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METHOD FOR REFINING HYDROCARBONS

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My invention relates to the treating of hydrocarbon oil and more particularly relates to a process for treating hydrocarbon oils whereby undesirable unsaturated compounds are oxidized to gums and polymers and separated.

It is well known that hydrocarbons, particularly those which have been subjected to a cracking condition contain unsaturated hydrocarbons. Certain of these unsaturated hydrocarbons are desirable as they give desirable characteristics to the hydrocarbons. However, other portions of the unsaturated components are highly objectionable inasmuch as they have the tendency on standing for a period of time, particularly when exposed to light, to polymerize and form gummy and resinous masses. Unsaturates of this type are, for example, the diolefines and terpenes. Apparently oxygen is absorbed and the action progresses to the formation of gummy masses from the more unstable components.

Various attempts have been made to remove these undesirable unsaturates. The most common method which has long been in use is refining the hydrocarbon fraction with sulphuric acid. The primary disadvantage of the use of sulphuric acid is that it reacts indiscriminately upon substantially all of the hydrocarbons, and thus, while it may remove a portion of the undesirable unsaturates, it also removes the desirable unsaturates, such as the olefines, and the desirable aromatic compounds. Even after a sulphuric acid refining treatment, hydrocarbon fractions of the type of cracked distillates will still change color and deposit gummy substances if stored for a long period.

One of the objects of my invention is to treat a hydrocarbon fraction to remove the polymerizing and gum forming unsaturates while retaining the more stable unsaturates.

Another object of my invention is to refine a hydrocarbon fraction with a minimum amount of sulphuric acid and with minimum refining losses.

A further object of my invention is to produce an oil free from potential gum forming components but containing the stable unsaturates and aromatics.

In general, my process consists in dispersing within the hydrocarbon fraction to be treated an agent capable of being rendered effective as an oxidant, in combination with an inert extending agent. I then mix with the hydrocarbon a substance capable of converting said dispersed agent to an oxidizing medium. The oxidizing agent then reacts with the undesirable unsaturates such as the diolefines and converts them directly to gums. The inert extending agent permits the reaction to take place at the surfaces of the particles which are uniformly dispersed throughout the hydrocarbon, thus avoiding localized overheating and over-oxidation. After settling, the treated hydrocarbon can be drawn off and subjected to any of the usual subsequent operations.

My process is particularly applicable to distillates containing large amounts of unsaturates, such as cracked distillates. It may also with advantage be used on heavier fractions such as lubricating oils. Such oils also contain unsaturated components which are very difficult to remove and which in time, in the presence of heat and air, form resins and polymers.

More specifically, my process for treating hydrocarbons to remove the gum forming components consists in adding to the oil to be treated an oxidizing agent, such as sodium potassium, calcium or similar bichromates in the dry form and in a finely divided condition. At the same time the bichromate is added I also add an inert extending agent, preferably graphite. The function of this inert extending agent will be pointed out later. I may use various extending agents provided they are unreactive to the added acid and oxidizing agent and are of such specific weight relative to the hydrocarbon treated or in such a powdered form as to permit a uniform dispersion and availability throughout the hydrocarbon body without immediate settling out. For example, powdered silica dioxide, powdered glass or powdered pure barium sulphate may be used. My preferred operation would be to grind the bichromate and graphite together in order to reduce them to a fine powdered form. They would then be added to the oil with thorough agitation so as to completely and uniformly disperse them throughout the body.

I now add to the hydrocarbon slowly and in small portions, concentrated sulphuric acid in amount sufficient to react with the bichromate to form an oxidizing medium. I prefer to use concentrated 66° Bé. acid in order to avoid the presence of water which would tend to form a solution with the bichromate. The amount of acid can be calculated on the basis of molecular proportions with the bichromate. The hydrocarbon body is again thoroughly agitated, from 20 minutes to a half hour usually being sufficient with a distillate, for example, to convert the undesirable unsaturates to gummy compounds.

