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(54) Process for the decontamination of used lubricating oil by the removal of contaminating metals and metal compounds.

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(73) Proprietor: **ASHLAND OIL, INC.**
R.C. Willson, Jr. P.O. Box 391, BL-5
Ashland Kentucky 41114 (US)

(72) Inventor: **Hettinger, William P., Jr.**
203 Meadowlark Road
Russell, KY 41169 (US)

(74) Representative: **Lambert, Hugh Richmond et al**
D. YOUNG & CO. 10 Staple Inn
London, WC1V 7RD (GB)

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Description

This invention relates to the removal of undesirable materials and ash from used or otherwise contaminated motor oil. The invention seeks to avoid environmental problems associated with disposal of heavy metal salts and other persistent pollutants contained in used motor oil, when the oil is dumped into the aquifers of landfills, sludge ponds or storage drums, which are themselves capable of deterioration.

Removal of degraded components and other contaminants from used motor oil can provide reclaimed and reusable motor oil, which is often formulated with some added amounts of detergent-inhibitor package or else blended as an inexpensive added basestock with new motor oil. Used motor oils, both with and without partial removal of contaminants and ash, have been used as rust inhibitors for equipment and machinery, as well as added components for hydrocarbon fuels.

Reclamation of used motor oil may be distinguished from re-refining in that no high-temperature distillation of motor-oil basestocks is involved. The process thus is usually less expensive than re-refining. In spite of the value of recovering lubricant basestocks, reclamation has been minimal because of the expense involved in collection of small amounts of oil drainings and their shipment to a central point. However, recent public awareness to the threat of water pollution by used motor oil has generated new incentives for reclamation.

Reclaiming motor oil normally involves treatment with a solvent containing an active purifying agent. Although motor oil of a purer nature is obtained, usually an appreciable amount of sludge is coproduced as the contaminated solvent by-product. This sludge must then be disposed of in some non-polluting fashion. Sometimes it is concentrated by relatively expensive flash distillation.

In US Patent Specification US—A—4,105,538, for example, a light paraffinic hydrocarbon fraction is added, along with a rather expensive amine. Subsequently, appreciable portions of heavy metal salts and other contaminants precipitate to the bottom as solids. Excess of light paraffinic fraction and amine must then be removed, although, with some amines, if attention is paid to the later use as motor oil, some amine can in practice be left in the reclaimed product.

In US—A—3,879,282 water-containing phosphate salts are used in a sealed autoclave at about 170 psig (1.17 MPa gauge pressure) and 132°C (270°F). Substantial amounts of contaminants and ash are precipitated in the water phase as insoluble metal phosphates. The preferred embodiment involves a specially constructed multistep facility using preheaters, vigorously agitated pressure vessels, a phase separator, a settlement tank, and filters. Gasoline and water remaining in the oil are removed by flash distillation. Recycled water is then purified sufficiently for recycle or else rigorously enough to be discarded into the environment. Filtration of the treated oil is carried out with silica gel in order to remove extraneous matter, especially tetraethyl lead, which is not removed by the prior treatment.

Petroleum refiners have been investigating means for processing reduced crudes, such as by visbreaking, solvent deasphalting, hydrotreating, hydrocracking, coking, Houdresid fixed bed cracking, H-oil, and fluid catalytic cracking. One or more approaches to the processing of reduced crude to form transportation and heating fuels, is that described in US—A—4,341,624, 4,347,122, 4,299,687, 4,354,923 and 4,332,673.

In the operation of the above identified patents, a reduced crude is contacted with a hot regenerated catalyst in a short-contact-time riser cracking zone, the catalyst and products are separated instaneously by means of a vented riser to take advantage of the difference between the momentum of the gases and that of the catalyst particles. The catalyst is stripped and sent to a regenerator zone, and the regenerated catalyst is recycled back to the riser to repeat the cycle. Owing to the high Conradson carbon values of the feed, coke deposition on the catalyst is high: it can be as high as 12 wt% based on feed. This high coke level can lead to excessive temperatures in the regenerator, at time in excess of 1400°F (760°C) and even as high as 1500°F (816°C), which can lead to rapid deactivation of the FCC catalyst through hydrothermal degradation of its active cracking component (crystalline aluminosilicate zeolites) and unit metallurgical failure.

