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PROCESS FOR FILM TREATMENT OF OIL

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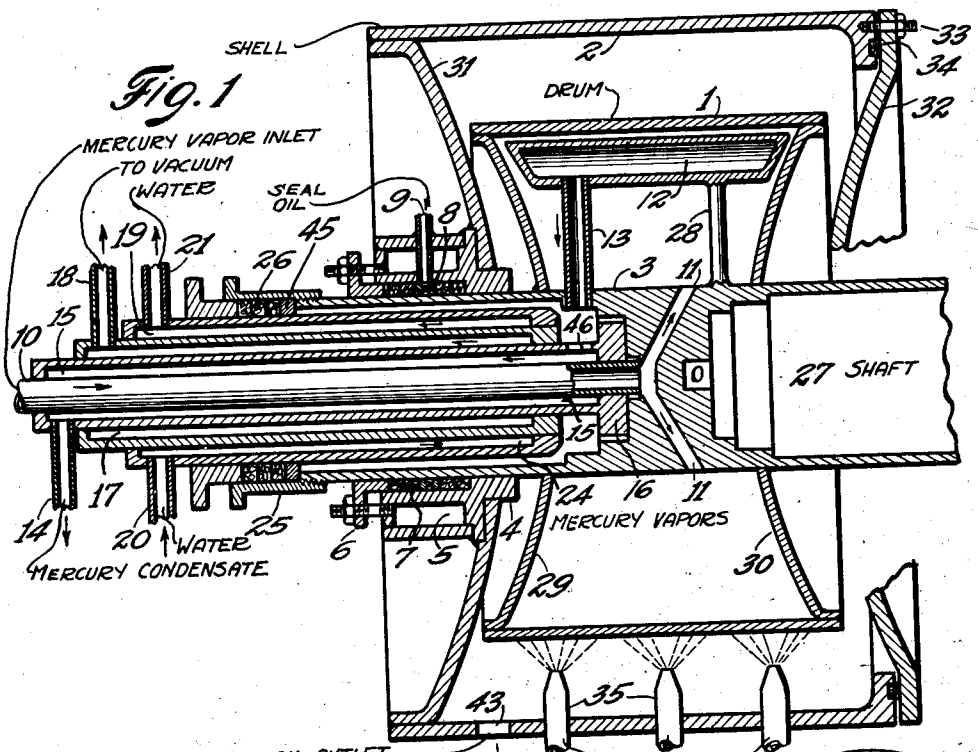


Fig. 1

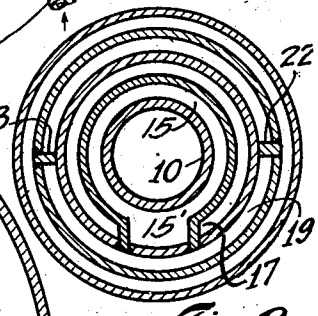


Fig. 2

Fig. 3

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PROCESS FOR FILM TREATMENT OF OIL

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14 Claims. (Cl. 196—79)

This invention relates to improvements in methods for transferring heat for such purposes as treating and distilling oil by means of mercury and other high boiling liquids. It further pertains to an improved method of applying vapors of such liquids to the distillation of oil to separate the oil in purified form from a residual mass containing an active agent and promoting such purification and more particularly to distillation as carried out by placing a thin film of oil with active agent on a heat transfer surface such as on the outside of a drum heated by internal application of mercury and similar vapors.

In the ordinary method of applying mercury and like vapors to treating and distilling oils of lubricating range or the like their use has been limited to jackets or heating pipes or trays or the like the latter permitting of the use of thin moving films with which residue is flowed away with the oil or otherwise prevented from accumulating and with which running down to dryness is prevented. With thin film vacuum evaporation from a drum as in drying milk for example, steam has been used and passed into the drum by means of a hollow shaft. Such steam has generally been close to atmospheric pressure. The construction of the drum and other features of units of substantial size have prevented the use of pressures of about 50 to 80 pounds. The temperature has thus been correspondingly limited. In such applications the matter of evaporation has been the objective and chemical or other changes has been especially avoided.

