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UNITED STATES PATENT OFFICE

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PROCESS OF REFINING HYDROCARBON OILS

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This invention relates to a process for the separation from hydrocarbon oils of a component or components thereof. The process may serve to separate from a hydrocarbon oil or mixture a valuable component thereof which is desired in a pure state or it may serve to separate from the oil a deleterious ingredient or impurity or it may serve for the separation of both types of components or components which are objectionable in the oil but valuable when separated from it.

The commercial application of the process contemplated at present is the purification of hydrocarbon mixtures of the motor fuel type and particularly those prepared from petroleum oils by cracking distillation processes and containing objectionable impurities such as sulfur and diolefines, and the invention will be illustrated hereinafter with reference to this application of the process, it being understood however that the invention is not limited to the treatment of any particular hydrocarbon oil or to the purification thereof or to the removal of any particular ingredient or ingredients thereof excepting as may be required in the appended claims.

The process of my invention is based upon the chemical precipitation of the ingredient of the oil to be removed therefrom and consists generally in treating the oil with the precipitating agent for the ingredient in the presence of a mutual solvent or reaction medium.

As stated, the process is applicable generally to hydrocarbon oils and under this expression I mean to include hydrocarbon liquids such as crude petroleum and products obtained therefrom such as distillates and products resulting from cracking operations, products of the destructive distillation of coal, shale, lignite and the like such as crude benzol, natural gas, gasolene, etc.

For the purpose of illustration let it be assumed that the hydrocarbon oil to be treated is a gasolene or motor spirit such as may be obtained by the cracking of a crude petroleum oil and that it contains sulfur, unsaturated compounds of the olefine series, acetylene hydrocarbons and diolefines. Such an oil has at least three objectionable features, to wit: (1) objectionable odor attributed to its sulfur content and perhaps also to its acetylene hydrocarbon content; (2) corrosive action when used as a motor fuel attributed to its sulfur content; and (3) gumming action usually attributed to the diolefine hydrocarbon content. The olefine hydrocarbons are now regarded as valuable components of the oil in its use as a motor fuel and their removal or destruction in the refining of the oil is undesirable. My invention therefore relates more particularly to the refining or purification of hydrocarbon oils by the removal therefrom of sulfur if present, acetylene hydrocarbons if present in objectionable quantity, and diolefine hydrocarbons and resinous or resin-forming bodies which tend to produce the gumming action referred to without injury to the remaining components of the oil, and particularly the olefine hydrocarbons.

In processes heretofore employed for the removal of sulfur from hydrocarbon oils, for instance the well known process of washing the oil with a water solution of a lead compound, the complete removal of sulfur apparently has been impossible or impracticable, and a substantial and objectionable residue of sulfur is found in oils so refined. Processes have also been devised for the removal of diolefines, for instance, by treatment with sulfuric acid, but this process is objectionable for a number of reasons, among which may be mentioned the incident removal from the oil of valuable olefine hydrocarbons.

By the process of my invention the impurities may be quickly and easily and completely removed without injury to the purified oil.

As stated above, the invention consists generally in treating an oil with a precipitant for an impurity or component to be separated in the presence of a mutual solvent or reaction medium. Obviously the invention may have numerous applications depending upon the impurity or component to be separated, the nature of the oil under treatment and the selection of precipitating agent and solvent. A suitable solvent capable of use with a variety of precipitants

is alcohol, either ethyl or methyl alcohol or mixtures thereof or denatured alcohol such as a mixture of ethyl alcohol and acetone.

The invention is amply illustrated by the following description of the treatment of a hydrocarbon oil of the motor fuel type referred to.

For the removal of sulfur the oil is mixed in any suitable manner, for instance, by agitation, with an alcoholic solution of a soluble lead compound, for instance basic lead acetate, lead nitrate, or sodium plumbite, preferably the latter, in quantity chemically equivalent to the sulfur content of the oil. The mixing may be carried out at atmospheric or other suitable temperature. The reaction between the lead and the sulfur content of the oil takes place quickly and completely with the formation of a precipitate which is removed in any suitable way as by filtration or sedimentation and decantation. The treatment described has been found to remove the sulfur content of the oil very completely so that not even a trace can be detected by ordinary methods. The foregoing step for the removal of the last traces of sulfur from the oil may advantageously be preceded by a treatment of the oil for the removal of the bulk of its sulfur content, for instance, by agitating the oil with a water solution of a lead compound. If the oil contains a relatively large amount of sulfur a portion of which is removable by the old process a considerable saving in the use of the alcoholic solution for the removal of the last traces of sulfur results.

