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METHOD OF TREATING HYDROCARBONS

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This invention relates to a method of treating hydrocarbon distillates for the refining thereof and removal of deleterious sulfur compounds, the stabilization of color, and the reduction and stabilization of gums.

Methods of distilling hydrocarbons currently in use produce distillates which contain relatively high proportions of materials which are generally designated by the oil refiner as unsaturates such as mono and di-olefines, and aromatic derivatives. Certain of these aromatics possess the valuable property of repressing or decreasing the "knocking" which is produced under certain operating conditions when a given petroleum distillate is used as fuel in an internal combustion engine. It is highly desirable, therefore, that any refining methods used upon petroleum distillates should be such that a loss of aromatics contained therein be kept as small as possible.

In addition to the aromatics, the petroleum distillates also contain sulfur in various chemical combinations. All of these particular sulfur combinations or derivatives possess certain inherent disadvantages which render petroleum distillates containing them less valuable than one in which there is no sulfur, or wherein there is contained only a small quantity of sulfur.

The presence of the unsaturated compounds is detrimental to the quality and marketability of the finished product, as it is generally accepted that these materials give use to poor color stability and to gum formation. Further they are very reactive, and are therefore susceptible to slow oxidation upon storage with formation of deleterious gums. This action is accelerated by the photochemical action or catalysis of the sun's rays.

In many of the processes currently used for removal of sulfur from hydrocarbon distillates, the valuable aromatic compounds and certain of the mono-olefines are either destroyed or removed coincidentally with the sulfur. Should the sulfur not be removed by a special process and the distillate given the usual acid and alkali wash, a small fraction of the sulfur compounds are removed during the sulfuric acid treatment, but on steam distillation, the final step in the refining process, the resultant distillate shows the presence of certain residual sulfur compounds by acquiring an off-color and/or an off-odor.

It is well known that certain of these sulfur compounds may be removed during sulfuric acid treatment, or may be removed by preliminary treatment with certain other chemical reagents. However, the chemical reagents react in both

cases, not only with the sulfur, but with a fairly large proportion of the aromatic substances in the distillate and remove these valuable materials as well.

The present invention provides a method of treating a given hydrocarbon distillate whereby a selective action is obtained upon the sulfur derivatives, producing a maximum removal thereof, while a minimum reaction and removal of the aromatic compounds is obtained with the consequent minimum removal of such compounds.

The present invention further comprehends the provision of methods for treating hydrocarbon distillates containing small quantities of aromatic compounds and further provides improvements upon the usual acid treatment of the distillate with sulfuric acid whereby gum formation is reduced to minimal quantities.

Other inventive features will be apparent from the disclosure in the following specification and claims.

In the production of hydrocarbon distillates from crude petroleum, the crude petroleum product may be treated under pressure at elevated temperatures whereby additional quantities of low boiling distillate are produced, which fraction contains substantially large amounts of unsaturated hydrocarbons and aromatic materials; or the petroleum may be distilled in contact with chemical reagents which possess the property of decomposing higher boiling fractions into low boiling fractions, with consequent increase in yield of the more economically desirable low boiling fractions.

These various petroleum fractions contain undesirable impurities and are usually given the well known acid and alkali wash in order to adapt them for use. This treatment consists of an agitation of the impure fractions with sulfuric acid which reacts with or dissolves the various impurities which are then removed with the acid since the latter is not soluble to any great extent in the hydrocarbon. The minute quantity of acid which remains dissolved in the hydrocarbons is then eliminated by agitation with a material capable of neutralizing the acid and which produces a substance either insoluble in the hydrocarbon, or which is soluble in water and which may be removed by a subsequent water wash. In usual standard practice, this step is effected by washing the hydrocarbons with an alkaline hydroxide subsequent to the acid treatment. This alkaline hydroxide wash produces water soluble alkali sulfate which is later removed by washing the hydrocarbons with water,

and the final treatment in the refining process consists of a distillation thereof, such distillation generally being by steam.

Where it is desired to entirely eliminate the sulfur compounds, very large quantities of sulfuric acid are required, and in such case, more and more of the valuable aromatic derivatives are removed from the hydrocarbons, either combined with or dissolved in the sulfuric acid together with a large fraction of the unsaturated di-olefines. By our method of treating and refining, we are able to reduce substantially the sulfur content of a hydrocarbon distillate of the type discussed above, and at the same time, decrease the consumption of sulfuric acid. We have found that we are able to produce a hydrocarbon distillate of very high purity, one containing only small quantities of sulfur; and one whose color is materially better than the original hydrocarbon, by treating and agitating the hydrocarbon with a chemical reagent which has the property of acting upon the sulfur contained therein in such fashion so as to render the same readily soluble in sulfuric acid. The reagents which we use are vigorous oxidizing agents such as the peroxides. The process lends itself to the treatment of hydrocarbons and petroleum fractions by means of existing apparatus, hence in one way of working the process, we may add this reagent to the hydrocarbons just prior to their entrance to an agitating chamber, such as a turbulence coil. In this method, we use hydrogen peroxide of fairly high concentration, such as 27% hydrogen peroxide or 100 volume hydrogen peroxide, in sufficient quantity to combine with the deleterious sulfur compounds present in the distillate. This mixture is thereafter advantageously treated in the turbulence coil whereby an intimate intermixture of hydrogen peroxide and distillate is secured, and a large contact surface for chemical reaction is provided.

The quantity of hydrogen peroxide necessary to cause the desired chemical reaction will necessarily vary according to the type of distillate treated. For distillates which have been produced from California crudes by a cracking process and which are high in sulfur, larger quantities of hydrogen peroxide must of necessity be used as compared with distillates which are low in sulfur and which are straight runs, produced without cracking from an original crude.

