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REFINING LIQUID HYDROCARBONS

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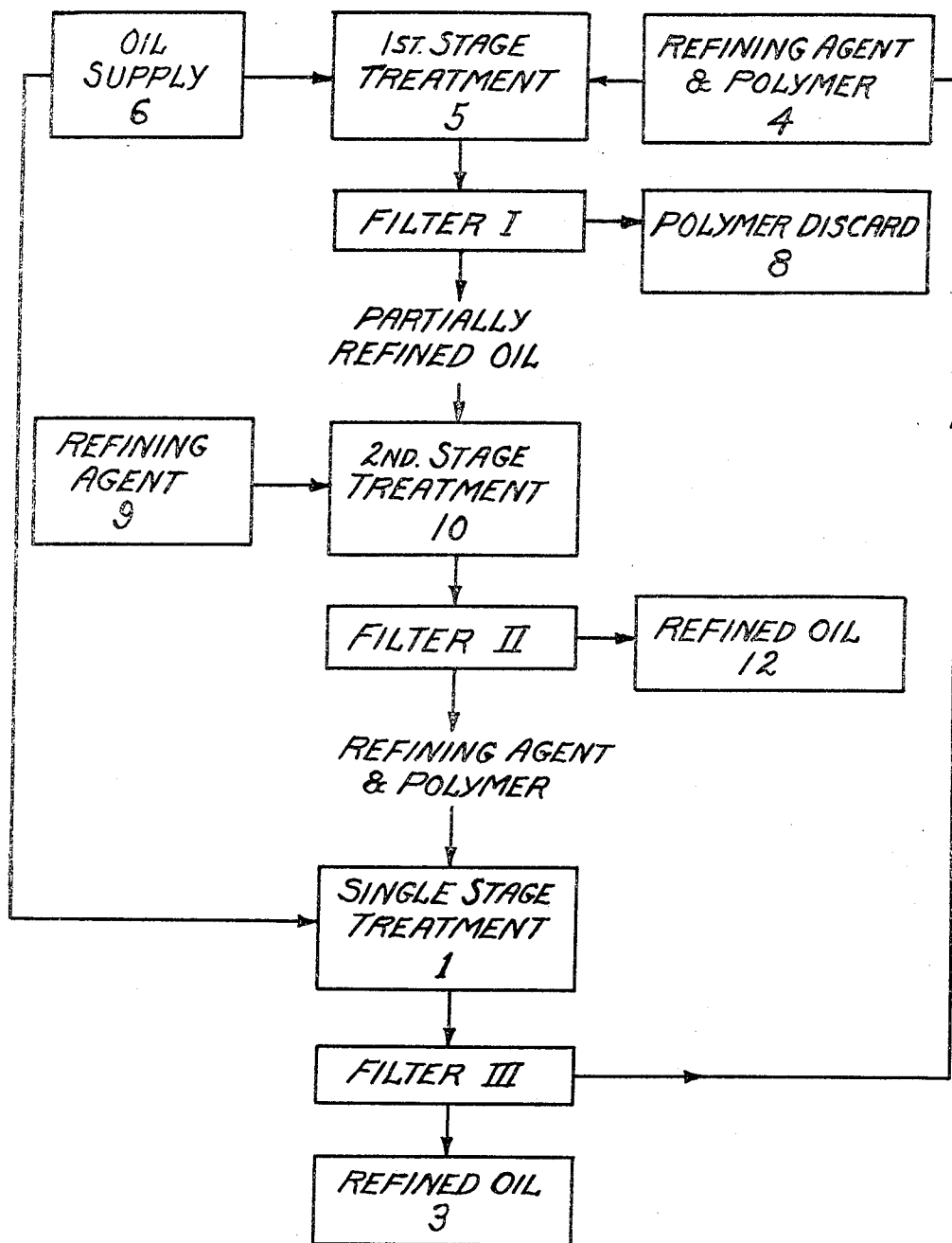


Fig. 1.

