30 said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said oil feed.

26. An oil made in a process comprising the step of passing an oil feed containing color contaminants and non-color contaminants through a permeable transition metal oxide membrane, wherein said oil that has passed through said transition metal oxide membrane has less color contaminants and non-color contaminants relative to said oil feed.

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