For the treatment of distillates of average sulfur capacity, we have found that a barrel of distillates may be economically and effectively treated by using in the neighborhood of 40 c. c. of 100 volume hydrogen peroxide, effecting a sulfur reduction equivalent to that obtained by using about 35 pounds of sulfuric acid per barrel; that is to say, with a distillate treated with sulfuric acid alone, in order to effect the same reduction in sulfur compounds, 35 pounds of sulfuric acid would have to be used, over and above that quantity which we find effective in order to obtain a material of comparable purity. After agitating the hydrocarbon with hydrogen peroxide, sulfuric acid is then added to the mixture of distillate and peroxide and agitated therewith in any suitable manner, such as in a turbulence coil as mentioned above. When the distillate is high in aromatic compounds, we find it advantageous to use a comparatively weak acid mixture such as 50 degree Baumé sulfuric acid. During agitation of the sulfuric acid with the hydrogen peroxide and hydrocarbon mixture, any water or hydrogen peroxide, or changed impurity,

for instance, sulfur compounds, are combined with or dissolved in the sulfuric acid which is insoluble in the hydrocarbon and may, therefore, be readily separated therefrom.

We have also found that we may remove sulfur compounds by a modified method of working. In this particular modification, the required amount of sulfuric acid in the form of oleum is added to the hydrocarbon prior to its entrance to the turbulence coil, and the hydrogen peroxide added immediately thereafter. The sulfuric acid, which has been thoroughly dispersed throughout the hydrocarbon distillate, dissolves the water solution of the peroxide and the reaction between that reagent and the sulfuric compounds occurs very rapidly, and the product of such reaction is to be found in the sulfuric acid which may be collected and removed. After an alkali wash, the hydrocarbon is in condition for final distillation and use.

By another variation of our method, we may make an acid reagent by treating sulfuric acid with the hydrogen peroxide and adding the mixed reagent to the hydrocarbon, agitating it therewith and finally removing the acid reagent, together with the excess peroxide and sulfur derivatives which have combined with or dissolved in sulfuric acid.

As in the first instance outlined above, if it be desirable to retain aromatic compounds in the hydrocarbon, a somewhat weak sulfuric acid is used; for instance, acid containing less than 80% sulfuric acid, and the hydrogen peroxide added thereto. When the distillate is treated with this chemical reagent, practically all of the aromatics remain in the distillate, while the sulfur derivatives are acted upon and removed.

However, where it is desired to treat with comparatively strong sulfuric acid, the hydrogen peroxide may be added to an acid of a specific gravity of 1.84 or to a fuming acid, for instance, a 103% sulfuric acid. This mixed reagent is immediately added to the distillate prior to its entrance into the agitating chamber or turbulence coil, and intimate contact of the reagent and distillate insured by passage through such coil.

As an example of the efficiency and practicability of our process, we may mention that we have treated distillates containing 0.26% sulfur which were found to contain 0.12% sulfur after treating with our method. We have also found that there is a reduction in the mercaptan sulfur content, such sulfur content falling from 0.12% to 0.02% after treatment. The significance of such a reduction of mercaptan sulfur content will be readily apparent since it is these undesirable sulfur containing materials which produce sour distillates after a final steam distillation, and which require a special doctor treatment in order to transform such sulfur into an innocuous disulphide. Coincident with the sulfur removal, there is found an improvement in the color of the product, rendering the same more readily marketable, and eliminating the necessity of further treatment for color reduction.

It will be readily apparent that one advantage of this process is a reduction in the consumption of sulfuric acid required to reduce sulfur contents to a definite desired minimum. For instance in the case cited above, a reduction of 0.14% in a sulfur content would have required about 35 pounds of sulfuric acid per barrel. We have been able to effect such a reduction by the use of approximately 45 c. c. of 27% hydrogen peroxide, with economies in operation and improvement of

product. It will therefore be apparent that our method effects material economy in process treatment and at the same time, produces a final product of superior quality for use, for example, in internal combustion engines, where excessive sulfur contents are detrimental to the delicate moving parts of the engine, when burned to an acid oxide.

What is claimed is:—

1. The method of refining liquid hydrocarbon distillates containing aromatic compounds which comprises adding hydrogen peroxide to the distillate, agitating the mixture to enhance chemical reactions occurring therein, agitating sulfuric acid with said mixture of a strength sufficient to dissolve the oxidized sulfur compounds but insufficient to combine with the aromatic compounds in the distillate, and separating the acid from the distillate.

2. The step in the refining of liquid hydrocarbon distillates containing aromatic compounds which includes adding to the hydrocarbon a mixture of hydrogen peroxide and sulfuric acid, the concentration of the acid being insufficient to react with the aromatic compounds but sufficient to dissolve the oxidized sulfur compounds, agitating the mixture

of distillate, acid and peroxide to insure intimate contact and thereafter separating the acid from the hydrocarbon.

3. The step in the refining of liquid hydrocarbon distillates containing aromatic compounds which includes agitation of the hydrocarbon with hydrogen peroxide in the presence of sulfuric acid insufficient in concentration to combine with the aromatic compounds but sufficient to dissolve the oxidized sulfur compounds.

4. The step in the refining of hydrocarbon distillate which comprises agitation of the hydrocarbon with hydrogen peroxide in the presence of sulfuric acid of a concentration of about 60° Baumé in order to dissolve the oxidized sulfur compounds.

5. The steps in refining of hydrocarbon distillates containing aromatic compounds which comprise adding hydrogen peroxide thereto prior to the final steam distillation for reducing the sulfur content thereof, and the removal of the peroxide and sulfur compounds with aqueous sulfuric acid of a concentration sufficient to dissolve the oxidized sulfur compounds.

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