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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbon compounds and mixtures thereof, including motor and heating plant fuels and lubricating oils, to improve them as to color, composition, properties and characteristics, and more particularly to their treatment for the purpose of removing objectionable impurities therefrom for rendering them more stable in composition and color, and, when the hydrocarbon compounds are lubricating oils, for also reducing the tendency of the oil to sludge or decompose under operating conditions such as in the crank case of an internal combustion engine. Among examples of the impurities which may be readily removed or rendered unobjectionable by this invention may be mentioned sulphur, whether in a combined or uncombined condition, gums and gum forming compounds, and unstable hydrocarbon constituents. Heretofore it has been common practice to partially remove some undesirable impurities, including sulphur compounds, from hydrocarbon compounds and mixtures thereof, including both motor and heating fuels and lubricating oils, some of which hydrocarbon compounds may be unsaturated, by various acidic treating agents such as the mineral acids. Sulphuric acid is the mineral acid or acidic treating agent most commonly used for this purpose, but anhydrous metallic halides, such as aluminum chloride, are acidic treating agents which have also been used for this purpose.

In the usual refining treatment of certain hydrocarbon mixtures, such, for example, as petroleum compounds and particularly the distillates from petroleum cracking stills, it has been found that the unsaturated hydrocarbons in those mixtures or distillates, that is, hydrocarbons containing less than the maximum amount of hydrogen which could be included in the combination, are, to a considerable extent, polymerized into undesirable hydrocarbon compounds, many of which are resinous in character, by the impurities removal agents heretofore employed. Such undesirable compounds when burned in an internal combustion engine are more likely to "knock" or detonate than are the unsaturated compounds before their polymerization.

Frequently these polymerized hydrocarbons have a higher boiling or vaporizing point than is desirable in an internal combustion engine fuel, and therefore are sometimes removed from the desulphurized or treated mixture and discarded, which decreases the yield of marketable fuel obtained from a given quantity of untreated hydrocarbon compounds. The polymerization of unsaturated compounds into compounds of higher molecular weight is frequently undesirable where the compounds are to be used in chemical reactions. For example, the unpolymerized and unsaturated compounds are usually chlorinated more easily than are saturated and polymerized compounds.

I have discovered that polymerization of the unsaturated compounds can be largely prevented or minimized, the impurities removal action greatly accelerated, and the percentage of impurities removed greatly increased, if the removal action is carried on in the presence of an accelerating or inhibiting agent or substance. According to my discovery, a more desirable product is obtained, and the impurities removal processes may be performed at higher temperatures not heretofore feasible or desirable. Various organic compounds have been found suitable as the accelerating or inhibiting agent, and may be used in the usual methods of removing impurities from hydrocarbon compounds.

The selection of the accelerating or inhibiting agent depends somewhat upon the exact nature of the impurities to be removed, the degrees of unsaturation of the hydrocarbon compounds from which the impurities are to be removed, the amount of impurities to be removed, and the conditions under which the removal is to be performed. In general, I have found that anhydrous treating agents yield better results than those in which water dilution occurs, and when sulphuric acid is used, I have found that in the presence of an inhibiting agent, a concentrated sulphuric acid as near as possible to a one hundred percent pure acid yields more satisfactory results than does commercial oil of vitriol acid, which is usually about ninety-five percent strength.

The amount of the inhibiting agent which it is desirable to use, while varying somewhat with the material to be treated, the impurities to be removed, and the character of the impurities removal agent, is in general less than the molal quantity of the impurities removal agent employed.

When the hydrocarbon compounds to be treated are viscous products, their treatment may be facilitated by first reducing their viscosity, either by heating the same first to reduce the viscosity or by mixing therewith the necessary amount of a thin liquid such as, for example, gasoline, which viscosity reducing addition agent, such as gasoline, can be removed readily by volatilization or other refinery practice after the

impurities removal treatment has been completed.

Among the various accelerating and inhibiting agents which may be satisfactorily employed, are the aldehydes including furfural and the aliphatic or aryl aldehydes. Outstanding examples of the aliphatic aldehydes which I have found to be very satisfactory in treating hydrocarbons in accordance with this invention are: acetaldehyde, acetaldol, paraldehyde, butyraldehyde, acrolein and crotolaldehyde.

Outstanding examples of the aryl aldehydes which are also satisfactory as the inhibiting agent in accordance with this invention are: citral, citronellal, amyl cinnamicaldehyde, anisicaldehyde, benzaldehyde, nitro-benzaldehyde, cinnamicaldehyde, phenylaceticaldehyde, piperonal, salicylicaldehyde, tolualdehyde, and vanillin.

The inhibiting agent may be added either to the impurities removal agent before the latter is added to the hydrocarbon mixtures, or to the hydrocarbon mixture before the impurities removal agent is added to the hydrocarbon mixture. I prefer to add the inhibiting agent to the hydrocarbon mixture first, and then add the impurities removal agent to this combined mixture, and the improved method of treatment may be of either the continuous or batch type.

