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TREATMENT OF HYDROCARBON OIL

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This invention relates to the treatment of hydrocarbon oils, and refers more particularly to the treatment of the lighter distillates produced in the cracking of heavy hydrocarbon oil mixtures though similar distillates produced in the straight run or non-cracking distillation of crude petroleums may also be treated by the process.

More specifically, the invention provides an improved process for the refining treatment of such distillates while in heated vaporous condition by a special method and means adapted to controllably reduce their content of gum-forming and corrosive sulfur compounds so that the distillates condensed following the vapor phase treatment are of sufficiently high quality to be utilizable as motor fuel with no further treatment other than a light neutralization or sweetening.

The detailed features of the process will be more fully disclosed hereinafter.

The most common practice in the production of refined gasoline by the cracking of heavy petroleum residua and distillates has been to produce a primary raw distillate containing major amounts of gasoline boiling fractions, this distillate being treated in liquid phase with sulfuric acid, caustic soda, pumbite or hypochlorite solutions and other chemical treating reagents and then subjected to redistillation for the production of a gasoline of a boiling point range desired and still bottoms which have been utilized as burning oil or returned to the cracking process for further treatment. The disadvantages inherent in this type of procedure are quite familiar to those engaged in the refining of petroleum, these being briefly as follows:

1. There is considerable heat loss due to the necessity for revaporizing distillates to distill the finished gasoline; with consequent increased cost.

2. There is considerable polymerization induced by the use of sulfuric acid which results in a loss by the production of high boiling from low boiling compounds.

3. The heavier portions of the raw distillate boiling higher than the end point desired in the finished gasoline are subjected to treatment along with the lighter portions, and since these higher boiling portions may at times constitute 25% of the raw distillate, a large amount of the acid is consumed in treating portions which will not appear in the finished gasoline.

4. The action of the sulfuric acid is not entirely selective in regard to the removal of the more highly unsaturated di and triolefins, but effects the removal also of mono olefins which are desirable constituents of the finished gasoline mixture on account of their anti-knock value.

5. The most careful neutralization and washing of acid treated distillates is not sufficient to completely remove acidic reaction products, these products decomposing during the rerunning operation if temperatures are allowed to rise above a certain point to result in the production of a sour distillate which must be finally neutralized and sweetened.

The desirability of a method of treatment which could be conducted upon cracked vapors prior to their condensation has been long recognized and a few processes are assuming a commercial status. It is with improvements in such processes that the present invention is concerned.

In one specific embodiment the invention comprises treating hydrocarbon oil vapors with aqueous solutions containing sulfuric acid, chromic acid, and salts of either or both acids.

Both sulfuric acid and chromic acid possess pronounced oxidizing properties in regard to organic materials such as the hydrocarbon compounds present in petroleum oils, particularly when the strong acids are used in excess and temperatures are allowed to rise above certain limits. Oxidation reactions properly controlled, however, have been definitely established as being of great value in inducing reactions of polymerization among highly unsaturated hydrocarbons and in transforming sulfur compounds such as mercaptans, sulfides, thiophenes, etc. into soluble oxygen derivatives removable by washing methods.

The present invention permits the use of controllable oxidation in treatments upon cracked hydrocarbon vapors as well as the simpler reactions of sludge formation characterized by the production of alkyl sulfates and normal sulphonic acids, since the concentration of either the sulfuric acid or the chromic acid may be varied independently within certain limits and the dilution factor controlled by the use of dissolved salts rather than the use of more solvent. This latter feature is of great importance, since if dilute aqueous solutions of either sulfuric or chromic acid or their mixtures are introduced into fractionating devices for the purpose of treating hydrocarbon vapors, a concentration ensues until equilibrium is established between liquid and vapor, this equilibrium corresponding to acids of fairly high concentration under the conditions of temperature and pressure necessary for maintaining cracked distillates in the vapor condition. By the use of soluble salts instead of

more solvent, the vapor pressure of the treating solution is depressed and concentrations may be maintained at the optimum point. The following tabulation shows the mutual solubility of sulfuric and chromic acids in water at ordinary temperatures:

Percent H_2SO_4	Percent CrO_3
20	30
40	14
61	1.0
80	0.8
90	1.0
100	0.076

The preceding solubilities indicate maximum values in the absence of other soluble salts, and the figures must be modified to some extent when other salts are present.

Reagents for use according to the process of the present invention may be prepared in a variety of ways, a few of which may be given as examples. In some cases aqueous solutions of sodium, potassium or other chromates may be added to solutions of sulfuric acid which commonly result in the preparation of a reagent in which the sulfuric acid is the chief acidic component though in some cases it may be present in minor amounts. At other times such solutions may be partly neutralized by caustic soda or the composition modified by the addition of normal or acid sulfates.

As another method of preparation, sulfuric acid may be added to solutions of dichromates such as sodium or potassium dichromate in amounts necessary to insure the presence of definite amounts of chromic acid.

As a further example of preparation of a reagent solution, commercially pure chromic anhydride may be added in regulated amounts to solutions of acid sulfates or of sulfuric acid.

