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METHOD OF REFINING HYDROCARBON OIL WITH A SLUDGE-FORMING REAGENT

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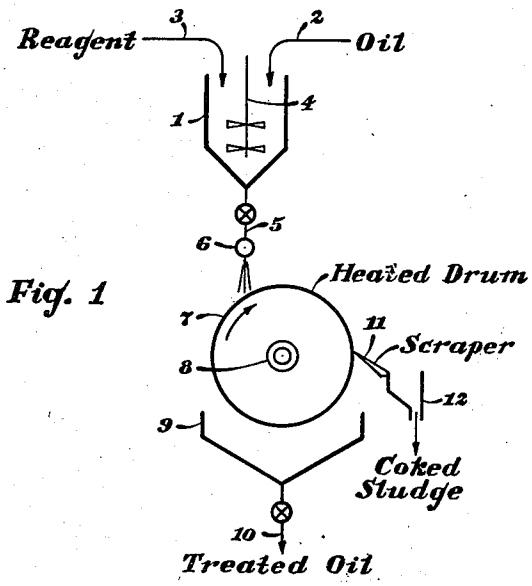

Fig. 1

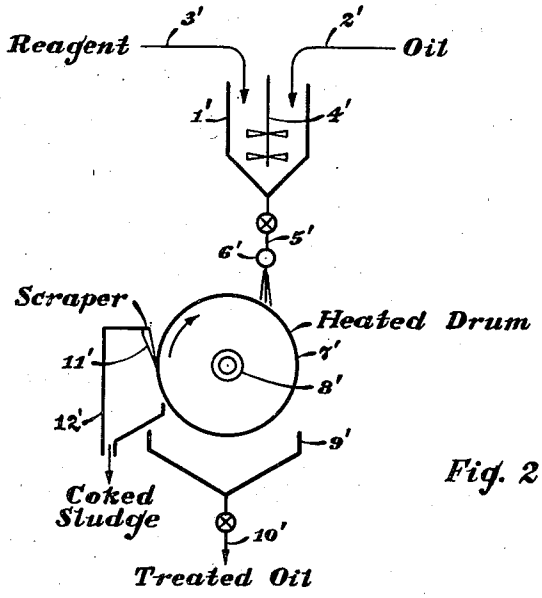

Fig. 2

Attest

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METHOD OF REFINING HYDROCARBON OIL WITH A SLUDGE-FORMING REAGENT

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The present invention relates to the refining of hydrocarbon oil, particularly lubricating oil, by treatment with a sludge-forming reagent at elevated temperature. This invention is especially adapted to the treatment of lubricating oil stocks with sulfuric acid or other reagent normally producing a sludge which will not settle readily and which is difficult to remove from the treated oil.

In accordance with the present invention, hydrocarbon oil is intimately mixed with a suitable quantity of a sludge-forming refining reagent, and the mixture is supplied, preferably in the form of a film, to an inclined stationary surface or to a rotating cylindrical surface heated to a temperature sufficient to coke or carbonize the sludge resulting from the reaction of the sludge-forming reagent with the oil but insufficient to deleteriously affect the oil. The rate of supply of the mixture as well as the rate of rotation of the cylindrical surface is controlled so as to effect deposition and coking of the sludge upon such surface, while the treated oil is drained therefrom and separately collected. The coked sludge is either continuously or periodically removed from the heated surface by scraping or other means in such a manner as not to contaminate the treated oil.

A variety of hydrocarbon oils may be treated, and include crude residuums or bottoms from the distillation of crude petroleum; lubricating oil distillate stocks; paraffinic or naphthenic oil fractions produced by the selective solvent extraction of lubricating oil distillates or reduced crudes; viscous hydrocarbon oils resulting from the destructive or non-destructive hydrogenation of crude oil or fractions thereof; and tars or tar distillates obtained in the cracking of petroleum for the production of motor fuel.

The refining agents which may be employed in the process of the present invention are sludge-forming substances such as concentrated sulfuric acid; 98% sulfuric acid; oleum or fuming sulfuric acid; chlorsulfonic acid; phosphoric acid; alkyl sulfates and acid sulfates such as mono- and dimethyl sulfate, and mono- and diethyl sulfate; and active metal halides such as aluminum chloride, tin tetrachloride, zinc chloride, ferric chloride, titanium tetrachloride, and the like. The quantity of refining agent employed varies considerably, depending upon the nature of the oil to be treated and the activity of the agent. Sulfuric acid in amounts of from 1% to 50% by volume of the oil may be used, while active metal halides are satisfactory in quantities of the order of 0.5% to 10%.