US—A—4,263,128 discloses a procss for decontamination of petroleum fractions with an adsorbent in a fluid bed technique with one FCC reactor and one regenerator. US—A—4,116,814 discloses two independent fluid catalytic cracking operations with two FCC reactors and one single regenerator for the regeneration of the catalyst used in both reactions. However, neither of these US Patent Specifications discloses or leads to the treatment of contaminated used lube oil by contacting it with sorbent particles in a contactor conventionally used for refining heavy crude feedstocks and there is no reference in the non-conversion art to a shared sorbent regenerator.

In accordance with the present invention, a continuous process for disposing of contaminated used lube oil by converting it to useful product comprises:

(a) contacting a particulate sorbent of low or no catalytic cracking capability with a carbo-metallic oil feed boiling at at least 343°C (650°F) and essentially free of used lube oil in a first contactor to form purified product and contaminated sorbent formed from contact with said carbo-metallic oil feed;

(b) separating the purified products from the said contaminated sorbent;

(c) regenerating the said contaminated sorbent by heating it at from 533°C to 683°C in a regenerator in the presence of oxygen-containing gases to form a regenerated particulate sorbent, the major part of which is recycled to the first contactor;

(d) withdrawing a minor portion of the regenerated particulate sorbent and passing it through a second contactor, which is smaller than the first;

(e) contacting the said minor portion of regenerated particulate sorbent in the second contactor with contaminated used lube oil for a period of time less then 3 seconds at a temperature below 500°C and converting the used lube oil to a substantially decontaminated hydrocarbon product;

(f) separating contaminated sorbent formed from contact with the used lube oil from the product formed in the second contactor; and

(g) returning the contaminated sorbent formed from contact with the used lube oil to the regenerator for regeneration and recycle to the first and second contactors.

The present invention can make use of existing petroleum refinery facilities which have been slightly modified for co-production of reclaimed motor oil. Especially useful for this purpose is a refining unit known as an carbon and metal removal system (MRS) such as the described in US—A—4,325,817 and 4,263,128.

In a preferred embodiment of the invention, spent lubricating oil is pumped to a small riser mounted along side a large MRS Unit under conditions which cause oil boiling in the range of 316°C to 510°C (600°F to 950°F) to be gently vaporized and lifted from the lubrication oil contaminants and ash and recovered for recycle to a lubrication-oil-processing plant. The ash-and-sludge-laden sorbent from the MRS treatment unit is disposed of or regenerated in much the same way as is the same sorbent when it has been spent (contaminated) in the process of use in an ordinary refining unit.

The apparatus used in the process of this invention can comprise a combustor, a first contactor, second contactor, a cooling means, and a receiving vessel. A preferred embodiment of the present invention is illustrated in the single figure of the accompanying drawings, which shows an apparatus that can be used for carrying out the process.

A carbo-metallic oil feedstock having an initial boiling point of 343°C or higher, such as residuum, is introduced via conduit 3 into a first contactor 22 where the feedstock is contacted with active solid sorbent particulate material having little, if any, cracking activity under the conditions used, which are those needed to thermally visbreak and reduce metal contaminants to a more acceptable lower level in conjunction with reducing the feed Conradson carbon value. The first contactor 22 comprises a riser reactor 5, hereinafter called the first riser, for selectively thermally contacting the oil feed comprising metal contaminants with the active solid sorbent particulate material of little or not catalytic cracking activity, in order to accomplish substantial removal of metals in the absence of excessive thermal cracking of the oil feed. Atomizing water is added by conduit 1 to the feed introduced by conduit 3 to the first riser 5 above the bottom portion thereof. Steam from conduit 7, and/or water from conduit 9, are/is admixed with circulated hot solid particulate material in the bottom portion of the first riser in amounts and under conditions selected to adjust the temperature of the hot solids obtained from the regeneration thereof and before contacting the oil feed particularly selected for charge to the first riser 5. If desired, a "wet gas" (e.g. light hydrocarbons) or other lift gas can be used to convey the particulate material through the first riser 5. The suspension passed through first riser 5 is discharged from the top or open end of the riser and separated so that vaporous hydrocarbons of thermal visbreaking material and gasiform diluent material are caused to flow through a plurality of parallel arranged cyclone separators 11 and 13 positioned about the upper open end of the riser contact zone. Hydrocarbon vapours separated from entrained solids by the cyclone separators 11 and 13 are collected in a plenum chamber 15 before withdrawal and recovery by conduit 17. Solid particulate material comprising spent sorbent particles containing accumulated metal deposits are carbonaceous material resulting from thermal degradation are collected in the bottom portion of vessel 21 comprising a stripping section 23 to which a stripping gas is charged by conduit 25. Stripped solid absorbent particulate material is passed by standpipe 27, which is provided with a flow control valve, to a fluidized bed of particulate material in the bottom portion of regeneration zone 29 of combustor 40. In like manner to that through standpipe 27, stripped solid particulate from second contactor 122 is passed by standpipe 1127 to a fluidized bed of particulate material in the bottom portion of regeneration zone 29.