In applying my invention, I prefer to establish a thin film and to definitely promote alteration during, or at about the time of, evaporation and to prevent the film supporting member from exceeding a predetermined temperature thus rendering assurance that alteration or reaction at higher-than-desired temperatures will not occur. The application of vapors of high boiling point and substantial latent heat, require special precautions or arrangement that continuity of operation and precise control may be had. For preferred operation back pressure during discharge as is ordinarily met with and tolerated must be eliminated or reduced to a negligible value.

The drawing illustrates a preferred arrangement which may be used for accomplishing the desired results. The heating medium is considered as being mercury. My Patents 1,760,095; 1,765,038; 1,847,542; and 1,886,436 and other applications describe means for the general application of mercury for distilling oil and otherwise.

In the illustration Fig. 1 is a sectional view parallel to the axis of the drum used for transferring heat to the thin film of oil. Fig. 2 is a detail of the tube used to supply the heating medium and Fig. 3 is an abbreviated section perpendicular to the axis of the drum illustrating the manner of elevating mercury condensate from the drum and removing residual matter from the drum.

A rotating drum 1 of metal impervious to the vapors is shown as being contained within a shell 2 adapted to contain hot oil vapors and to withstand vacuum or pressure. The drum is carried therewithin by a shaft 3 revolving within bearing 4. Another such bearing not shown is provided for the right hand end of the shaft. This bearing is provided with a jacket 5 for temperature control liquid and gland 6 with packing 7 and ring 8 with connecting pipe 9 through which oil or other liquid being treated is passed to maintain a seal and for lubrication in the aforesaid manner. I prefer to use treated oil for lubrication when shell 2 is under vacuum so that inleakage will not unduly pollute the charge. If treated oil is not used for lubricating the above bearing, I prefer to have an internal drip pan or the like to flow lubricant to an outside vacuum receptacle and to otherwise prevent the untreated oil from contaminating treated or partially treated oil.

Mercury vapors or the like are flowed in through line 10 to outlets 11 within the drum 1. Condensate of the mercury is lifted by scoops 12 and elevated to a height to produce rapid flow and poured into line 13 whereby it reaches outlet 14 which is preferably arranged as previously described. I prefer that 12 should be free from 1. In its passage mercury flows through annular opening 15. Dam 16 serves to guide and direct the flow of condensate mercury into passageway 15 which preferably has an enlarged opening 15' to facilitate discharge. The lower end of 13 may be extended close to opening 46. In this manner plugging, back pressure and other undersirable features are substantially avoided. If the companion unit of similar design but for insertion in space 27 is used free vapor passage is always had.

About the mercury condensate and gas passageway 15 is an evacuated or gas filled space 17 with connection 18, which retards heat transfer between the condensate and the water or other jacket 19 provided with connections 20 and 21 to contain flowing or boiling liquid. Baffles 22 and 23 are provided to direct the flow from 20 to the remote zone at 24 and back to outlet 21. This

jacket is preferably carried at a temperature between about 80° C. and 130° C. It operates as to assure proper lubrication of and to prevent "feezing" of stuffing box 25 as it rotates with shaft 3 while the tube structure and shell 2 remain stationary. The packing 26 may be liquid sealed as by a ring similar to 8 not shown. In this manner the mercury vapors are introduced and mercury condensate and non-condensible gas are removed. Vapors of mercury can flow inwardly and mercury condensate outwardly at the same time. As an alternate design which I consider as less desirable, one tube set may be used for inflow of heating medium and the second set for outflow.

The second similar tube set may be placed in the right hand end of the drum 1 as in the shaft 3 indicated as being hollow to form the receiving chamber 27. In some cases I prefer to reverse the relative position of the vacuum and the water spaces. At times one or the other of these may be omitted for example a workable although less effective system may permit mercury condensate space to be in thermal contact with the cooling jacket, liquid flowing through 15' and gaseous fluid through 15.