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REFINING LIQUID HYDROCARBONS

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3 Claims. (Cl. 196—23)

This invention relates to the refining of hydrocarbon materials, and more particularly to refining by metallic agents.

Various metals, including the alkali metals, have been used or proposed as refining agents for hydrocarbon materials. During the treatment of hydrocarbons by sodium for example, some polymerization of certain constituents takes place. Some of these polymers may be soluble in the hydrocarbon and cause no difficulty, other polymers however, separate out as more or less sticky, oily masses which contaminate the solid treating agent, such as sodium. For effective treatment with such metals as sodium it is preferable to use considerable excesses of metal at the end of the refining period, this excess of sodium can be removed from the oil mixed with the solid polymer, but the recovery of the metal from the contaminating polymer is difficult.

An object of this invention is to provide a method for refining hydrocarbons by treatment with a metallic substance whereby the treating agent may be economically and substantially completely utilized. A further object is to provide such a process which is applicable to the refining of hydrocarbons having relatively high viscosities as well as the lighter hydrocarbons. Other objects will be hereinafter apparent.

These objects are accomplished by a novel combination of a two-stage refining process and a single-stage refining process. By "two-stage refining process", I mean a process for refining hydrocarbon wherein the hydrocarbon is first treated with a relatively small amount of refining agent whereby the amount of agent added is substantially entirely consumed and the hydrocarbon is only partially refined, ("first stage treatment") then this partially refined hydrocarbon, after removal of insoluble treatment by-product, is treated with an excess of refining agent ("second stage") until the desired degree of refinement is obtained. By "single stage refining process", I mean a single treatment of hydrocarbon material with excess of refining agent until the desired refinement is obtained. The novel combination of such processes according to my invention comprises using the mixture of unreacted refining agent and insoluble treatment by-product resulting from the second stage of a two-stage process as treating agent in a single-stage process and then using the insoluble material recovered from the single-stage process, which material comprises treatment by-products mixed with relatively small amounts of refining

agent, as treating agent in the first stage of a succeeding two-stage process.

The drawing is a diagrammatic representation of one form of my invention, showing the flow of materials through the various steps of the process.

One method of carrying out my invention will be described with reference to the use of alkali metal as refining agent. The hydrocarbon to be refined is treated by agitating it preferably at a temperature of from 175–275° C., with a sludge consisting of alkali metal and treatment by-products from a prior operation. The amount of sludge used is so adjusted that by this treatment substantially all the metal is reacted and the hydrocarbon is only partially refined. The sludge is then removed and the hydrocarbon is subjected to the second stage treatment, which consists in treating it with a great excess of alkali metal. After the desired degree of refinement has been obtained, the refined hydrocarbon is filtered off. The remaining sludge, containing a considerable excess of refining agent, is used as treating agent in a single-stage treatment of a fresh batch of hydrocarbon, which treatment consists in agitating the sludge with the hydrocarbon, preferably at 175–275° C., until the desired degree of refinement is obtained. The ratio of hydrocarbon to sludge in this single stage treatment must be such that there is an excess of alkali metal over that which will react in producing the desired refinement. The sludge recovered by filtration from the single stage treatment contains a relatively low proportion of unreacted metal and is used as refining agent in the first stage of the two-stage treatment of fresh hydrocarbon previously described.

The above described process may be more fully understood by reference to the drawing, which shows, by means of arrows, flow of materials through the various steps. The mixture of refined oil, polymer and unreacted treating agent from the single stage treatment (1) is passed to filter III where the refined oil is separated and passed to the refined oil storage (3). The polymer, containing unreacted refining agent (4), is sent to the first-stage treatment (5), where it is mixed with oil from the oil supply (6). After the first-stage treatment is completed, the mixture is filtered in filter I where the partially refined oil is separated from the insoluble polymer (8), which contains substantially no refining agent and is discarded. The partially refined oil is treated with excess refining agent, drawn from the refining agent supply (9), in the second-stage

treatment (10). The mixture passes from this operation to filter II and the refined oil there separated is transmitted to refined oil storage (12). The mixture of polymer and unreacted refining agent separated in filter II is sent to the single-stage treatment (1), where it is used to treat fresh oil drawn from the oil supply (6); and the cycle is then repeated.

