

[54] **REMOVAL OF LEAD AND OTHER  
SUSPENDED SOLIDS FROM USED  
HYDROCARBON LUBRICATING OIL**

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208/187, 251, 184, 179; 423/92**

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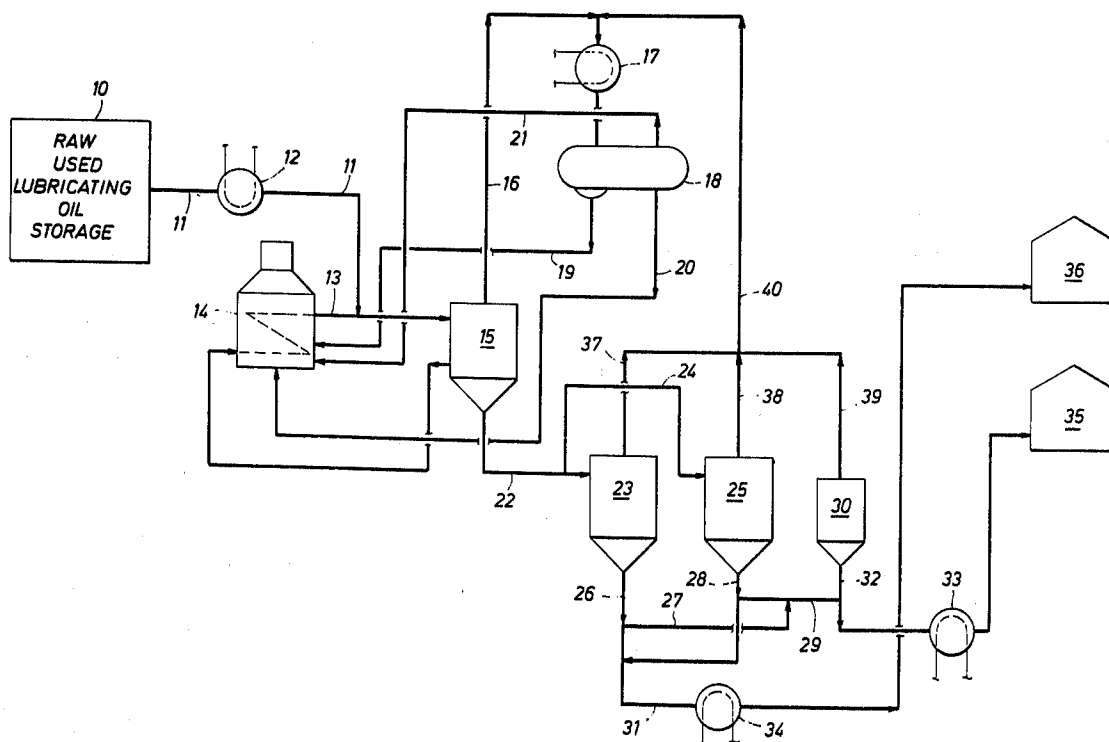
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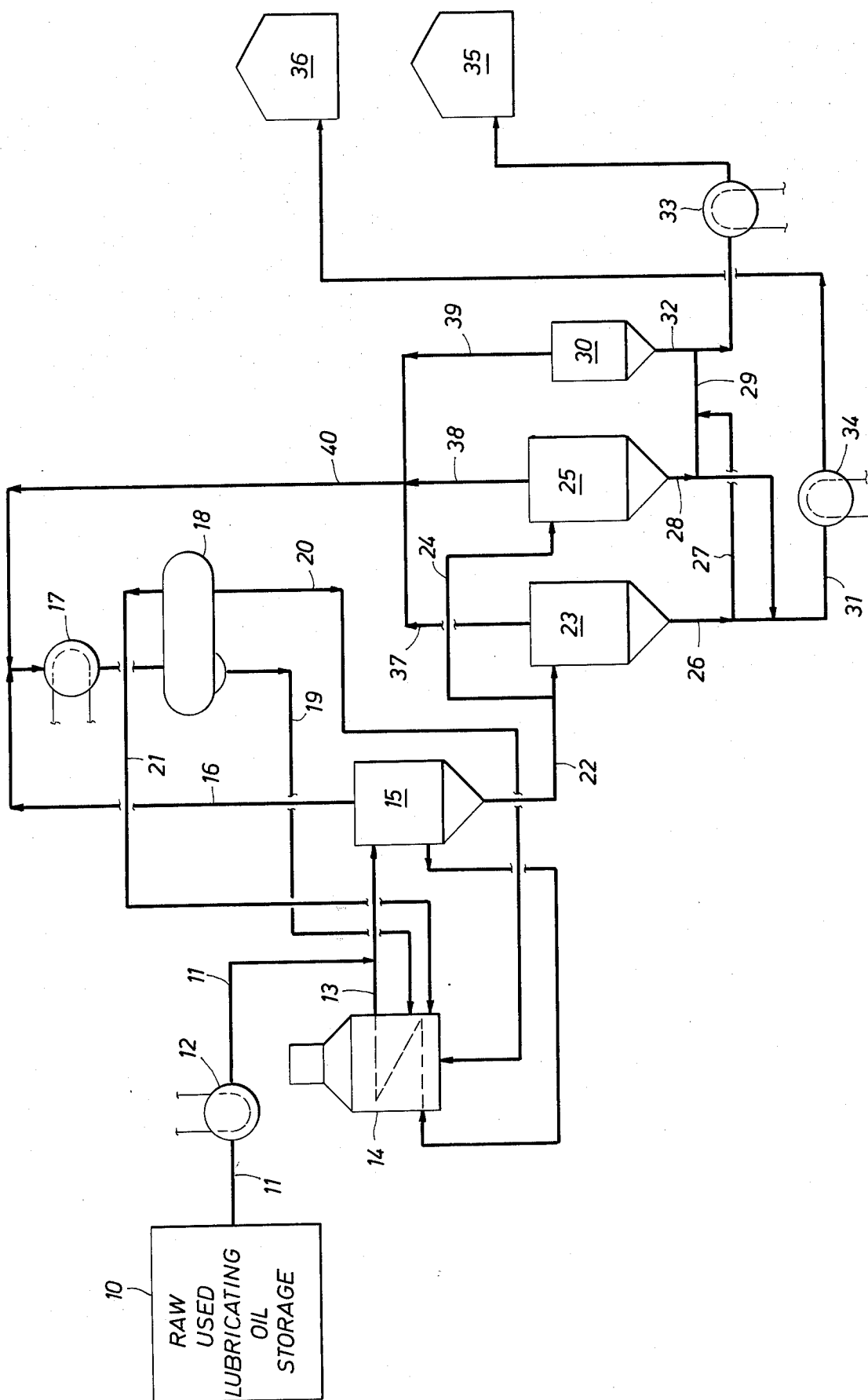
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[57] **ABSTRACT**