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The temperature necessary to coke or carbonize the sludge resulting from the reaction of the reagent with the oil varies with the reagent employed depending upon the activity thereof and the character of the sludge. In general, a temperature between 250° F. and 600° F. may be used. With concentrated or 66° Bé. sulfuric acid, a temperature between 400° F. and 600° F. is preferred, although temperatures as low as 250° F. may be used provided the coking time is extended.

The method of the present invention may be carried out either batch-wise or continuously, the latter mode being preferred. In batch-wise operation, for example, a lubricating oil stock such as a reduced crude having a Saybolt Universal viscosity of 160 seconds at 210° F., is intimately mixed with a suitable quantity of refining agent, such as 1.0% by volume of 66° Bé. sulfuric acid, and the mixture is supplied to the upper end of a stationary iron plate inclined at an angle of about 60° to the horizontal and electrically heated to a temperature of about 500° F. As the oil-acid mixture descends over the plate in the form of a film, the reaction between the oil and the acid is completed, the resulting acid sludge depositing on the heated plate and coking or carbonizing thereon, while the treated oil substantially free of sludge flows down the plate and is drained from the lower edge thereof into a suitable receptacle. The rate of flow of the oil-acid mixture is regulated so that all of the sludge is deposited upon the plate by the time the treated oil reaches the lower edge of the plate. At such time as the deposit of coked sludge upon the plate becomes appreciable, for example, $\frac{1}{16}$ inch in thickness, the supply of oil-acid mixture is shut off and the coked sludge is removed from the plate by scraping with a blade or wire brush. After the plate has been cleaned, the oil treating operation may be resumed. From the above operation there was obtained a yield of 88% by volume of decolorized, sludge-free, substantially neutral oil, and slightly less than 12% of dry, porous coked sludge.

My invention may be further illustrated with reference to the accompanying drawing, in which Figures 1 and 2 represent diagrammatically oil treating systems suitable for carrying out my process.

Referring to Figure 1, a hydrocarbon oil stock and a suitable quantity of sludge-forming reagent, such as concentrated sulfuric acid, is continu-

ously introduced into mixing vessel 1 by means of pipes 2 and 3, respectively. The oil and acid is thoroughly mixed in vessel 1 by means of stirrer 4, and the mixture of oil and acid, including some acid sludge, is withdrawn from the vessel by valve-controlled pipe 5 and delivered to a perforated pipe or manifold 6, which functions to distribute the mixture along the length of a heated drum or cylinder 7 rotating clockwise on the hollow axle 8. The drum 7 may be electrically heated by means of internal resistance heaters, or may be heated by circulation of a hot gas or liquid supplied through the perforated hollow axle 8. Since the actual method of heating is of no concern in the present invention, the inclusion of heater details is omitted. Suffice to say that the surface of the drum 7 is maintained at a temperature between 250° F. and 600° F., and preferably about 500° F. when the refining treatment involves the use of concentrated sulfuric acid. The mixture of oil and acid, with incidental sludge, is spread as a film over the surface of the drum immediately under the distributing manifold 6, and the reaction between the oil and the acid is completed upon the heated surface of the drum. The acid sludge is deposited on the surface of the drum and undergoes coking or carbonization. As the drum rotates clockwise, the treated oil substantially free of coked sludge flows downwardly counterclockwise over the drum and drains from the lowest point thereof into the collecting vessel 9, from which it may be removed by means of valve-controlled pipe 10 as desired. The rate of feed of oil-acid mixture to the surface of the drum and the rate of rotation of the drum is controlled so that little or no oil is carried in a clockwise direction to contaminate the coked sludge on the upper right quadrant of the drum, and at the same time the acid sludge is completely coked and does not drain off with the treated oil. The coked sludge deposited on the surface of the drum is continuously removed therefrom by contact with a scraper or blade 11 extending lengthwise of and in close proximity to the surface of the drum. The coked sludge thus dislodged is collected in the hopper 12 from which it may be removed and disposed of as desired. The coked sludge is usually obtained in the form of a powdery, friable scale which may be used for fuel or other purposes. The treated oil removed from vessel 9 is substantially sludge free and neutral, most of the sulfuric acid initially associated with the oil being removed therefrom in the form of sludge or sulfur dioxide. The treated oil, by virtue of the acid treatment, is partially decolorized, and may be finished by conventional methods such as clay filtration, dewaxing, etc.