The optimum proportion of refining agent to use in the second-stage treatment and the amount of hydrocarbon which can be efficiently treated in the single-stage treatment will be found to vary somewhat according to the nature of the hydrocarbon being treated and may be determined by trial runs. These quantities also depend on the desired degree of refinement which must be likewise determined. The temperature to be maintained in the various treating operations should be above the melting point of the refining agent. For treating hydrocarbons having relatively high viscosities, for instance lubricating oils, I prefer to maintain the treatment temperature at 175°-275° C.

In some cases the amount of by-product formed and the viscosity of the hydrocarbon are such that the refining agent is rapidly fouled and is consequently not completely consumed in the first stage of a two-stage treatment. This difficulty is avoided by sub-dividing the first stage into a plurality of treating operations. In each operation a fraction of the amount of refining agent sludge desired in the first stage is added. After each such fraction has been substantially entirely consumed, insoluble by-product is removed and treatment is continued with the next fraction of refining agent. In this way substantially all of the refining agent is consumed in the first stage treatment.

Oils of relatively high viscosity are sometimes difficult to refine because the by-product and the oil tend to form a gelatinous mass which prevents complete utilization of the refining agent and makes it difficult to recover the refined oil. In such cases, I may dilute the oil with a suitable solvent, for instance, a lighter hydrocarbon such as kerosene. Such dilution may be made at any point in the refining process, but I prefer to dilute the oil prior to its treatment. The diluent may be removed from the refined oil by distillation.

In the following example the term "barrel" is used to designate a unit of 42 gallons.

Example

An acid refined, asphalt base oil was further refined by the process illustrated diagrammatically by the drawing. A quantity of insoluble residue, obtained by filtration of the mixture from a previous single-stage treatment of the same oil, containing 18.7% of metallic sodium, was mixed with untreated oil in the proportion of 82.25 lbs. of residue per barrel of oil, corresponding to about 7 lbs. of metallic sodium per barrel of oil and the mixture was agitated at 215°-225° C. until tests showed that substantially no metallic sodium remained. This required about 12 hours. The mixture was then filtered and the residue, consisting of insoluble polymer and some oil, was discarded. The filtrate, consisting of partially refined oil, was agitated at 215°-225° C., for 7½ hours with 24.5 lbs. of metallic sodium per barrel of oil. The insoluble polymer and unreacted sodium were then filtered off from the refined oil. The characteristics of the oil before and after treating by the above two-

stage treatment are shown in the following table. The characteristics were determined by the standard methods of the American Society for Testing Materials.

Characteristics	Before treatment	After treatment
Neutralization No.	0.00	0.00
Color N.P.A. No.	2	1
Color Saybolt.		+18 ("Prime white")
Sligh oxidation No.	14.1	1.7
Steam emulsion No.	200	15
Viscosity at 100° F.	150 sec.	146 sec.
Flash point.	325° F.	330° F.
Fire point.	365° F.	370° F.

The residue from the above two-stage treatment contained 31% of metallic sodium. It was mixed with a fresh quantity of oil in the proportion of 79 lbs. of residue per barrel of oil, corresponding to about 24.5 lbs. of metallic sodium per barrel of oil. The mixture was agitated at 215°-225° C. for 12 hours and then filtered. The refined oil thus obtained had the following characteristics:

Neutralization No.	0.00
Color N. P. A. No.	1
Color Saybolt.	+10
Sligh oxidation No.	5.5
Steam emulsion No.	59
Viscosity at 100° F.	154 sec.
Flash point.	325° F.
Fire point.	370° F.

The residue from the filtration, contained 13.5% of metallic sodium and was used as treating agent in the first stage of a succeeding two-stage treatment.