After the hydrocarbon compounds or mixtures thereof have been treated with the impurities removal agent and the inhibiting agent, the complete mixture may be agitated continuously until the reaction is complete. The reaction I have found is usually completed within about ten minutes when the acid treatment is used for the removal of sulphur, and within approximately one half hour if a metallic halide is used as the removal agent. After the reaction is complete, the combined mixture is left quiescent, whereupon the residue separates out carrying the impurities and the treating agent, which then may be removed in any suitable manner such as by draining off the supernatant liquid, or by treatment with fuller's earth or other adsorbent material, or by washing with water. This treated material may then be subjected to any further neutralization or treatment as desired to finish it for the market and to remove any viscosity reducing agent. The residue may be then disposed of as usual in the industry, or treated for the recovery of any valuable components thereof.

Without the use of the inhibiting agent or material, the acidic impurities removal treatment often required several hours or days in order to get a high percentage of removal of the impurities. The use of the inhibiting agent also speeds up the reaction and makes the removal of impurities more complete, without undesirable polymerization or alteration of the hydrocarbons. I have found that by the use of the inhibiting agent, the action is more rapid at the same temperatures, and one may use higher temperatures during the removal reaction in order to speed up the reaction without materially increasing the polymerization of the unsaturated compounds, which polymerization or alteration always heretofore occurred to a very great extent whenever the impurities removal reaction was speeded up by the use of the higher temperatures.

Removal of impurities with such an inhibiting agent may be applied to hydrocarbon mixtures in any stage of refinement or in crude form, and produces a product which I have found will stand exposure to light more satisfactorily than products obtained by similar removal processes without the use of the inhibitor. The removal of sulphur, for example, when accomplished in the presence of the inhibitor, is more complete for a given amount of the sulphur removing agent than is possible without the use of an inhibitor, and the inhibitor may be used without any change in the apparatus used heretofore for sulphur removal. The amount of acidic treating agent can be increased to the desired point, impractical otherwise, in order to secure desired refining results. For example, in treating Pennsylvania lubricating oils, such quantities of 98% sulphuric acid as 30 pounds per barrel or more can be used successfully and to advantage without excessive loss of the lubricating material itself.

When motor fuels, such as gasolines, are treated in accordance with this invention, the resulting product is non-corrosive, lower in gum content, very much more stable as evidenced by the distillation test residues which are relatively light colored, and has better color and color stability. When heavier petroleum products such as lubricating oils are treated in accordance with this invention, the color, non-corrosiveness, tendency to "sludge" or decompose under operating conditions, particularly under the conditions existing in the crank cases of internal combustion engines, and the resistance to heat are improved in a similar manner. I have also discovered that lubricating oils intended for use in automotive engine lubrication can be given still greater color stability and resistance to sludging by the admixture with the oil of the desired, and preferably a relatively small, amount of quinhydrone. When the quinhydrone is used even in such small amounts as .001% by weight, the results have been found satisfactory and effective in some cases, but usually a larger percentage of the quinhydrone is preferred up to a percentage which is soluble in the oil.

In the foregoing description, reference has been made to sulphur as one of the impurities that may be removed or rendered unobjectionable in accordance with this invention, but it will be understood that the exact composition of the impurities which are found in petroleum hydrocarbons is not definitely known, but sulphur is one of the major impurities found in such petroleum products which can be removed or rendered unobjectionable by this invention. It is also believed that the removal of undesirable nitrogen compounds is facilitated by this invention.

I claim as my invention:

1. A lubricating oil of the type useful in lubricating internal combustion engines and having increased resistance to sludging in the crank case of such engines, greater color stability and greater resistance to decomposition under crank case conditions, which comprises a petroleum lubricating oil having mixed therewith a relatively small amount of quinhydrone.

2. The method of treating petroleum lubricating oils of the type intended for crank case lubrication of internal combustion engines to increase their color stability and resistance to decomposition and sludging, which comprises mixing with said lubricating oil a relatively small quantity of quinhydrone.

3. An improved lubricating composition of low tendency to sludge, comprising a petroleum lubricating oil of the type having a normal tendency to form objectionable sludge and change color in

the crank case of an internal combustion engine and containing as an addition agent a relatively small amount of quinhydrone.

4. An improved lubricating composition for crank cases of internal combustion engines and which in use is relatively stable as to color and has maximum resistance to heat and minimum corrosiveness, comprising a petroleum lubricating oil of the type known as crank case oil and having a normal tendency to form objectionable sludge, cause corrosion and change color in use, and a relatively small amount of quinhydrone as an addition agent.

5. An improved lubricating composition for crank cases of internal combustion engines and which in use is relatively stable as to color and has maximum resistance to heat and minimum corrosiveness, comprising a petroleum lubricating oil of the type known as crank case oil and having a normal tendency to form objectionable sludge, cause corrosion and change color in use, and quinhydrone as an addition agent in an amount which is soluble in the oil and above approximately .001% by weight.

6. The method of treating a petroleum lubricating oil of a viscosity suitable for use in the crank cases of internal combustion engines, to reduce its tendency to form sludge when used in the crank cases of said engines, to stabilize its color, and to reduce its corrosiveness, which comprises incorporating in said oil a relatively small amount of quinhydrone as an addition agent in an amount which is soluble in said oil and above approximately .001% by weight.

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