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TREATMENT OF HYDROCARBON OILS

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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 heavier oils although similar distillates produced from the primary or non-cracking distillation of crude petroleums may also be treated.

More specifically the invention relates to the treatment of such hydrocarbon mixtures while in a heated vaporous condition, a process being disclosed which accomplishes the necessary refining of such vapors prior to their condensation and substantially eliminates the necessity for extensive treatment of the distillates and their subsequent rerunning, thus effecting much needed economies.

It has been recognized for some time by those engaged in the oil industry that the usual method of treating cracked distillates with sulfuric acid followed by neutralization and rerunning to produce end point gasoline possessed numerous inherent disadvantages due principally to the need for special auxiliary treating equipment and the necessity of rerunning the treated distillates. Even though distillates of gasoline end point are treated, rerunning or redistillation is usually necessary on account of the formation of high boiling polymers, sulfoxy compounds, et cetera, which raise the final boiling point of the gasoline and render the distillates unstable with respect to color and given formation. Of the proposed vapor phase treating methods thus far tried one or two only have attained commercial status, notably treatments with solid adsorbents such as fuller's earth. As yet, however, it cannot be said that any one type of vapor phase treatment has been found which is efficient enough to completely supersede the customary acid treating and rerunning of cracked distillates. The present invention provides an improvement over existing commercial processes which possesses marked advantages over those now in use, the details of the invention being set forth in the following paragraphs.

In one specific embodiment the invention comprises treating hydrocarbon oil vapors, particularly cracked hydrocarbon oil vapors, with liquid mixtures of sulfuric acid and organic acids and/or salts of organic acids with inorganic bases. The organic salt may react and form the corresponding acid and a sulphate. Inorganic salts such as those of ammonium, sodium, potassium, etc., may also be added to the mixture.

It will be evident from the preceding paragraph expressing the preferred embodiment of the invention that it comprises essentially a modification of the idea of using relatively dilute aqueous sulfuric acid, the range of use of the latter being limited due to the fact that under the conditions of temperature and pressure common to fractionators which are handling cracked vapors that any dilute aqueous sulfuric acid which may be added thereto is rapidly concentrated to a strength which is undesirable because of its powerful oxidizing and charring effect, producing thus cokey sludges and too severe an effect upon the vapors. The use of the organic acids and salts mentioned enables the use of sulfuric acid in the necessary diluted condition for proper vapor treatment, since the vapor pressure of the organic materials is lower than that of water and they are not lost by evaporation during the progress of treatments.

As examples of organic acids which may be employed may be mentioned such acids as benzene, sulphonic acid, acetic acid, chlor-acetic acids, other aliphatic carboxylic acids such as propionic, butyric, hexoic, isobutylacetic, dimethyl ethyl acetic, heptoic, et cetera. Dicarboxylic acids such as oxalic, succinic, tartaric, maleic, et cetera, can seldom be used owing to the decomposing effect of hot sulfuric acid which produces water and oxides of carbon. However, the carboxylic acids of aromatic or hydroaromatic groups are readily utilizable, such acids including benzoic acid, the toluic and xylidic acids as well as phthalic, isophthalic and terephthalic acids. In the majority of instances such aromatic spacing agents will be partially sulfonated in the course of the treatments.

It is also comprised within the scope of the invention to use as diluent or spacing agents the salts of acids of the types enumerated, particularly the salts with the alkali metals and ammonia, when the properties of the compounds permit. While in most cases the virtue of the treating solution employed is due principally to the sulfuric acid, it is recognized that the other acids and salts may at times exert a definite chemical influence upon the reactions other than merely moderating the effect of the sulfuric acid. It will be also evident that the selection of any particular compound or mixture of compounds for use with the sulfuric acid will be determined by solubility relations, the extent of refining treatment necessary upon the vapors, the general operating conditions and the matter of economy in the cost of the reagents. However, such prob-

lems will be solved by those familiar with the treating art without great difficulty.

The process may be conducted in any type of apparatus suitable for efficiently contacting vapors with liquid treating reagents. A filled tower containing crushed rock, fragments of porcelain, Raschig rings or metallic filler is readily utilizable, the scheme of operation in such a case being to pass the vapors upwardly through the tower counter-current to the descending treating solution which has been introduced above the baffling material through distributing means to assist in securing intimate contact of oil vapors and liquid. Other devices for efficiently contacting the vapors with the treating reagent, such as orifice columns, may be employed. At other times greater advantage may be gained by passing the vapors downwardly along with the treating solution, this serving in some instances to allow better separation and disposition of sludge and heavy reaction products. Treatments of high efficiency may be obtained by utilizing towers of the spaced-tray type, the trays being perforated, or arrangements being made for the down flow of liquids and up flow of vapors. Towers may be lined with lead or other materials, or be made of corrosion resistant materials, to minimize corrosion effects or suitably chosen corrosion resisting metals may be employed in their construction.

Another type of operation which may be successfully employed involves the simple expedient of merely allowing the vapors to rise through a pool of treating solution, the solution being circulated to insure thorough mixing and used until substantially spent, at which time the vapors undergoing treatment may be diverted to a fresh supply of reagent in parallel connected towers, thus insuring substantially continuous operation.

Owing to the possibility of varying the composition of the treating solutions over a wide range, the process is adaptable for use under practically all conditions of temperature and pressure encountered in the vapor zones, cracking, primary distilling or rerunning operations upon vapors containing large amounts of gasoline boiling range fractions. The temperatures prevailing in such distillations are usually included within the range of 200 to 600° F. and pressures from atmospheric or slightly superatmospheric to high superatmospheric, such as for example, pressures in the neighborhood of 300 pounds per square inch, or higher.

