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## PROCESS FOR REFINING HYDROCARBON OILS

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1

This invention relates to the art of treating hydrocarbon oils. It pertains more particularly to a process for removing undesirable substances such as ash-forming constituents and/or asphaltic substances from hydrocarbon oils, especially oils of the character of mineral lubricating oils and residual hydrocarbon oils for use as fuel for, e. g., gas turbine installations.

The use of residual hydrocarbon oils, either alone or mixed with, for example, oil distillates, as fuel for, e. g. gas turbine installations, is attractive for economical reasons. The ash-forming constituents, however, and to a smaller degree also the asphaltic substances, generally occurring in residual hydrocarbon oils, constitute a drawback to the use of the latter as fuel oil for this purpose. The ash-forming constituents which, it will be understood, are inorganic-containing substances and form non-volatile mineral or inorganic compounds upon combustion, have a fouling effect on the installations in which said oils are used. As a result, the installation soon begins to operate less smoothly and too soon for economical reasons the operation must be stopped for a thorough cleaning of the installation.

The asphaltic substances have the drawback in such fuel oil that they greatly increase the viscosity of the oil, so that in general it is necessary to dilute the oil with a considerable proportion of less viscous and more expensive distillate materials.

It has already been proposed to refine oils, particularly mineral lubricating oils, containing asphaltic substances with certain combinations of extraction agents which bring about the removal by extraction of the asphaltic substances, for example, with the combination propane-phenol (and/or cresol), or with the aid of a combination such as antimony trichloride-ethyl ether, or even with a solvent extraction proportion of liquefied antimony trichloride. Application of solvent extraction for the removal of asphaltic substances from residual oils in the production of cheap fuels is too expensive to be considered. Furthermore, even the application of solvent extraction with liquefied antimony trichloride to the refining of more valuable lubricating oils is not entirely satisfactory, particularly from the standpoint of economy.

It is a principal object, therefore, of this invention to provide an improved process for treating heavier hydrocarbon oils. A further object is to provide a process wherein asphaltic substances are more economically removed from hydrocarbon oils. Another object is to provide a

2

process for readily, economically and effectively removing ash-forming constituents and/or asphaltic substances from heavier hydrocarbon oils, such as residual hydrocarbon oils. Still another object is to provide an improved process for the removal of asphaltic substances from mineral lubricating oils. These objects will be more clearly understood and other objects will be evident from the detailed description of the invention.

Now, in accordance with the present invention, it has been found that the above and other objects may be realized by a process wherein a heavier hydrocarbon oil which contains undesirable impurities such as ash-forming constituents and/or asphaltic substances is treated with a minor but effective precipitating and/or coagulating amount of a precipitating and/or coagulating agent for said impurities followed by separation of the resulting precipitated or coagulated matter together with said agent. In some cases, this treament may be combined with other subsequent treatments to provide advantageous combination treatments or processes wherein the above described treatment is in the nature of a pretreatment.

Generally described, the present invention provides an improved process for refining hydrocarbon oils, particularly residual hydrocarbon oils which contain ash-forming constituents and asphaltic substances and hydrocarbon lubricating oils which contain asphaltic substances, which process comprises treating the impurity-containing oil with an added, small amount of one or more of an agent from the halides, oxyhalides and sulfohalides of antimony, arsenic and phosphorus, which agent does not react with the hydrocarbon oil under the conditions of the treatment, thereby precipitating the ash-forming constituents and/or the asphaltic substances, and separating the precipitated impurities from the hydrocarbon oil. With the application of this treatment to a hydrocarbon lubricating oil fraction, the separated oil fraction may be advantageously further treated as by a solvent extraction process with a selective solvent such as a phenol, furfural, liquid sulfur dioxide, liquefied antimony trichloride, a sulfolane, etc. In that case, the combination of the first or pretreatment operation with the subsequent refining treatment as by solvent extraction materially decreases the amount of selective solvent required in the solvent extraction to an extent that there are realized economies in the overall process over the required solvent extraction when that is used alone without the advantages of the described pretreatment. Thus, when

the pretreatment and subsequent extraction are effected by the same agent, for example antimony trichloride, a substantially smaller amount of the antimony trichloride is required in total than when the pretreatment is dispensed with and sufficient antimony trichloride is utilized alone in the extraction operation to produce an oil raffinate of similar quality.

In some applications of the present invention such as to residual hydrocarbon oils, such a small quantity of the treating agent may be used as will suffice to practically completely precipitate the ash-forming constituents, but to leave a part of the asphaltic substances dissolved in the oil.