The hydrocarbon body is then allowed to stand to permit the polymers and gummy compounds to settle out with the reacting agents and the inert material. The clear hydrocarbon body can then be drawn off or otherwise separated from the settled material. In operating with a light distillate, it may, if desired, be re-run to obtain a more complete separation of the distillate from the gummy components in view of their change in boiling point. If the treatment is carried out with a more viscous hydrocarbon, such as one within the lubricating oil range, it may be necessary after a preliminary settling to filter the hydrocarbon. Of course, the usual water washes and other operations customarily performed after a treating operation may be carried out.

In operating with a hydrocarbon within the lubricating oil range, I preferably heat the oil before adding the bichromate and graphite. This is done for the purpose of reducing the viscosity of the oil to obtain a better dispersion and also to facilitate the oxidizing action.

By means of my process I am able to carry out an effective oxidizing action within a body of hydrocarbon material without danger of localized overheating explosions, or over-oxidation. Thus, I am also able to use by means of my process an oxidizing medium in a concentrated form. The graphite acts as a dispersing medium for the bichromate and also acts as an extended surface upon which the action between the sulphuric acid and the bichromate can take place as well as a surface on which the oxidizing action takes place. The surface tension between the reacting substances is minimized. Therefore, the fineness of the graphite and the uniformity and completeness of the dispersion of the graphite and bichromate within the hydrocarbon body are important factors in the carrying out of my operation. In view of the fact that the oxidizing action takes place at this extended surface, its action is uniform and complete. Localized overheating which otherwise might result in an explosion is thus avoided. Also the oxidation of compounds other than those which it is desired to remove is minimized.

I prefer to have the bichromate and the graphite ground to a condition in which they will pass through a sieve of 0.01 mm. mesh although an even finer powder is desirable. A coarser powder may be used and an advantageous operation secured but considering all factors might not equal the operation with a very fine powder of bichromate and graphite.

I have given below two examples for carrying out my process with a gasoline fraction and a lubricating oil fraction. These specific examples, however, as well as the other examples given, are only for the purposes of illustration and are not to be considered as limitations upon my invention.

Example 1

1000 cc. of untreated gasoline was thoroughly mixed with about 4 grams of a finely ground mixture composed of 2 grams of potassium bichromate and 2 grams of graphite. The bichromate and graphite were in a homogeneous condition and passed through a sieve of 0.01 mm. mesh. The amount of the mixture added, namely, the 4 grams, was determined by previously ascertaining the oxidation capacity of the gasoline and then taking from 30 to 35% excess of bichromate over the theoretical quantity based on the oxidation capacity. The bichromate and graphite were thoroughly mixed with the gasoline by stirring. Then 4 cc. of 66° Bé. sulphuric acid was added slowly and in small increments. After stirring for several minutes, the mixture was allowed to settle for one hour and the treated gasoline decanted.

Example 2

1000 cc. of a mineral oil within the lubricating oil range was heated to about 50° C. To this warm oil there was added 6 grams of a mixture of 3 grams of graphite and 3 grams of potassium bichromate. The bichromate and graphite were thoroughly mixed and in a finely divided dry condition capable of passing through a mesh of 0.01 mm. The mineral oil was stirred for about ten minutes to thoroughly distribute the graphite and bichromate throughout the mass. The temperature had dropped to about 35° C. due to cooling. 7 cc. of concentrated 66° Bé. sulphuric acid was then added slowly in small portions and with constant stirring. Agitation was kept up for about one quarter of an hour and the oil then allowed to settle for one hour. The treated mineral oil was removed by decanting and subjected to the usual operations subsequent to treating.