Regeneration gas or combustion-supporting gas such as oxygen-modified gas or air is charged to the bottom of the regeneration zone 29 by conduit 31 through a plenum distribution chamber 33 which supports a plurality of radiating gas distributor pipes 35. Regeneration of the spent sorbent particulate to its active form is accomplished by burning deposited carbonaceous material, on and in the spent sorbent, in an oxygen-containing gas to CO, CO_2 and/or other combustion products. Combustion product gases and catalyst pass from upper level 37 of a fluidized bed of particulate material in flue gases to an upper enlarged portion of the regeneration vessel where solid particulate material and product flue gases are separated by a combination of hindered settling and cyclone separator means. The separate particulate material is collected as a fluidized bed of material 41 in an annular zone about restricted passageway 39. Flue gas separated from solids passes through a plurality of cyclones 43 positioned about the open upper end of passageway 39 for removal of entrained fines. The flue gases then pass to plenum chamber 45 for withdrawal by conduit 47. Regenerated, that is, active, solid sorbent particulate material is passed by standpipe 49 to the bottom portion of the first riser 5 for use herein proposed.

In like manner to that through standpipe 49, active solid sorbent particulate material is passed by standpipe conduit 1149 to the second contactor 1122. A portion of the hot active sorbent is withdrawn by conduit 51 for passage to a heat exchanger 53 where 450lb steam (i.e. steam at 3.1 MPa pressure) generated by indirect heat exchange with charged boiler feed water. The thus partially cooled solid particulate material is withdrawn by conduit 59 for passage to a bottom portion of the fluidized bed of particulate material in the bottom of the regeneration zone 29 for temperature control of the metals-contaminated particulate material being regenerated.

The decontaminator system comprises the second contactor 1122 which is connected by the conduits 1127 and 1149 to the combustor 40 in like manner to that of the first contactor 22. A contaminated specialized hydrocarbon feedstock, such as used motor oil, preferably having an initial boiling point of 100°C or higher, is introduced via conduit 113 into the contactor 1122 where the contaminated specialized hydrocarbon is contacted with active solid sorbent particulate material having little, if any, cracking activity under the conditions used, which are those needed to substantially decontaminate the contaminated specialized hydrocarbon by reducing metal and other contaminants that boil higher than the initial boiling point of the contaminated specialized hydrocarbon. The second contactor 1122 comprises a riser reactor 115, hereinafter called the second riser, for selectively thermally contacting the contaminated specialized hydrocarbon feed comprising metal-containing and other high-boiling contaminants with the active solid sorbent particulate material of little or not cracking activity, to removal substantially all contaminants without excessive thermal cracking of the specialized hydrocarbon. Atomizing water is added by conduit 111 to the contaminated specialized hydrocarbon feed introduced by conduit 113 to the second riser 115 about its bottom portion. Steam in conduit 117 and/or water in conduit 119 are/is admixed with circulated hot solid particulate material at a temperature in the range 350°C to 500°C in the bottom portion of the second riser in amounts and under conditions to adjust the temperature of the hot solids obtained from the regeneration thereof and before contacting the contaminated specialized hydrocarbon feed particularly selected for charge to the second riser. If desired, "wet gas" (e.g. light hydrocarbons) or other lift gases can be used to convey the particulate material through the second riser 115. The particular combination of diluents admixed with solids permits of imparting a vertical velocity component to the solids before contact with dispersed contaminated specialized hydrocarbon feed material in the riser under selected temperature and pressure conditions. A suspension of solid sorbent particulate and atomized contaminated specialized hydrocarbon feed of low partial pressure in the steam diluent at a temperature below 500°C, preferably 350 to 500°C, from riser 115 at a velocity providing a hydrocarbon residence time of less than 3 seconds and preferably within a range of 1 to 3 seconds. The second riser 115 is provided with a plurality of vertically spaced apart reed inlet means to accomplish the above change in hydrocarbon residence time. The weight ratio of active sorbent to contaminated specialized hydrocarbon feed is preferably within the range 3:1 to 12:1. The suspension passed through riser 115 is discharged from the top or open end of the riser and separated so that vaporous hydrocarbons and gasiform diluent material are caused to flow through a plurality of parallel arranged cyclone separators 1111 and 1113 positioned about the upper open end of the riser contact zone. Atomized hydrocarbons and/or hydrocarbon vapours separated from entrained solids by the cyclone separators are collected in a plenum chamber 1115 before withdrawal or recovery by conduit 1117 at a temperature at or below 480°C. The entrained hydrocarbon is communicated to receiving vessel 1172, by passing through conduit 1176 and cooling means 1170 if desired. Solid particulate spent sorbent comprising accumulated metal deposits and carbonaceous material is collected at the bottom portion of vessel 1121, which comprises a stripping section 1123, to which stripping gas is charged by conduit 1125 at a temperature of at least 200°C. Higher stripping temperatures up to 580°C are also contemplated. Stripped solid absorbent particulate material is passed by standpipe 1127, which is provided with a flow control valve, to a fluidized bed of particulate material in the bottom portion of regeneration zone 1128 in a like manner to that of the standpipe 27 communicating from the first riser 5. Regenerated, that is, active, sorbent is passed from standpipe 1149 to the second riser 115, for use herein proposed, in like manner to that through standpipe 49 to the first riser 5.