Examples of substances which may be used in accordance with the invention as the treating agent are antimony trichloride, arsenic trichloride, arsenic tribromide, phosphorus trichloride, phosphorus sulfochloride, antimony pentachloride, antimony oxychloride, etc.

The quantity by weight in which the treating agents of the invention are added to the hydrocarbon oil depends on the quantities of ash-forming constituents and asphaltic substances occurring in the oil to be purified. In general, amounts of not more than about 10% by weight of the oil to be thus treated, and in many cases not more than 5% by weight of the oil, effect the required precipitation of the impurities and refinement of the oil.

The precipitation and/or coagulation treatment is not confined to any particular temperature or narrow temperature range. Normal or elevated temperatures may be applied. When applying normal or slightly elevated temperatures the precipitated ash-forming constituents and/or asphaltic substances generally do not settle out readily in the case of relatively viscous oils but may be easily separated from the oil by centrifugation. If, on the other hand, the precipitation is effected at a temperature of from about 150° C. to 250° C., the precipitates obtained will settle fairly quickly and the oil can be easily separated therefrom by decantation.

After removal of the precipitated ash-forming constituents and asphaltic substances the treating agent used for this purpose may be recovered from the oil by distillation or by shaking the oil with a solvent for the agent, which solvent is at least partially immiscible with the oil. The separated solvent solution of the agent may then be separated by distillation and any of the solvent dissolved in the oil may be separated therefrom by distillation.

When the halides, oxyhalides and sulfohalides of antimony, arsenic and phosphorus are entrained to any considerable extent by the precipitate separating from the oil, it is in many cases profitable to recover these agents also from the precipitate. This may, for example, be effected by distillation under reduced pressure, or the precipitate may be treated with an inert diluent, such as naphtha and/or with a solvent for the agent such as a concentrated aqueous solution of hydrogen chloride, etc.

In the event the foregoing described treatment to precipitate impurities is applied to a lubricating oil fraction such as a hydrocarbon distillate, the thus pretreated oil may in some cases be subjected to a solvent extraction treatment with a solvent amount of the same agent, for example, when the agent is antimony chloride. In that event the agent remaining in the oil after the first or pretreatment need not be recovered therefrom prior to the solvent extraction. Even when the precipitating agent and the selective solvent are not the same, it often is not necessary to remove the precipitating agent remaining in the oil before effecting the solvent extraction unless the solvent is reactive with said agent, which, in general, is not so. In some cases where the agent and solvent are different the small amount of agent dissolved in the oil enhances the selectivity of the solvent toward the various types of hydrocarbons present in the oil.

After the extraction proper has been carried out, both the raffinate phase and the extract phase are liberated of the added substance (solvent) or substances (solvent and agent). It will generally be deemed desirable to recover the solvent and agent separately for the treatment of a fresh quantity of oil. The most suitable method of procedure will depend on the particular circumstances for each given case; more particularly on the boiling points of the components and the temperature concentration relationships of the various systems to be considered in this respect.

The following examples representing the practice of the present invention as applied to the treatment of exemplary materials illustrate the invention but are not to be construed as limitative thereof:

*Example I*

To a Colon residue, i. e. a residue from Venezuelan oil, there was added 3% by weight of $SbCl_3$ at 200° C. and the mass was kept at this temperature for half an hour. The oil, forming the upper layer, was then decanted from the precipitate which had formed and settled. The $SbCl_3$ was recovered from the oil by first diluting the latter with benzene and then shaking it out with a hydrochloric acid solution. The two liquid layers thus formed were separated and the benzene was distilled off from the oil layer. As a result of the treatment the ash-content of the Colon residue was lowered from a value of 0.06% by weight to a value less than 0.01% by weight; the asphaltene content was lowered from 8.8% by weight to a value of only 0.5% by weight.

Practically the same results were obtained by treating another sample of the same residue with 3% by weight of $AsBr_3$ instead of an equal quantity of $SbCl_3$, the other conditions, operations, etc. being the same.

*Example II*

A Venezuelan oil residue obtained by distilling off from a Venezuelan crude oil the constituents boiling above about 380° C. (atmospheric pressure) and which residue had an asphaltene content of 8.8% by weight, was thoroughly mixed at 200° C. with 3% by weight of antimony trichloride and then was allowed to stand for half an hour. The oil was separated from the sediment obtained by decantation. It still contained 0.5% by weight of asphaltenes and was subsequently extracted in countercurrent with 40% by volume of liquefied antimony trichloride at 80° C. in an apparatus provided with three mixing- and settling-tanks. The raffinate phase, after being freed from antimony trichloride, consisted of an oil with a viscosity $E_{50}=17.4$, a viscosity index of 97 and a Conradson-carbon figure of 0.75.