Lead and other dispersed solids present in used hydrocarbon lubricating oil which also contains water and light hydrocarbon impurities are removed by a process wherein agglomeration of the suspended lead and other solids is induced by heat treatment of the used oil at about 500 to 700°F after flashing off the water and light hydrocarbon material. The agglomerated solids are readily separated from the heat treated oil by conventional physical separation techniques such as centrifuging or gravity settling to afford a used oil substantially free, i.e., at least 90% lead removal, of lead and other solid contaminants.

**5 Claims, 1 Drawing Figure**





# REMOVAL OF LEAD AND OTHER SUSPENDED SOLIDS FROM USED HYDROCARBON LUBRICATING OIL

## BACKGROUND OF THE INVENTION

This invention relates to purification of used hydrocarbon lubricating oil. More particularly, this invention is directed to a process for renovating hydrocarbon oils used as lubricants in internal combustion engines, i.e., crankcase oil, wherein substantially all of the lead and other dispersed solids are separated from the used oil.

The disposal of the approximately 500 million gallons of used crankcase oil produced annually in the United States by environmentally acceptable techniques is becoming an increasingly significant challenge to both the private and public sectors of modern day society. In the past much of this waste oil has been disposed of by means such as pouring it onto the ground or into sewers, oiling roads, burning it directly as fuel, etc. However, primarily because of the accumulated solid impurities such as combustion derived inorganic materials, particularly lead compounds, which remain dispersed in this crankcase oil due to the very effective dispersant characteristics of modern day lubricating oil additives, many of the crankcase oil disposal techniques, such as those mentioned above, are becoming unacceptable in today's environmentally conscious society.