Treatments may be employed alone or in combination with other types of vapor phase treatment. For example, the vapors may be subsequently treated with ammonia or alkali solutions to neutralize and remove hydrogen sulfice, after which the process of the invention is applied and vapors after the treatment may be further neutralized, subjected to filtering or sedimentation to remove entrained particles or further neutralized and filtered to remove substantially all acidic reaction products. While it is contemplated that the process of the invention is in general sufficient to produce finished gasoline from cracked vapors in one step it may be at times necessary to subject the condensed gasoline to a mild neutralizing action which is easily accomplished by injecting minor amounts of caustic soda into the rundown line to storage.

The vapors treated may receive sufficient fractionation during the treatment depending upon the type and capacity of treating tower employed or they may be subsequently fractionated in separate equipment, with return of intermediate refluxes to the primary cracking stage for further conversion, or removing them from the system together with, or separately from, reagent sludges.

The sludges produced by the process of the invention will also vary in character depending upon the numerous factors entering into the treatment and the steps necessary for their recovery for further use will necessarily be modified accordingly. In most instances the general procedure commonly employed in recovering sludge from liquid phase sulfuric acid treatments is applicable, the sludge being diluted to a proper point with water to cause separation of oily material, and the aqueous solution being concentrated and receiving further addition of chemicals to restore it to the proper composition for use. It is contemplated to continuously regenerate used treating solutions as a step in the treating process.

Numerous examples of operation and the results obtainable therefrom might be given but a few will suffice to indicate the feasability of the operation from a commercial standpoint. As one example of operation, the gasoline range boiling vapors from a cracking process operating upon the Mid-Continent residuum may be passed under pressure of approximately fifty pounds per square inch counterflow to a descending solution containing approximately 40% of sulfuric acid, 35% of sodium salt of trichloracetic acid and 25% water. The temperature at the vapor exit at the top of the tower may be held at approximately 325° F. and the vapors further passed in a downwardly direction through a stationary filter bed consisting of a mixture of finely divided fuller's earth and lime, or be subsequently neutralized after the primary treatment. The final fractionation of the treated vapors may produce a gasoline suitable in all respects for commercial use. The following tabulation of comparative properties of a raw gasoline produced without vapor phase treatment and that produced by the refining operation just described will show the effect of the treatment:

	Raw gasoline	Treated gasoline
Gravity A.P.I.	55.2	55.5
Final boiling point	410° F.	410° F.
Color, Saybolt	Yellow.	Plus 30
Color after 4 hours exposure		25
Gums, mg./100 cc.	390	20
Sulfur	0.28	0.16

The continuous regeneration of treating solution from the sludge produced in the preceding example, and the circulation of reagent through the tower to enable its efficient utilization may make possible the treatment to the point shown in the tabulation by using as low as five pounds of reagent solution per barrel of gasoline, which is well within the required economy since the auxiliary treating reagent may be substantially unaffected in the treating and regenerating steps so that the only constituent needing replenishment is the sulfuric acid.

As another example illustrative of the operation of the process, a similar operation to the one given may be conducted upon the vapors produced from cracking a California residuum. The reagent solution employed in this case may contain as the diluting or spacing compound approximately 30% of acetic acid. By utilizing the same general steps already outlined and an amount of reagent amounting to seven pounds per barrel of finished gasoline improved results

indicated by the following tabulation may be brought about:

	Raw gasoline	Treated gasoline
Gravity A.P.I.	54.0	54.5
Final B.P.	400	400
Color, Saybolt	10	30
Color after 4 hours exposure	Yellow.	25
Gums, mg./100 cc.	450	25
Sulfur	0.39	0.12

The foregoing specification and examples have sufficiently disclosed and illustrated the process of the invention and made its features and advantages evident in comparison with existing processes. While the description and examples are accurate, the invention is not confined thereto but includes many other examples and modes of operation within its generally broad scope though it has not been deemed necessary to go into further detail for purposes of disclosure.

I claim as my invention:

1. In the art of refining petroleum distillate, a step which comprises subjecting petroleum distillate in heated vaporous condition to the action of sulphuric acid in the presence of a chloracetic acid.

2. In the art of refining petroleum distillate, a step which comprises subjecting petroleum distillate in heated vaporous condition to the action of an aqueous solution predominating in sulphuric acid to which benzene sulphonic acid has been added prior to the contact of the vapors with the acid.

3. In the art of refining petroleum distillate, a step which comprises subjecting petroleum distillate in heated vaporous condition to the action of sulphuric acid in the presence of phthalic acid.

4. In the refining of hydrocarbon oil, the step which comprises treating the oil in vapor phase with an aqueous solution predominating in sulphuric acid to which has been added prior to contact with the vapors a compound selected from the group which consists of benzene sulphonic acid, acetic acid, the chlor-acetic acids, the aliphatic carboxylic acids, the carboxylic acids of aromatic and hydroaromatic groups, and the salts of said acids.

5. In the refining of hydrocarbon oil, the step which comprises treating the oil in vapor phase with an aqueous solution predominating in sulphuric acid to which has been added prior to contact with the vapors a compound selected from the group which consists of the chloracetic acids, benzene sulphonic acid, the phthalic acids, and the salts of said acids.

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