Without applying a pretreatment as described above, a similar result with a countercurrent extraction in the same apparatus and under the same conditions was obtained only when the ex-

traction had been effected with about 75% by volume of antimony trichloride.

Thus, the combination process represented an economy of 35 volumes of $SbCl_3$ extractive solvent out of 75 volumes, for a pretreatment outlay of only three volumes of $SbCl_3$.

Thus, it is seen that the present invention provides an improved process for the removal of ash-forming constituents and/or asphaltic substances from hydrocarbon oils. The invention is of particular utility in refining residual hydrocarbon oils so that they may be used advantageously, alone or in mixtures with a content of at least 50% by weight of such residual oils, the rest being made up of, for instance, mineral oil distillates, synthetically prepared ash-free types of oil, benzene, etc., as fuel for operating gas turbine installations. Furthermore, the embodiment of the invention wherein a pretreatment as described herein is combined with a subsequent solvent extraction operation has utility as a process of greater economy for the refining and production of lubricating oils.

I claim as my invention:

1. In a process for the refinement of mineral lubricating oils which contain impurities of the character of asphaltic substances, wherein the mineral oils are subjected to solvent extraction with a selective solvent for various hydrocarbons present therein, the improvement which comprises preceding said solvent extraction by treating said mineral oil containing the asphaltic substances with a minor but asphalt-precipitating amount up to about 10% by weight of antimony trichloride as sole active precipitating agent under conditions to precipitate at least a substantial portion of said impurities, and separating the resulting precipitated impurities from the oil prior to the solvent extraction operation.

2. In a process for the refinement of mineral lubricating oils which contain impurities of the character of asphaltic substances, wherein the mineral oils are subjected to solvent extraction with liquefied antimony trichloride as a selective solvent for various hydrocarbons present therein, the improvement which comprises preceding said solvent extraction by treating said mineral oil containing the asphaltic substances with a minor but asphalt-precipitating amount up to about 10% by weight of antimony trichloride as sole active precipitating agent at a temperature of from about 150° C. to about 250° C., thereby precipitating at least a substantial portion of said impurities, and separating the resulting precipitated impurities from the oil prior to the solvent extraction operation.

3. In a process for the refinement of mineral oils which contain asphaltic substances, wherein the mineral oils are subjected to solvent extraction with a selective solvent for various hydrocarbons present therein, the improvement which comprises preceding said solvent extraction by treating said mineral oil containing the asphaltic substances with a minor but asphalt precipitating amount not more than about 10% by weight of a halide agent selected from the group consisting of the trihalides of antimony, arsenic and phosphorus and mixtures thereof, as the sole active precipitating agent, under conditions to precipitate at least a substantial portion of said asphalt substances, and separating the resulting precipitated asphaltic substances from the oil prior to the solvent extraction operation.

4. A process for removing ash-forming impurities from residual hydrocarbon fuel oils, which process comprises treating said impurity containing fuel oils with a minor but impurity-precipitating amount not more than about 10% by weight of a halide agent selected from the group consisting of the trihalides of antimony, arsenic and phosphorus and mixtures thereof, as the active impurity-precipitating agent, under conditions of temperature, time and proportions to precipitate a substantial portion of said ash-forming constituents, and separating the resulting precipitated impurities from an improved fuel oil.

5. A process for removing ash-forming impurities from residual hydrocarbon fuel oils containing also asphaltic substances, which process comprises treating said impurity-containing fuel oils with a minor but impurity-precipitating amount not more than about 10% by weight of a halide agent selected from the group consisting of the trihalides of antimony, arsenic and phosphorus and mixtures thereof, as the active impurity-precipitating agent, at a temperature up to about 250° C., and with proportions selected to selectively precipitate substantially completely said ash-forming impurities while leaving a substantial portion of the asphaltic substances dissolved in said oil, and separating the resulting precipitated impurities from an improved fuel oil.

6. A process for removing ash-forming impurities from residual hydrocarbon fuel oils containing also asphaltic substances, which process comprises treating said impurity-containing fuel oils with a minor but impurity-precipitating amount not more than about 10% by weight of antimony trichloride, as the active impurity-precipitating agent, at a temperature up to about 250° C., and with proportions selected to selectively precipitate substantially completely said ash-forming impurities while leaving a substantial portion of the asphaltic substances dissolved in said oil, and separating the resulting precipitated impurities from an improved fuel oil.

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