The invention is not to be limited by the description of the above specific embodiment. For example, the single catalyst, combusting contactor could supply several specialized hydrocarbon decontaminator combustors attached in parallel to it. Also, several decontaminators could be attached in series so as to partially decontaminate the specialized hydrocarbon in several steps. If desired, the solid sorbent material having very little catalytic activity could be diluted with other types of particulate material which would interact with the specialized hydrocarbon or with essentially inert material. Not all contactors need be simultaneously in use. The active and spent catalyst conduits may proceed from and to the combustor independently or in manifold fashion. There may be multiple second contactors in parallel connection, with respect to the first contactor, to the combustor. Many other variations are possible both in hardware design and process operation.

Claims

1. A continuous process for disposing of contaminated used lube oil by converting it to useful product, comprising:

(a) contacting a particulate sorbent of low or no catalytic cracking capability with a carbo-metallic oil feed boiling at at least 343°C (650°F) and essentially free of used lube oil in a first contactor 22 to form purified products and contaminated sorbent formed from contact with said carbometallic oil feed;

(b) separating the purified products from the said contaminated sorbent;

(c) regenerating the said contaminated sorbent by heating it at from 533°C to 683°C in a regenerator 29 in the presence of oxygen-containing gases to form a regenerated particulate sorbent, the major part of which is recycled to the first contactor 22;

(d) withdrawing a minor portion of the regenerated particulate sorbent and passing it through a second contactor 1122, which is smaller than the first;

(e) contacting the said minor portion of regenerated particulate sorbent in the second contactor 1122 with contaminated used lube oil for a period of time less than 3 seconds at a temperature below 500°C and converting the used lube oil to a substantially decontaminated hydrocarbon product;

(f) separating contaminated sorbent formed from contact with the used lube oil from the product formed in the second contactor 1122; and

(g) returning the contaminated sorbent formed from contact with the used lube oil to the regenerator 29 for regeneration and recycle to the first and second contactors 22 and 1122.

2. A process according to Claim 1 in which the contaminated use lube oil comprises contaminated motor oil.

3. A process according to Claim 1 or 2 in which from 3 to 12 kilograms of the particulate sorbent is used to contact each kilogram of the used lube oil.

4. A process according to any one of Claims 1 to 3 in which, in stage (e), the period of time is 1 to 3 seconds and the temperature is 350 to 500°C.