The drum 1 is further provided with a secondary support 28 for the scoop 12 and ends 29 and 30 tightly welded to the shell 3 the surface of which is preferably ground smooth. The shell 2 is evacuated for high boiling oils and the like. It is shown as having a fixed end 31 and a removable end 32 fastened as by studs 33. A recessed gasket 34 is shown as meeting a machined surface of 32. Cover plate 32 may carry a bearing similar to 4 although in some instances as when a single set of tubes is used I prefer to have a fixed bearing inside of the cover plate so that the cover plate may be removed without disturbing drum 3. In some cases I prefer to use both bearings at the end with removable cover. In some instances it is advisable to weld 32 to 2. The drum 1 may be rotated by internal application of power from a shaft of smaller size which may pass through end 31, or otherwise, so as not to materially interfere if at all with the position of drum 3 and the step of removal of 32. An internal gear set or chain on sprocket set or the like may be used for such drive.

For purposes of illustration the liquid oil to be evaporated is shown as being applied by means of spray nozzles 35 which are preferably located between the illustrated points and the trough 39. A pan or trough for contact with or without rotating paddles may be used. Plates 36 and 37 are shown as being used to confine the applied liquid oil. One or both may be adjustable as to spacing and clearance. Thus 37 may be used to adjust the maximum thickness of applied liquid. Scrapper 38 is preferably adjustable and discharges the dried material into trough 39 with discharge conveyor 40 leading to a receiver under the same pressure as are within shell 2. Arms or paddles for mixing is preferable to break up lumps or to mix in a liquid. A pressure control line and vapor outlet may be applied to shell 2 in the well known manner and at suitable distance from the end and circumferentially placed about as indicated by the opening 41. As pointed out in the co-pending applications the treated oil is required to be quickly fractionated and liquefied to prevent undesirable alterations and formation of portions of desired boiling point. A sight glass or preferably a number of them may be provided along shell 2 to show operations therewithin and circumferentially about as indicated by center line 42. Liquid oil may be returned by a line connecting with the opening 43 for recirculation through the pump feeding nozzles 35 which are preferably made removable and adjustable from the outside. In general I prefer to have a heater in the circulating or in the feed system (or both) so that upon entering the chamber the temperature will be such that an appreciable portion of more volatile components of the oil will evaporate by virtue of heat applied external to the drum. Thus vapors may pass from the zone of the sprayed liquid to the vapor outlet at 41. The outside shell 2 itself is preferably heated as by a jacket although with electric power at reasonable cost, I prefer to use a frequency electricity of between about 60 and 500 cycles and to induce currents into shell 2 and a further amount into drum 1 whereat internal vaporous heating and induced electric heating are thus simultaneously applied. The electrical and magnetic effects both in the oil film and in the space within the drum 1 and the shell 2 may thus be utilized to benefit the distillation as is evidenced by small but often noticeable betterment in the distilled product and in some instances in the character of the carbonaceous residue delivered by the drum. In applying the induced heating I prefer to impose a very high magnetic flux circumferentially about shell 2 and between the center lines of the three nozzles 35. An emission as of ultraviolet or infra red range may be applied to the vapors or to the film. An electrical discharge may be promoted under the preferred high vacuum as between two electrodes or one electrode and the drum 1 or the shell 2 or both for promoting change.

As an alternate or added feature the drum shaft may be cooled as by hot water within the bearing, the jacket for this purpose rotating with the shaft. Other similar equivalents may be provided.

As an example of the application of the general methods above described, I give the treatment of oil with metals with one unpaired electron such as sodium. As shown in Serial No. 660,031 clay-like or equivalent substance may be added to facilitate treatment. The type of apparatus of Ser. No. 613,151 may be used, the last stage of treatment being with or without substantial amounts of free metal. My preferred process involves the use of about a quarter or a half of a pound of free metal per barrel of oil treated during distillation as from a thin film as elsewhere described.

It is preferred that lubricating oil be previously treated with alkali metal at between about 200° C. and 400° C. to remove impurities and promote rearrangement to form light hydrocarbon from the lubricant to the extent of between about 5% and about 20% and that from about five to about twenty pounds of sodium or alkali metal be consumed during such treatment the time element, temperature and other factors being controlled as found by experiment to promote such consumption of the metal. An oxidation step is preferably applied, as for example, just before or shortly before passage into the zone of distillation from a thin film in the presence of alkali metal. Oil so treated is consistently and exceptionally stable, of low or no color and of increased viscosity index.