The hydrocarbon to be refined may be previously treated by any known process; for instance, treatment with sulfuric acid, fuller's earth, aluminum chloride, or other known refining agent. Such pre-treatment, preceding refining with metallic refining agent is often desirable because it decreases the amount of metal consumed.

My invention is not restricted to the use of alkali metal as refining agent, but may be applied to the use of any metallic refining agent which undergoes chemical reaction with the hydrocarbon during the treating process and which causes the formation of an insoluble by-product. The invention is also not restricted to any particular means of contacting the hydrocarbon with the refining agent.

My invention may be used to refine any hydrocarbon material in liquid state, including solutions of hydrocarbons. It is especially adapted for the treatment of petroleum hydrocarbons, regardless of their source or previous treatment. It may be used for the lighter grades of such hydrocarbons, such as gasoline and kerosene and is particularly adapted for refining hydrocarbons of relatively high viscosity, such as lubricating oils.

The chief advantage of my invention is that by it a hydrocarbon material may be refined to practically any desired degree with complete utilization, and therefore without waste, of metallic refining agent. A further advantage is that it affords a means for using the residues from the alkali metal treatment of hydrocarbons when such residues contain free alkali metal. A still further advantage is that the process is equally applicable to the lighter hydrocarbons and those of relatively high viscosity.

In the specification and claims, the terms "oil" and "hydrocarbon oil" mean a liquid hydrocarbon material having an S. U. V. viscosity of 50 seconds or more at 100° F. For the sake of brevity, the term, "reactive metal" is used in the claims to mean a metallic refining agent capable of chemically reacting with the constituents and impurities of the hydrocarbon or hydrocarbon oil treated therewith. Likewise, the term "polymer" is used in the claims to designate the insoluble treatment by-products formed during the treatment of a liquid hydrocarbon material with "reactive metal", as defined above.

I claim:

1. A cyclic process for refining liquid hydrocarbons comprising treating said liquid with alkali metal-polymer mixture at a temperature above the melting point of the alkali metal until substantially complete consumption of said metal is obtained, removing polymer, completing the refining of said liquid by treating with a fresh supply of the alkali metal in large excess, separating refined liquid, utilizing the recovered metal-polymer mixture for complete refinement of an amount of untreated liquid hydrocarbon insufficient to use up the molten alkali metal in said mixture, separating refined liquid, and utilizing the residual metal-polymer mixture and a new batch of liquid to renew the cycle.

2. A process for refining a liquid hydrocarbon comprising agitating a mixture of polymer and alkali metal recovered from a previous refining operation with said hydrocarbon at 100-275° C. until the metal is substantially entirely consumed,

separating partially refined hydrocarbon from polymer, agitating said partially refined hydrocarbon with a large excess of alkali metal at 100-275° C. until the desired degree of refinement is obtained, separating a mixture of polymer and unreacted metal from refined hydrocarbon, agitating said separated mixture at 100-275° C. with an amount of unrefined hydrocarbon insufficient to use up said unreacted metal until the desired degree of refinement is obtained, separating a mixture of polymer and unreacted metal from refined hydrocarbon and using the last said mixture to refine partially a fresh quantity of the hydrocarbon.

3. A process for refining a liquid hydrocarbon comprising agitating a mixture of polymer and sodium recovered from a previous refining operation with said hydrocarbon at 100-275° C. until the sodium is substantially entirely consumed, filtering to remove partially refined hydrocarbon from polymer, agitating said partially refined hydrocarbon with a large excess of sodium at 100-275° C. until the desired degree of refinement is obtained, filtering to remove a mixture of polymer and unreacted metal from refined hydrocarbon, agitating said separated mixture at 100-275° C. with an amount of unrefined hydrocarbon insufficient to use up said unreacted metal until the desired degree of refinement is obtained, filtering to remove a mixture of polymer and sodium from refined hydrocarbon and using the last said mixture to refine partially a fresh quantity of the hydrocarbon.

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5	80
10	85
15	90
20	95
25	100
30	105
35	110
40	115
45	120
50	125
55	130
60	135
65	140
70	145
75	150