The oil from which sulfur has been removed may be treated next for the removal of acetylene hydrocarbons. This treatment consists simply in mixing the oil at ordinary atmospheric temperature with an alcoholic solution of a copper compound in quantity just equivalent to the precipitatable acetylene hydrocarbon content thereof and separating the resulting precipitate. A suitable copper containing solution for use in this step may be prepared by suspending a copper salt, such as the chlorid, nitrate, or acetate, in alcohol and saturating the mixture with ammonia.

The next step of the complete process for the purification of the oil under consideration is the treatment for the removal of diolefines. This step consists in mixing the oil at ordinary or other suitable temperature with an alcoholic solution of a mercury compound for instance mercuric chlorid, nitrate, or acetate, in quantity only sufficient to precipitate the diolefine hydrocarbon content of the oil. The resulting precipitate which contains the mercury and the diolefines is curdy and preferably is separated from the oil by decantation.

The next step in the process is for the removal of resinous materials. This is accomplished by treating the oil with an alcoholic solution of caustic soda, for instance by agitating the oil with an alcoholic caustic soda solution at atmospheric temperature, and then adding a relatively small amount of water, agitating, and decanting or otherwise separating the clarified oil. The clarified oil may then be washed with water to remove dissolved alcohol therefrom and the alcohol recovered by fractionation of the wash water and the purified oil is finally steam distilled.

The several precipitates formed may if desired be treated by methods known or obvious to a chemist for the recovery therefrom of the precipitating agents and the precipitated materials.

In the foregoing description I have referred to the use of the several precipitating agents or chemicals in quantity only sufficient to accomplish the desired precipitation. This is important not only from the standpoint of economy in the use of the reagents and further in that the contamination of the oil with excess of reagent which would make necessary a purifying step for its removal is avoided, but also, particularly in the step for the removal of diolefines, removal or destruction or undesired conversion of the olefine hydrocarbon content of the oil is avoided. For instance in the sulfur removing step if an excess of the lead precipitating agent is employed the excess or some of it will remain in the oil and necessitate a washing treatment for its removal. In the diolefine hydrocarbon removing step if an excess of the mercury precipitating agent is used some of the olefine hydrocarbons in the oil may be destroyed by oxidation or converted into undesirable resinous bodies which, as is stated above, are objectionable, due to their gumming action, and must be removed, this objectionable feature being in addition to the loss of valuable olefine hydrocarbons. This use of the precipitating agents in quantity only sufficient to accomplish the desired precipitation without contamination of the oil is made possible by the use in accordance with my invention of a mutual solvent or reaction medium for the oil and the precipitant because in the presence of such a reaction medium the reaction between the precipitating agent and the component of the oil to be precipitated proceeds to completion quickly without the use of an excess of reagent. The quantities of the reagents necessary in each step are readily determined by a laboratory titration on a sample of the oil under treatment to the precipitation end point in the known manner.

The procedure described in the foregoing specific example is preferred for several reasons, among which may be mentioned the fact that if the sulfur and acetylene hydro-

carbon content of the oil are not removed prior to the diolefine hydrocarbon precipitation they will combine with the mercury compound employed in this step, thus producing a composite precipitate from which the several precipitated components are not readily recoverable. The step by step method is systematic and thorough. However, it is to be understood that the invention is not limited in this respect. Within the scope of my invention several components of the oil may be precipitated simultaneously by a single precipitating agent or by the use of a mixture of the precipitating agents for the several components or the several components may be precipitated successively by the successive addition of the several precipitating agents without the separation of the individual precipitates formed.