As the mass containing active treating agent is concentrated there is a critical point reached

whereat residual mass nearly devoid of the oil becomes exceptionally active as regards the vapors with which it is then contacted. Furthermore the amount of oil close to the heating surface becomes very small or nil and heat transfer must be through a mass of particles of relatively low heat conductivity or through superheated vapors which are rarified under the preferred condition of vacuum distillation. Ordinarily, heat is applied by a means which permits of a rise in temperature of the heating medium as the liquid is removed from the contacting film. Thus the active agent of or contained in the residue is applied at undesired high temperatures whereat they react unfavorably. To prevent this the heat transfer surface must be absolutely fixed as to its upper operating temperature range. My invention is not to be confused with thin film distillation for the primary purpose of preventing change at the time of distillation. I impose conditions to promote desirable change. Such change is that due to association with and evaporation from alkali metal or its equivalent and may include lowering of molecular weight of unstable portions, increase of viscosity index, increase in stability and removal of gum forming and colorizing impurities of oil.

While, I have disclosed a drum heater other approximately equivalent means may be used to dry the active residue from oil treated therewith. For example an electric heated belt giving an added advantage of flexure or other means may be used. With mercury vapors I prefer to maintain a small vacuum on the mercury system such conditions give a temperature of about 350° C. or a little below. Ordinarily the advantages of this could not be realized on account of the high temperature of evaporation when heavy oil is treated, however by providing a lighter oil to the mass either by preferably mixing or by spraying a mist or vapors thereon, the temperature of mercury vapors produced by boiling mercury under small vacuum is sufficient. With heavy oil shell **2** is preferably under high vacuum. With some oil the absolute pressure therein is preferably less than about two millimeters of mercury. In attaining high vacuum I prefer to immerse the shell in a liquid bath or to apply a liquid seal to all joints and leakable parts. Immersion may be in a metal such as mercury contained in a tank. Oil similar to that treated may be used for immersion or sealing. By utilizing a closed outer vessel to surround vessel **2** or leakable parts thereof, I am able to establish a reasonable vacuum exterior to ends **31** or to the whole and to then apply a very high vacuum to the interior. In such manner units of practical size may be well operated about a millimeter or less, obviously desirable with very heavy oils. Such arrangement is also of advantage in high pressure operation as for combination of light molecules. Mercury may be used as a lubricant and preferably after the metal parts have been "wetted" as by high vacuum treatment combined with hot vaporous treatment by a metal. Electrolysis may be used to obtain wetting.

The tube set may be tightly fixed to the outside chamber as by welding or special gasketed joint. The motor drive may be contained in the outer chamber and provided with heat abstraction means desirable to dissipate the heat generated. The jacketed heat control means may be used to maintain the parts at elevated temperature when regular operation is not carried on. With the double chamber construction, I prefer to have the glands adjustable by outside means.

During operation, the mass may be run down to a consistency of a tarry liquid or thereabouts by other or by similar apparatus and means and a more volatile oil mixed therewith and the mixture passed in thin film on a heating surface and preferably without appreciable motion as regards the surface of heat transfer. In this manner the more volatile oil carries most of the heavy oil with it. Similarly the oils with active substance in concentrated form may be treated with a light oil and a light stable liquid may be used to continuously remove the residue. In doing this I prefer to first cool the residue and to keep the temperature below the boiling point of most of the light liquid. This feature may be more readily understood by reference to Ser. No. 613,151 whereat the formation of such a mass and the concentration is illustrated. The added more volatile oil is preferably one which has been treated by the same or an equivalent agent so as to be of the same general condition as regards equilibrium if the heavy oil is to be later separated therefrom for use in its purified form.

The apparatus and method hereof or their equivalent may be otherwise utilized for the purposes generally indicated in connection with the processes and steps of the following applications, 613,080; 613,151; 627,171; 660,031; 661,095; 663,369 and 664,382. I do not limit my claims to the specific means and methods illustrated and I recognize that other equivalent ones may be used for similar purpose. Substances other than oils may be similarly treated.