The insoluble, solid materials contained in a typical used crankcase oil include sub-micron size carbon particles, inorganic materials such as atmospheric dust, metal particles, lead and other metal compounds originating from fuel combustion. Besides lead, which is generally present at concentrations of 1.0 to 2.5%w, appreciable amounts of zinc, barium, calcium, phosphorus and iron are also present in the used crankcase oil. Examination of the used oil under an optical microscope at 600 magnifications reveals the very effective dispersant characteristics of modern day lube oils. The particle size of the particulates is estimated from this microscopic examination to be 0.1-1.0 microns with virtually no occurrence of agglomerates in the oil.

Although this extremely effective dispersing action of today's typical lube oil is advantageous when the hydrocarbon oil composition is employed as a lubricating agent, it also provides a distinct obstacle to the development of an environmentally acceptable means of disposing of the used oil, in that it prevents the separation of lead from the used oil by simple and relatively inexpensive methods, a prerequisite to any viable disposal means. For example, conventional physical separation techniques such as gravity settling, centrifugation or filtration of the undiluted waste oil which might be suitable from economic and ease of operation standpoints are not effective in facilitating the desired separation. Other separation methods have been previously proposed. However, many of these methods require the addition of a coagulating agent which is either not re-usable, e.g., see U.S. Pat. No. 2,568,583, or recoverable only through the employment of a supplemental recovery scheme with the associated costs of auxiliary equipment and process control, e.g., see U.S. Pat. No. 3,763,036. Further, in crankcase oil purification methods such as that described in U.S. Pat. No. 2,305,464 wherein no extraneous coagulating agent is added (hydrolytic action of water apparently relied on), it is an essential requirement that volatile materials in the used oil (including water) be maintained in the used oil

phase during a heat treatment period to coalesce solid impurities. This, of course, requires the use of expensive high pressure resistant equipment as well as exposing operators of the process to the hazards associated with such high pressure operation.

## SUMMARY OF THE INVENTION

It has now been found that suspended lead and other dispersed solids in used hydrocarbon lubricating oil can be readily agglomerated and separated from the used oil by conventional physical separation techniques if the used oil is subject to heat treatment at a critically high temperature range, i.e., 500° to 700°F, subsequent to removal by volatilization or equivalent means of substantially all of the water and volatile hydrocarbons contained in the used oil. Accordingly, the instant invention provides a process for removing lead and other dispersed solids from used hydrocarbon lubricating oil which comprises

- a. heating the used hydrocarbon lubricating oil under temperature and pressure conditions at which substantially all the water and volatile hydrocarbon materials boiling below about 500°F at atmospheric pressure will volatilize out of the used oil to afford a used hydrocarbon lubricating oil substantially free of water and said volatile hydrocarbons, said water and volatile hydrocarbons being removed as a gaseous overhead,
- b. subjecting the used hydrocarbon lubricating oil substantially free of said water and volatile hydrocarbons to further heat treatment at a temperature between about 500° and 700°F for about 1 to 12 hours, thereby agglomerating the lead and other dispersed solids contained in the used oil and
- c. separating the agglomerated solids from the used hydrocarbon lubricating oil.

In a preferred aspect of the invention the removal of lead and other dispersed solids from the used hydrocarbon lubricating oil is effected in continuous fashion by recycling a portion of hot used oil with water and volatile hydrocarbons removed from the zone in which volatilization occurs through a separate used oil heating zone and introducing fresh used oil feedstock into this recycle line at a point subsequent to the used oil heating zone but prior to recycle of the hot used oil into the devolatilization zone. In this continuous process the agglomeration and separation of agglomerated solids (lead and other solid impurities) is preferably effected by passing the devolatilized used oil into at least two gravity separation zones (settlers) operated in parallel; one settler being filled with hot used oil while the other settler filled with hot oil is utilized to effect the heat treatment for the time required to agglomerate and gravity separate the lead and other dispersed solids. In this aspect all settlers operated in parallel are maintained at a temperature in the 500° to 700°F range required to agglomerate the suspended solids.