It is further noted that the invention is not limited to the removal from a hydrocarbon oil of the particular components heretofore referred to excepting as may be required by the appended claims. The process of my invention may be applied for the removal of any single or any particular group of components, for instance, for the removal of sulfur or acetylene hydrocarbons or diolefines, or resinous matter, or any combination thereof or any other impurity or material in any hydrocarbon oil for the precipitation of which a suitable reagent and reaction medium may be found.

In the appended claims reference is made to the mutual solvent or reaction medium as a solvent for the precipitant which is soluble in the oil. The reference to the solubility of the solvent for the precipitant in the oil is intended to cover any condition of miscibility or of mutual solution as between the oil and the solvent for the precipitant.

I claim:

1. Process of purifying a hydrocarbon oil containing sulfur, diolefine hydrocarbons, acetylene hydrocarbons, olefine hydrocarbons and resinous material which comprises removing the bulk of the sulfur by treating the oil with an aqueous solution of a lead compound, removing the last traces of sulfur from the oil by mixing it with an alcoholic solution of a lead compound and separating the resulting precipitate, removing acetylene hydrocarbons from the oil by mixing it with an alcoholic solution of a copper compound and separating the resulting precipitate, removing diolefine hydrocarbons from the oil by mixing it with an alcoholic solution of a mercury compound and separating the resulting precipitate, and removing resinous material from the oil by treatment with an alcoholic solution of caustic soda and then washing with water.

2. Process of purifying hydrocarbon oils which comprises precipitating sulfur therefrom by treatment thereof with a lead compound in the presence of a solvent for said lead compound which is soluble in the oil, precipitating diolefine hydrocarbons by treatment with a mercury compound in quantity not substantially in excess of the quantity necessary to precipitate said diolefines in the presence of a solvent for said mercury compound which is soluble in the oil, and thereafter removing resinous material from the oil by treatment with an alcoholic caustic soda solution and washing with water.

3. Process of purifying a hydrocarbon oil containing sulfur, diolefine hydrocarbons, acetylene hydrocarbons, olefine hydrocarbons and resinous material which comprises treating the oil for the removal of sulfur compounds therefrom and thereafter removing acetylene hydrocarbons from the oil by mixing it with an alcoholic solution of a copper compound and separating the resulting precipitate, removing diolefine hydrocarbons from the oil by mixing it with an alcoholic solution of a mercury compound and separating the resulting precipitate, and removing resinous material from the oil by treatment with an alcoholic solution of caustic soda and then washing with water.

4. Process of purifying hydrocarbon oils which comprises treating the oil for the removal of the sulfur content thereof and thereafter precipitating diolefine hydrocarbons by treatment with a mercury compound in quantity not substantially in excess of the quantity necessary to precipitate said diolefines in the presence of a solvent for said mercury compound which is soluble in the oil, and thereafter removing resinous material from the oil by treatment with an alcoholic caustic soda solution and washing with water.

5. Process of purifying a hydrocarbon oil containing diolefine and acetylene hydrocarbons which comprises removing the acetylene hydrocarbons from the oil by mixing it with an alcoholic solution of a copper compound and separating the resulting precipitate, and removing the diolefine hydrocarbons from the oil by mixing it with an alcoholic solution of a mercury compound and separating the resulting precipitate.

6. In a process of purifying a hydrocarbon oil the step which comprises removing an impurity of the group consisting of sulfur, diolefine hydrocarbons and acetylene hydrocarbons by mixing the oil with an alcoholic solution of a mercury compound and separating the resulting precipitate.

7. In a process of purifying a hydrocarbon oil the step which comprises removing diolefine hydrocarbons by mixing the oil with an alcoholic solution of a mercury compound and separating the resulting precipitate.

In testimony whereof, I affix my signature.

ALEXANDER S. RAMAGE.

CERTIFICATE OF CORRECTION.

Patent No. 1,771,350. July 22, 1930.

ALEXANDER S. RAMAGE.

It is hereby certified that the name of the assignee in the above numbered patent was erroneously described and specified as "Gyro Process Corporation" whereas said name should have been described and specified as Gyro Process Company, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of March, A. D. 1934.

F. M. Hopkins

(Seal) Acting Commissioner of Patents.