Patentansprüche

1. Verfahren zur Entseuchung von gebrauchtem Schmieröl durch Entfernung der verunreinigenden Metalle und Metallverbindungen, gekennzeichnet durch:

(a) Inberührungbringen eines teilchenförmigen Sorbens mit niedriger oder keiner katalytischen Spaltfähigkeit mit einer carbometallischen Ölbeschickung, die bei wenigstens 343°C siedet und in wesentlichen frei von gebrauchtem Schmieröl ist, in einer ersten Berührungszone 22, um gereinigte Produkte und verunreinigtes Sorbens, das bei der Berührung mit der carbometallischen Ölbeschikkung erhalten wird, zu bilden;

(b) Abtrennen der gereinigten Produkte von dem verunreinigten Sorbens;

(c) Regenerieren dieses verunreinigten Sorbens vermittels Erhitzen bei 533 bis 683°C in einem Regenerator 29 in Gegenwart eines sauerstoffhaltigen Gases unter Ausbildung eines regenerierten, teilchenförmigen Sorbens, dessen Hauptteil zu der ersten Berührungszone 22 zurückgeführt wird;

(d) Abziehen eines kleinen Teils des regenerierten, teilchenförmigen Sorbens und Führen desselben durch eine zweite Berührungszone 1122, die kleiner als die erste ist;

(e) Inberührungbringen des kleinen Anteils des regenerierten, teilchenförmigen Sorbens in der zweiten Berührungszone 1122 mit verunreinigtem, gebrauchtem Schmieröl eine Zeitspanne von weniger als 3 Sekunden bei einer Temperatur unter 500°C und Umwandeln des gebrauchten Schmieröls in ein praktisch gereinigtes Kohlenwasserstoffprodukt;

(f) Abtrennen des verunreinigten Sorbens, das bei der Berührung mit dem gebrauchten Schmieröl erhalten wird, von dem in der zweiten Berührungszone 1122 ausgebildeten Produkt und

(g) Rückführen des verunreinigten Sorbens, das durch die Berührung mit dem gebrauchten Schmieröl erhalten wird, zu dem Regenerator 29 zwecks Regenerierung und Zurückführung in die erste und zweite Berührungszone 22 und 1122.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das verunreinigte gebrauchte Schmieröl verunreinigtes Motoröl enthält.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass 3 bis 12 kg des teilchenfoermigen Sorbens zum Inberuehrungbringen mit jeweils einem Kilogramm des verunreinigten Schmieroels verwendet werden.

4. Verfahren nach Anspruechen 1 bis 3, dadurch gekennzeichnet, dass in der Stufe (E) die Zeitspanne 1 bis 3 Sekunden und die Temperatur 350 bis 500 Grad Celsius betraegt.

Revendications

1. Un procédé en continu pour écouler de l'huile lubrifiante usée contaminée, par conversion de celle-ci en produit utile, consistant à:

(a) mettre en contact un sorbant particulaire présentant une aptitude au craquage catalytique faible ou nulle, avec une charge d'huile carbométallique bouillant à au moins 343°C (650°F) et sensiblement exempte d'huile lubrifiante usée, dans un premier contacteur 22, afin de former des produits purifiés et du sorbant contaminé issu du contact avec ladite charge d'huile carbométallique;

(b) séparer les produits purifiés dudit sorbant contaminé;

(c) régénérer ledit sorbant contaminé par chauffage de celui-ci entre 533°C et 683°C dans un régénérateur 29, en présence de gaz contenant de l'oxygène, afin de former un sorbant particulaire régénére, dont la majeure partie est recyclée dans le premier contacteur 22;

(d) soutirer une fraction mineure du sorbant particulaire régénéré et la faire passer à travers un second contacteur 1122, qui est plus petit que le premier;

(e) mettre en contact ladite fraction mineure de sorbant particulaire régénéré dans le second contacteur 1122 avec de l'huile lubrifiante usée contaminée, pendant une période de temps de moins de 3 secondes, à une température inférieure à 500°C, et convertir l'huile lubrifiante usée en un produit hydrocarboné sensiblement décontaminé;

(f) séparer le sorbant contaminé issu du contact avec l'huile lubrifiante usée, du produit formé dans le second contacteur 1122; et

(g) renvoyer le sorbant contaminé issu du contact avec l'huile lubrifiante usée, au régénérateur 29 en vue de la régénération et du recyclage aux premier et second contacteurs 22 et 1122.

2. Un procédé selon la revendication 1, dans lequel l'huile lubrifiante usée contaminée comprend de l'huile de moteurs contaminée.

3. Un procédé selon la revendication 1 ou 2, dans lequel de 3 à 12 kilogrammes du sorbant particulaire sont utilisés pour la mise en contact avec un kilogramme de l'huile lubrifiante usée.

4. Un procésé selon l'une quelconque des revendications 1 à 3, dans lequel, à l'étape (e), la période de temps est de 1 à 3 secondes, et la température est de 350 à 500°C.

FIG. 1

MRS UNIT - CONTACTOR / DECONTAMINATOR SYSTEM