In conducting operations comprised within the scope of the invention, hydrocarbon vapors from any source, for example, direct from a cracking process and in general from any distillation process including substantially atmospheric pressure distillation of crudes or re-run distillations upon primary distillates may be passed through towers containing filling or baffing material if desired either counter-current to or concurrent with a solution containing regulated proportions of sulfuric acid, chromic acid and their salts. The treating solution may be introduced in the form of a spray or mist from sprays, atomizers or nozzles to insure intimate contact with the vapors undergoing treatment, or it may be, for example, introduced onto the top tray of a series of superimposed plates to flow downwardly countercurrent to a rising stream of vapors. In some cases it may be sufficient to introduce the vapors into the bottom of a pool of treating reagent so that their upward passage therethrough effects the desired treatment. In any case of operation the treating reagent may be introduced, the vapors withdrawn and the sludge reaction products removed continuously by utilizing any of the well-known treating and fractionating devices common to the oil industry.

Treatments may be employed alone or as a step along with other separate treatments such as treatment with fuller's earth and preliminary or final neutralization or sweetening of the vapors with ammonia or liquid alkali solutions, sodium plumbite, etcetera, to insure the neutralization of acidic compounds. Other types of treatments which may be conducted as preceding or succeeding steps following the application of the treating process of the invention are such treatments as those accomplished by the use of metals, metal oxides, lime, and ordinary or special treating reagents.

In a preferred operation of the process the vapors treated are preliminarily fractionated so that their boiling range approximates that of commercial gasoline so that the reagent is not wasted upon portions of the vapor mixture which are too heavy for use as motor fuel.

The sludge from the treatment may at times be recirculated, particularly in the case of treatments involving counterflow of reagent solution and vapors through a filled tower, such recirculation being employed to insure maximum efficiency in the use of the particular solution employed. It is further contemplated to insert a regeneration step so that sludge produced may be used as a basis for making fresh reagent. For example, it may be diluted to separate and partially hydrolyze dissolved and emulsified oils and acid organic compounds, the aqueous solution reconcentrated to desired strength and replenished by the addition of calculated amounts of the compound necessary to restore it to the proper composition for its effective use.

The chemical reactions involved in treatments comprised within the scope of the invention have already been partly disclosed and to summarize, it may be stated that their net result is to effect controllable polymerization of undesirable unsaturates and reduction of sulfur content, with resultant increased stability of the gasoline produced and a lessening of its corrosive properties due to its sulfur content. The strength of the reagent solutions can obviously be varied over a wide range by regulating the proportions of the two acid constituents, that is, sulfuric and chromic, and controlling their respective dilution by the use of dissolved salts. The more strongly reactive reagents will be reserved for treatment of vapors containing large percentages of gum-forming and sulfur compounds, while weaker solutions will be used upon vapors produced from cracking stocks of a better nature or the vapors produced from operations under milder conversion conditions. In any case, the type and strength of reagent solution under conditions of operation may be suitably modified to produce the best results.

The composition of treating reagents which may be utilized in the process disclosed in the preceding specification may be varied considerably according to the degree of treatment required and the particular conditions employed. The example will be illustrative of results to be expected and serve to clearly define the commercial value of the process.

Operations may be conducted upon the vapors of approximate gasoline boiling point range evolved from the final fractionator of a cracking process operating upon California residuum. The treating solution employed may have the following approximate composition:

	Percent
Sulfuric acid H_2SO_4	30
Sodium acid sulfate $NaHSO_4$	30
Chromic anhydride CrO_3	5
Water	35

This solution may be passed downwardly counterflow to an ascending stream of end boiling point

vapors at a temperature of approximately 300° F. at the vapor outlet and a slight superatmospheric pressure to insure flow at the proper rate through the succeeding condenser and receiver. By suitable recycling of the solution amounts equal to approximately 2½% of the volume of the condensed gasoline may be needed to secure effective treatment. The comparative properties of the gasoline normally produced and that produced by the vapor phase treatment of the process of the invention may be seen from the following tabulation:

	Normal gasoline	Treated gasoline
Gravity	54.5	54.7
End point	410	410
Gums (copper dish)	500	15
Color, Saybolt	12	plus 30
Color after 4 hours in sunlight		25
Sulfur percent	0.5	0.16

The invention has particular application to cracked distillates of high sulphur content, e. g. those of California, Venezuela and Mexican origin, although it is obvious that other types of distillates may be treated.

The foregoing specification and example will serve to define the invention and show its commercial possibilities, but inasmuch as the example is merely specific to the case selected and many others might be given, it is not intended that either the exact details of the specification or the example shall act in a limiting manner upon the scope of the invention.

I claim as my invention:

1. In the art of refining petroleum distillate, a step which comprises subjecting said distillate in heated vaporous condition to the action of a solution containing sulphuric acid, chromic acid, and a salt of one of said acids in amount adequate to effect substantial dilution of the acids.

2. In the art of refining petroleum distillate, a step which comprises subjecting said distillate in heated vaporous condition to the action of a solution containing sulphuric acid and a salt of chromic acid in amount adequate to effect substantial dilution of the sulfuric acid.

3. In the art of refining petroleum distillate, a step which comprises subjecting said distillate in heated vaporous condition to the action of a solution containing sulphuric acid, a sulphate and chromic acid, the sulphate being in amount adequate to effect substantial dilution of the acids.

4. A process for refining hydrocarbon oil vapors which comprises treating the same with a solution containing chromic acid and a sulphate in amount adequate to effect substantial dilution of the acid.

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