## DETAILED DESCRIPTION OF THE INVENTION

In the first step of the process of the invention raw used hydrocarbon lubricating oil which can contain up to 30%/w water and up to 40%/w volatile hydrocarbons, i.e., gasoline and gasoline boiling range fractions, in addition to the suspended lead and other dispersed solids is subject to a flashing or devolatilization treatment under temperature and pressure conditions at which substantially all of the contained water and vola-

tile hydrocarbons are distilled away from the used oil. The specific temperature and pressure conditions employed in this devolatilization operation may vary within fairly wide limits dependent on factors such as the specific concentration of water and volatile hydrocarbons in the raw used oil, the rate of devolatilization desired, the heating and vacuum facilities available, etc. For typical used lubricating oil feedstocks, which contain 5–15%/w water and 15–35%/w gasoline range volatile hydrocarbons, the flashing operation is suitably carried out at pressures ranging from a mild vacuum, e.g., 2.5 psia up to 150 psia and at temperatures ranging from about 500° up to about 700°F; the upper temperature limit being dictated by the temperature at which thermal decomposition of the lubricating oil becomes significant and/or loss of 500°F+ boiling material becomes excessive. In any case, the temperature, pressure and flashing residence times should be selected such that the used oil product of the flashing operation is substantially free of any entrained water and volatile hydrocarbons boiling below 500°F at atmospheric pressure. It is very advantageous to recover the volatile hydrocarbon materials, which are distilled overhead in this flashing operation, by means of conventional condensing facilities for use in the flashing step, discussed below, where they can supply all or part of the heat requirement of this step.

After removal of substantially all of the contained water and volatile hydrocarbons, the used lubricating oil is subject to heat treatment at a temperature in the range of about 500° to about 700°F for a time sufficient to cause agglomeration of a substantial portion of the lead and other dispersed solids contained in the used oil. While the basis for the occurrence of this agglomeration phenomenon is not completely understood, it is believed that heating of the used oil to this critically high temperature range causes thermal decomposition of the peptizing agents which hold the dispersed lead and other solids in colloidal suspension. With this heat treatment procedure it is possible to agglomerate substantially all of the dispersed lead and other solids contained in the used oil such that reductions in lead content in excess of 90% can be readily obtained on subsequent separation of the agglomerated solids by conventional physical separation techniques. Since substantially all of the water and volatile hydrocarbons have been previously removed from the used lubricating oil, this heat treatment step can be very suitably carried out at atmospheric pressure thereby avoiding the use of high pressure equipment as required in the prior art procedures. The specific residence time employed in this heat treatment step is dependent, in part, on factors such as the solids content of the lubricating oil, the quality of oil to be treated, etc., which vary somewhat in any given practical application. However, in most instances it has been found that heat treatment residence times ranging from about 1 to about 12 hours will facilitate the high degree of agglomeration contemplated by this invention.

The agglomerating heat treatment can be suitably carried out in a reaction zone under an air or inert gas, e.g., nitrogen, atmosphere. In this same connection it has been found that the heat-induced agglomeration of the lead and other dispersed solids can be enhanced by the addition of either H<sub>2</sub>S or NH<sub>3</sub>. Accordingly, in a preferred aspect of this invention, H<sub>2</sub>S or NH<sub>3</sub> is admixed with the used oil after removal of water and vola-

tile hydrocarbons. In this instance it is adequate to operate at atmospheric pressure since low concentrations of H<sub>2</sub>S or NH<sub>3</sub> suffice.

In the final step of the process the heat treated lubricating oil is subject to a physical separation procedure by which the agglomerated solids are removed from the used lubricating oil. Heat-induced agglomeration according to the process of the invention affords agglomerated solid particles of a particle size sufficient that any conventional physical separation technique may be employed to effect this final separation. For example, suitable separations are effected by centrifuging, filtration, gravity settling and like techniques. For simplicity and economy of operation, it is preferred that the separation be effected in one or more gravity settling zones. With this technique the agglomerated solids are collected in the bottom of the first settling zone as a sludge-like material which can be drained away from the purified oil and disposed of directly or passed into a second gravity settling zone for further separation and recovery of purified oil. Suitably the gravity settling is carried out at a temperature which approximates that employed in the heat treatment zone, i.e., 500°–700°F with a residence time of 1 to 12 hours. Most preferably the heat treatment step and the gravity settling separation step are carried out in a single processing step wherein the lead and other dispersed solids are allowed to settle as they agglomerate. In this most preferred case the combined residence time required for both agglomeration of dispersed solids and settling of the agglomerated solids ranges from 1 to 12 hours, depending upon the geometry of the vessel and the degree of particulate removal which is desired.