My process requires a minimum amount of sulphuric acid in view of the fact that there is no loss of sulphuric acid in reacting with other than those hydrocarbons which it is desired to remove. For example, from 0.2% to 0.3% sulphuric acid may be sufficient for treating fractions within the gasoline range and 0.3% to 0.7% for fractions within the lubricating oil range dependent upon their source. In other words, from 2 to 3 kilograms of sulphuric acid are used per 1000 kilograms of gasoline as compared with 45 to 50 kilograms of sulphuric acid which are necessitated by the present methods.

Also, it should be noted that only very small residues are formed by my process for I remove only those components which are of the undesirable polymerizing and gum-forming type. There is no loss of other valuable components such as is the case in the usual sulphuric acid processes which remove aromatic compounds and stable olefines. I have found that the refining losses by my process average approximately 50% less than with the usual sulphuric acid refining process in connection with the treatment of gasolines, and in connection with the treatment of oils within the lubricating oil range, I have found that my losses may run from 50 to 80% less as compared with the usual sulphuric acid refining process. It will be noted that the components removed are immediately converted to the gummy state and thus are rapidly separated.

I have found that the gum-forming components of an auto-oxidizing nature are substantially completely removed so that there is very little further formation of gummy compounds even after long storage periods. On the other hand, it is well known that any gasolines treated by the usual sulphuric acid refining process will continuously break down into gummy compounds. For example, in a benzine produced from Pechelbronn crude and refined with sulphuric acid I have found that after one month 20 milligrams of gummy substances per 100 cc. of gasoline were formed. After three months the amount was 75 milligrams per 100 cc., and after six months, the amount of gummy material had increased to 150 milligrams per 100 cc. In comparison, gasoline from the same source was treated by my process and after one month, there were 2 milligrams of gum sub-

stances per 100 cc. of gasoline; after three months there were 4 milligrams per 100 cc., and after six months there were only 7 milligrams per 100 cc. It was also important to note in connection with this comparative test with benzine from Pechelbronn that the material when treated by my process was found to have a higher octane number than the material from the same source treated by the usual sulphuric acid process. This is because of the fact that my refining process does not remove the aromatic hydrocarbons as does the sulphuric acid treatment. It was well known that this type of compound had certain anti-knock properties. Thus by means of my process, the natural anti-knock characteristics of a distillate are retained.

It will be apparent that there are other modifications and extensions of my process disclosed herein which, however, are within the scope of my invention. I do not wish this specific disclosure therefore to be interpreted as limiting my invention as defined in the appended claims.

I claim:

1. A method for refining hydrocarbons containing undesirable unsaturated components whereby said undesirable components are converted to polymers and gums easily separated from the hydrocarbon, comprising mixing an alkaline bichromate in a dry powdered form with said hydrocarbon in the presence of powdered graphite, thoroughly agitating the mass to obtain a uniform dispersion of the bichromate oxidizing agent and the graphite extending agent, slowly adding to said hydrocarbon mixture with agitation concentrated sulphuric acid, allowing the hydrocarbon mixture to settle, and separating the treated hydrocarbon substantially free from undesirable polymers.

2. A method for refining hydrocarbons with an oxidizing agent whereby over-oxidation and localized heating is avoided, comprising mixing a dry powdered alkaline bichromate and powdered graphite, adding said powdered mixture to the hydrocarbon to be treated with agitation to obtain a uniform dispersion of the powdered mixture, slowly adding with agitation concentrated sulphuric acid in an amount sufficient to render effective the bichromate as an oxidizing means, allowing the reactant mixture to settle, and separating the treated hydrocarbon.

3. A method for refining hydrocarbons with an oxidizing agent whereby over-oxidation and localized overheating is avoided, comprising mixing a dry powdered alkaline bichromate, and a dry powdered extending agent, adding said powdered mixture to the hydrocarbon to be treated, with agitation to obtain a uniform dispersion of the powdered mixture, slowly adding with agitation concentrated sulphuric acid in an amount sufficient to render effective the bichromate as an oxidizing means, allowing the reactant mixture to settle, and separating the treated hydrocarbon.

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