I claim:

1. In vacuum evaporation of an oil of lubricating range containing treating agent in thin film on a moving heat transfer surface contacting vapors of mercury, the method of applying the oil as a thin film to the external surface of a slowly revolving drum heated by vapors of mercury under controlled pressure which vapors are flowed through the axis of the drum, surrounding the flow of mercury vapors with separately contained mercury condensate and gaseous fluid held in indirect heat transfer relation and flowing in a direction opposite to the main flow of vapors flowing towards the drum, and surrounding the mercury condensate and gaseous fluid by heat abstracting liquid and so abstracting heat therefrom and preventing substantial transfer of heat to a surrounding zone while simultaneously removing vapors evaporated from the oil film and avoiding excessive and irregular temperatures normally inherent to such distillation and maintaining the approximate established equilibrium during distillation.

2. For purifying and evaporating oil of lubricating range from residual active alkali metal treating agent under vacuum, the method of spreading the oil and residue containing about one half of a pound of alkali metal per barrel of oil on a closed drum as a thin surface layer contained within a chamber of reduced pressure, applying mercury vapors under controlled pressure to the interior of the drum to promote evaporation of the oil at about 350° C. or a little below, rotating the drum so that an element thereof repeatedly passes through established zones of film formation, evaporation and residue removal, elevating metal condensed within the drum and dropping it and flowing it axially to the outside through an annular stationary member heated internally by hot mercury vapors

flowing to the drum and externally by heat abstracting means to retard heat transfer from the stationary parts to the moving parts, and collecting and recovering lubricating oil from the oil evaporated from the film to yield a fraction of high viscosity index, improved stability and substantially lowered color.

3. In evaporating oil of lubricating range in contact with an active alkali metal to promote removal of impurities of oil and molecular rearrangement to increase the viscosity index of the oil and to decolorize the oil and to substantially prevent over action of the metal while separating oil from the alkali metal by evaporation, the process which comprises applying mercury vapors to a rotating member carrying oil and agent in thin film by flow of the mercury vapor through a stationary tube, withdrawing mercury condensate by flow through an annular passage parallel with and adjacent to the flow of mercury vapors in the tube while preventing transfer of heat from mercury condensate to parts external of the said passage by flowing a heat exchange fluid therebetween so promoting uniform simultaneous treatment and evaporation of the oil and withdrawing formed oil vapors and recovering oil of lubricating range therefrom with increased viscosity index and decreased color.

4. The process of simultaneously treating and evaporating oil in thin film form held under appreciable vacuum which comprises holding mercury vapors under controlled pressure in indirect heat exchange relation with oil of lubricating range which has been treated with alkali metal and which oil contains in substantially uniform admixture roughly one half of a pound of free metal per barrel of oil treated, and evaporating oil and forming dry residual alkali metal treating agent admixed with residual by-products of treatment and removing the residue of the film after drying while removing vapors and recovering therefrom lubricant so improved in viscosity index, color and stability.

5. The process of simultaneously treating and evaporating oil in thin film form held under appreciable vacuum which comprises holding mercury vapors under controlled pressure in indirect heat exchange relation with oil of lubricating range which has been treated with alkali metal and which oil contains in substantially uniform admixture roughly one half of a pound of free metal per barrel of oil treated, and evaporating oil at about 350° C. or a little below and forming dry residual alkali metal treating agent admixed with residual by products of treatment and removing the residue of the film after drying while removing vapors and recovering therefrom lubricant so improved in viscosity index, color and stability, and wherein the periods of forming film, evaporating and removal of dried residue are continuously maintained as by rotation of a drum and wherein heat is applied by mercury vapors passed uninterruptedly through an axially disposed tube and into the mercury vapor chamber of the drum and wherein mercury condensate is periodically removed by flow through an annular chamber concentric with the tube and protecting the mercury vapors from loss of heat and which chamber is likewise protected by an annular concentric evacuated chamber.