The process of the invention may suitably be carried out in either batch or continuous fashion. In batch operation the raw used lubricating oil is passed into a suitable heating vessel having a bottom discharge for product, e.g., a cone bottom tank equipped with a bottom discharge valve, and a suitable means for heating the raw used oil — e.g., in tank stream coils, electrical heaters, etc. After receiving the desired charge of raw used oil, the heating vessel is heated to a temperature sufficient to distill off the contained water and volatile hydrocarbons, e.g., 500°F at atmospheric pressure, which are collected in an overhead condensing system. Optionally, during the water and light hydrocarbon flashing operation a partial vacuum can be placed on the heating vessel to reduce the heat and temperature requirements of the flashing step. After removal of contained water and volatile hydrocarbons, the used oil is subject to further residence time in the heating vessel at a temperature in the range of 500° to 700°F to induce agglomeration of the dispersed lead and other solids. In normal operation this heating vessel will also function as a gravity settling vessel and as such will effect separation of most of the agglomerated solids which collect as a sludge in the bottom of the tank from the used oil. The total residence time for agglomeration of dispersed solids and separation of most of the agglomerated solids from the used oil suitably ranges from 1 to 12 hours. At the end of the heating cycle the sludge is drained from the bottom of the heating vessel into a smaller vessel, e.g., cone bottom tank, where further settling and separation takes place. In this manner considerably more than 90% separation of dispersed lead and other solids from the used oil can be effected.

Preferably, the process of the invention is carried out in a continuous manner. To facilitate understanding of this preferred mode of operating the process of the invention, reference will be made to the Figure which shows, in schematic fashion, a suitable apparatus for continuous operation of the process of the invention. For the sake of simplicity, auxiliary equipment such as valves, pumps, vacuum facilities and the like are not shown in this figure.

Raw used lubricating oil feedstock is passed from storage tank 10 via line 11 through a feedstock pre-heater 12 in which it is heated to a temperature in the range of 300° to 500°F. This preheated oil is then introduced into the recycle loop 13 which cycles hot used oil from the used oil flasher 15 through the primary used oil heater or furnace 14 and back into the flasher. At its point of introduction into the recycle loop 13, which introduction is suitably accomplished by means of a mixing T positioned on the recycle line 13 at a point subsequent to passage of the recycled oil through the heater but prior to its introduction back into the flasher, the raw used oil is admixed with the hot recycled oil at a ratio selected to give the desired temperature in the flasher, e.g., 600°F, without overheating the recycle oil. In the flasher 15, which may suitably be a cone bottomed insulated vessel, the water and volatile hydrocarbon components of the raw used lubricating oil are distilled overhead via line 16 through a heat exchanger-condenser 17 into a water and light hydrocarbons accumulator 18. This distillation or flashing operation may be accomplished under partial vacuum conditions, e.g., 300 mm Hg furnished by appropriate vacuum facilities (not shown). In the accumulator 18 the water and volatile hydrocarbon overhead are phase separated and passed via lines 19 and 20, respectively, back into the primary used oil heater 14 where the hydrocarbons supply at least a portion of the heat requirement of that heater. Also, the water is incinerated in this heater for disposal. Any non-condensed vapors, i.e., light hydrocarbons which may also be present in the accumulator are also passed back into the heater 14 via line 21 to furnish a portion of the thermal requirement for that heater. The primary used oil heater 14 is suitably constructed as a hydrocarbonaceous fuel furnace wherein hydrocarbons are completely combusted in the presence of the waste water. In this manner, the recycled oil is heated to maintain the flasher at a temperature in the range of 500° to 700°F.

To affect agglomeration of the lead and other dispersed solids in the used oil and concomitant separation of such agglomerated solids, a stream of hot flasher bottoms is taken off the bottom of flasher 15 and passed via lines 22 and 24 into two gravity settling vessels operated in parallel. This stream of hot flasher bottoms is substantially free of both water and volatile hydrocarbons. Procedurally, the used oil is passed via line 22 into settler 23 until it is filled to the desired level after which the used oil is diverted by means of appropriate valving on line 22 into line 24 for passage into settler 25. In this manner the hot used oil is given the desired agglomeration and settling residence time in one of the settlers during the time period when the other settler is filling with used oil. Gravity settlers 23 and 25 are of similar size and construction, both suitably being cone bottomed insulated tanks. During the solids agglomeration and settling residence time in each of the settlers, the temperature of the used oil is maintained