In Figure 2 of the drawing, there is shown a modification of the apparatus employed in Figure 1. In Figure 2, the mixture of oil and sludge-forming reagent, such as sulfuric acid, is supplied to the right upper quadrant of drum 8' and flows clockwise in the direction of rotation of the drum. The treated oil, free of coked sludge, drains from the lower-most portion of the drum and is collected in vessel 9', while the coked sludge is scraped from the drum by means of longitudinally disposed blade 11'. Here again the rate of supply of the oil-acid mixture to the surface of the drum and the rate of rotation of the drum are controlled to give complete deposition and coking of the sludge without entrainment of sludge in the treated oil or entrainment of treated oil in the coked sludge removed by the scraper 11'.

While the present invention has been described particularly with reference to the use of sulfuric acid as the treating agent, it is obvious that other sludge-forming reagents may be used in lieu thereof, with consequent adjustments of temperature, rate of flow, etc. When the mixture of oil and sludge-forming reagent supplied to the drum 8 or 8' is too viscous to flow by gravity from the mixing vessel 1 or 1' to the perforated distributing manifold 6 or 6' and thence to the surface of the drum, a pump may be installed in series with valved-controlled pipe 5 or 5' to deliver the oil-reagent mixture at the proper rate of flow, such pump being of the type customarily employed in handling viscous, corrosive materials.

I claim:

1. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with a sludge-forming reagent, supplying said mixture in the form of a film to an inclined surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sludge-forming reagent with the oil but insufficient to deleteriously affect the oil, depositing and coking the sludge upon said heated surface, and separately removing said coked sludge and the treated oil from said surface.

2. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with a sludge-forming reagent, supplying said mixture in the form of a film to a rotating surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sludge-forming reagent with the oil but insufficient to deleteriously affect the oil, depositing and coking the sludge upon said heated rotating surface, and separately removing said coked sludge and the treated oil from said surface.

3. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with a sludge-forming reagent, supplying said mixture in the form of a film to a rotating surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sludge-forming reagent with the oil but insufficient to deleteriously affect the oil, controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of the sludge upon said surface, and separately removing said coked sludge and the treated oil from said surface.

4. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with a sludge-forming reagent, supplying said mixture in the form of a film to a rotating cylindrical surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sludge-forming reagent with the oil but insufficient to deleteriously affect the oil, controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of substantially all of the sludge upon said surface, draining the treated oil substantially free of sludge from said surface, and separately removing said coked sludge from said surface.

5. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with sulfuric acid, supplying said mixture in the form of a film to an inclined surface heated to a temperature sufficient to coke the sludge resulting from the reaction of sulfuric acid with the oil but insufficient to deleteriously affect the oil, depositing and coking the sludge upon said heated

surface, and separately removing said coked sludge and the treated oil from said surface.

6. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sulfuric acid with the oil but insufficient to deleteriously affect the oil, depositing and coking the sludge upon said heated rotating surface, and separately removing said coked sludge and the treated oil from said surface.

7. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sulfuric acid with the oil but insufficient to deleteriously affect the oil, controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of the sludge upon said surface, and separately removing said coked sludge and the treated oil from said surface.

8. The method of refining hydrocarbon oil, which comprises intimately mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating cylindrical surface heated to a temperature sufficient to coke the sludge resulting from the reaction of the sulfuric acid with the oil but insufficient to deleteriously affect the oil, controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of substantially all of the sludge upon said surface, draining the treated oil substantially free of sludge from said surface, and separately removing said coked sludge from said surface.

9. The method of refining hydrocarbon oil, which comprises mixing said oil with sulfuric acid, supplying said mixture in the form of a film to an inclined surface heated to a temperature between 250° F. and 600° F., depositing and coking the resulting acid sludge upon said heated surface, and separately removing said coked acid sludge and the treated oil from said surface.

10. The method of refining hydrocarbon oil, which comprises mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating surface heated to a temperature between 250° F. and 600° F., depositing and coking the resulting acid sludge upon said heated surface, and separately removing said coked acid sludge and the treated oil from said surface.

11. The method of refining hydrocarbon oil, which comprises mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating surface heated to a temperature between 250° F. and 600° F., controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of the resulting acid sludge upon said heated surface, and separately removing said coked acid sludge and the treated oil from said surface.

12. The method of refining hydrocarbon oil, which comprises mixing said oil with sulfuric acid, supplying said mixture in the form of a film to a rotating cylindrical surface heated to a temperature between 250° F. and 600° F., controlling the rate of supply of said mixture and the rate of rotation of said surface to cause deposition and coking of substantially all of the acid sludge upon said heated surface, draining the treated oil substantially free of sludge from said surface, and separately removing said coked sludge from said surface.

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