6. The process of refining oil of lubricating range which comprises treating oil of lubricating range with an alkali metal so as to rearrange unstable portions thereof into light vapors while simultaneously altering and removing impurities and increasing the viscosity index by flowing purified oil and residual mass containing about one half pound of metal per barrel of oil into contact with a rotating drum so as to form a film of oil and metal thereon, applying heat to the film on the drum from the interior of the drum so as to form vapors under the influence of the metal, holding the temperature of the surface of the drum at about 350° C. or a little below and controlling the drum speed so as to retain a film and promote undisturbed distillation and applying a vacuum to the atmosphere surrounding the film so as to volatilize substantially all of the oil during a single revolution of the drum, and so producing a substantially solid residue and oil vapors which are improved in viscosity index, stability and color and wherein heat is applied to the drum by flow of mercury vapors under controlled pressure, said flow being through a hollow axle of the drum while condensate of said vapors is removed through a concentric annular channel separated from the bearing of the drum by an annular heat-insulating space and wherein scoops are used to elevate condensate mercury and flow it outwardly through the condensate line.

7. In refining oil of lubricating range to render it more stable and to increase the viscosity index thereof while reducing the color, the process which comprises treating the oil with alkali metal at about 350° C. or a little below to promote rearrangement and formation of light hydrocarbons from unstable portions of lubricating range and to simultaneously increase the viscosity index and remove impurities coloring the oil while contacting the oil and the metal with a rotating drum which is precisely heated and in a manner to evaporate oil from a film under the influence of metal therein and under vacuum, and thereafter quickly fractionating and condensing oil so treated to form a portion of lubricating range which has been substantially stabilized and improved as to viscosity index and color and wherein the amount of metal added is such that during evaporation in film form on the drum there is present roughly one half of one pound of alkali metal per barrel of oil treated and evaporated and wherein impurities collected by the metal are retained in the film by the presence of adsorptive clay-like substance applied to the oil before the same is spread in film form on the drum.

8. The process of refining heavy oil of petroleum which comprises forming a mixture of the heavy oil to be treated and a more volatile oil which has been previously treated with alkali metal and applying said mixture to a precisely heated metallic surface as a thin film and in the presence of a small amount of alkali metal, transferring heat from the surface to oil of the film and evaporating said oil in substantially its entirety at about 350° C. or a little below, quickly fractionating and liquefying the vapors and while maintaining a substantially reduced pressure thereon.

9. For increasing the viscosity index of lubricating oil and improving the color thereof, the method of spreading a mixture of the oil containing a small amount of alkali metal upon a precisely heated metallic surface in film form, avoiding motion between the film and the surface while transferring heat from the surface into the oil to promote evaporation of substantial portions thereof while purifying the oil and forming light hydrocarbons from portions thereof,

quickly passing the formed vapors to a zone of fractionation and quickly liquefying and isolating the purified portions of lubricating range.

10. The process of refining heavy petroleum which comprises evaporating the petroleum under substantial vacuum and from a thin film containing alkali metal in small amounts and quickly liquefying the vapors of the oil so treated and wherein the thin film is precisely heated at about 350° C. or a little below.

11. In refining petroleum of lubricating range, the method comprising spreading the oil and small amount of alkali metal in film form over a precisely controlled heat transfer surface in a manner to evaporate substantial portions of the oil at about 350° C. or a little below while purifying the same and wherein the zone of evaporation is maintained under an absolute pressure of about a millimeter or less and the formed vapors are quickly liquefied.

12. The process of refining petroleum which comprises forming a mixture of petroleum of lubricating range and a substantially more volatile hydrocarbon, and alkali metal, spreading the mixture in a thin layer upon a precisely heated metallic surface designed to evaporate oil from the mixture and to run the residue down to substantial dryness, forming vapors by transferring heat from the surface to the film, and quickly fractionating the vapors and quickly liquefying and isolating improved oil of lubricating range therefrom and wherein the alkali metal is applied to the oil being treated at temperature resulting from holding the metallic surface at about 350° C. or a little below.

13. The method of claim 12 wherein evaporation is carried out under substantial vacuum.

14. In refining heavy hydrocarbons, the steps comprising mixing the hydrocarbon to be treated with a small amount of alkali metal and a clay like substance, applying the mixture in film form to a precisely heated surface, transferring heat from the surface into the film to evaporate the hydrocarbon, controlling the temperature of the film at about 350° C., and maintaining a vacuum on said film.

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