at between 500° and 700°F. With the combined agglomeration and settling residence times contemplated by the instant invention, i.e., 1 to 12 hours, the desired temperature range is suitably maintained by means of appropriate insulation on the settlers since the hot flasher bottoms are already at temperatures in this range. However, if desired, additional heat may be supplied to the settlers by means of heating coils, e.g., high pressure steam or electrical, located in the walls of the settlers. Upon completion of the desired agglomeration and settling residence time in either of the settlers 23 or 25, the settler is drained via a bottom outlet into lines 26 and 28, respectively, wherein the first portion of the drained material, containing the agglomerated solids and a minor portion of oil in the form of a sludge, is diverted via appropriate valving into lines 27 and 29, respectively. This sludge is passed by lines 27 and 29 into a sludge pot 30 where additional settling could be achieved, if desired. The used oil which remains after draining off of the sludge is passed from the settler 23 and 25 via lines 26 and 28, respectively into line 31 where the combined settler effluent, now substantially free of lead and other dispersed solids, is cooled via heat exchanger 34 and passed into a purified oil storage tank 36. The sludge present in the sludge pot 30 after being given the desired settling time, e.g., 1 to 12 hours, at temperatures which may be lower than those maintained in the settlers is drained from the sludge pot via line 32 through a heat exchanger 33 where it is cooled and passed into a concentrated solids storage tank (35). Any additional purified oil which may separate in the sludge pot is diverted on draining of the sludge pot from line 32 into line 29 which connects with the purified oil storage via line 28. Any volatile materials, e.g., volatile hydrocarbons, which may conceivably carry over into the settlers 23 and 25 and the sludge pot 30 from the flashing operation are passed via overhead lines 37, 38 and 39, respectively, into line 40 which joins line 16 at a point prior to its introduction into the flasher overhead condenser 17.

Through operation of the process of the invention in the continuous manner hereinbefore described, it is possible to remove in excess of 90% of the lead and dispersed solids present in the used hydrocarbon lubricating oil. The purified oil obtained by operation of this continuous process may be suitably employed in many industrial applications of such heavy oils, e.g., fuel oil, without risk of environmental contamination such as lead emissions on combustion which plagues the possible use of the unpurified used lubricating oil. Further, the concentrated metal sludge obtained from the process can be dispensed to suitable metal reclaimers for recovery of the valuable metals contained therein or, alternatively, can be utilized in amounts consistent with acceptable environmental standards in asphalt manufacture.

What is claimed is:

1. A process for removing suspended lead and other dispersed solids from used hydrocarbon lubricating oil which comprises:

- a. heating the used hydrocarbon lubricating oil under temperature and pressure conditions at which substantially all the water and volatile hydrocarbon materials boiling below about 500°F at atmospheric pressure will volatilize out of the used oil in a devolatilization zone to afford a used hydrocarbon lubricating oil substantially free of water and

said volatile hydrocarbons, said water and volatile hydrocarbons being removed as a gaseous overhead,

- b. subjecting the used hydrocarbon lubricating oil substantially free of said water and volatile hydrocarbons to further heat treatment at a temperature between about 500° and 700°F for about 1 to 12 hours in a heat treatment zone thereby agglomerating the lead and other dispersed solids contained in the used oil and
- c. separating the agglomerated solids from the used hydrocarbon lubricating oil.

2. The process according to claim 1 wherein the separation of agglomerated solids from the used hydrocarbon lubricating oil is effected in one or more gravity settling zones.

3. The process according to claim 1 wherein the heat treatment step and the agglomerated solids separation step are carried out in a single processing step in one or more gravity settling zones wherein the lead and other dispersed solids are allowed to settle as they agglomerate.

4. The process according to claim 1 wherein the vola-

tilization of water and volatile hydrocarbons contained in the used hydrocarbon lubricating oil is effected continuously by recycling a portion of the used hydrocarbon lubricating oil substantially free of water and volatile hydrocarbons from the devolatilization zone through a separate used oil heating zone and continuously introducing fresh used hydrocarbon lubricating oil feedstock into this recycle line at a point subsequent to the used oil heating zone but prior to recycle of the used oil into the devolatilization zone.

5. The process according to claim 4 wherein the agglomeration of the lead and other dispersed solids and at least partial separation of said agglomerated solids are effected continuously by passing the used oil substantially free of water and volatile hydrocarbons into a heat treatment zone comprising at least two gravity separation zones operated in parallel, one separation zone being filled with said used oil while the other separation zone filled with said used oil is utilized to effect the heat treatment for the time required to substantially agglomerate and at least partially separate the lead and other dispersed solids.

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