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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 petroleum industry that the usual method of treating cracked distillates with sulphuric acid followed by neutralization and rerunning to produce end point gasoline possesses numerous inherent disadvantages due principally to the need for special auxiliary treating equipment and the necessity for rerunning the treated distillates. Even though distillates of gasoline end point are treated, rerunning is usually necessary on account of the formation of high boiling polymers, sulphuric acid derivatives, sulfoxy compounds, etc. which raise the final boiling point of the gasoline. Of the proposed vapor phase treating methods thus far tried a few 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 vogue, the details of the present invention being set forth in the following paragraphs.

In one specific embodiment the invention comprises the treatment of hydrocarbon vapors, particularly cracked hydrocarbon oil vapors, with liquid sulphuric acid solutions of various concentration containing substantially neutral organic compounds or the reaction products between these compounds and sulphuric acid.

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 dilute aqueous sulphuric acid, the range of use of the latter being very 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 sulphuric 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 spacing agents of the types mentioned in the preceding paragraph enables the use of sulphuric acid in a sufficiently diluted condition for efficient vapor phase treatments since the vapor pressure of such compounds, properly selected with regard to their physical and chemical properties, may be considerably lower than that of water so that the tendency to change the composition of the solution due to evaporation of the solvent is lessened.

The invention contemplates the use of sulfonic acids of compounds of a substantially neutral nature or at most only slightly acid or alkaline. For example, it includes the use of sulfonic acid of benzol and its homologs and also the sulfonic acids of multi-ring compounds such as naphthalene, anthracene, phenanthrene, etc. when the sulfonic acids of these compounds are of proper chemical and physical characteristics. The invention further contemplates the use of sulfonic acids of the chlor, nitro and hydroxyl derivatives of the aromatic or ring hydrocarbons mentioned. For example, diluting or spacing reagents may be made by sulfonating monochlorbenzol, mononitrobenzol, or phenol. Poly-substituted compounds and mixed substitution compounds may also be employed as bases for the manufacture of sulfonic acids. For example, metadichlor benzol may be sulfonated, or paradinitrobenzol or resorcinol may be used. Compounds similar to cresols and other phenols of homologs of benzol may also be used as starting materials when their sulfonic acids have the right properties. Suitable compounds for use as diluent or spacing agents may be formed by reacting upon unsaturated chain compounds with sulfuric acid, the product of these reactions being compounds of the type of mono or dialkyl sulfates. The particular olefins available for the manufacture of such compounds will in general be those which do not suffer extensive polymerization such as the mono olefins corresponding to the normal paraffins.

Another class of compounds which may be utilized and which may or may not undergo sulfonation during their use are the aldehydes and

ketones of ring compounds such as, for example, benzaldehyde, diphenyl ketone, etc.

From the statements just made concerning the types of compounds which may be employed as diluting or spacing materials it will be evident that a large number of reagent treating solutions of varying composition may be made up to suit the needs of different treatments. While in most cases the virtue of the treating solution employed is due principally to the sulfuric acid, it is recognized that the organic compounds used as spacing agents may at times exert a definite chemical influence upon the reactions other than merely moderating the effect of the sulfuric acid. It will also be evident that the selection of any particular compound or mixture of compounds for use with the sulphuric 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 problems 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 countercurrent 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. 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 supporting bubble caps such as are commonly employed in fractionating towers in the oil industry. Towers may be lined with lead or other 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 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 lbs. per sq. in. or higher.

Treatments may be employed alone or in combination with other types of vapor phase treatment. For example, the vapors may be treated with ammonia or alkali solutions to neutralize and remove hydrogen sulfide, 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.

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 feasibility 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 50 lbs. per sq. in. counterflow to a descending solution containing approximately 45% of sulfuric acid, 35% of benzene sulfonic acid and 20% of water. The temperature at the vapor exit at the top of the tower may be held at approximately 345° 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. 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
Gr. A. P. I.	53.9	54.3
Final B. P.	412° F.	413
Color, Saybolt	Yellow	+30
Color after 4 hrs. exposure		26
Gums, mg/100 cc	405	17
Sulfur	0.35	0.12

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 5 lbs. of reagent solution per bbl. of gasoline, which is well

within the required economy since the sulfonic acid is substantially unaffected in the treating and regenerating steps and 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 the sulfonic acid of mononitrophenol. By utilizing the same general steps already outlined and an amount of reagent amounting to 7 lbs. per bbl. of finished gasoline improved results indicated by the following tabulation may be brought about:

	Raw gasoline	Treated gasoline
Gravity A. P. I.	53.2	53.7
Final B. P.	405	406
Color, Saybolt	12	30
Color after 4 hrs. exposure	Yellow	25
Gums, mg/100 cc.	465	22
Sulfur	0.41	0.15

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, however, the broad scope of the invention is not limited by the exact details of the specification nor the particular examples given.

I claim as my invention:

1. In the refining of light petroleum distillates of the character of gasoline, the step which comprises treating the distillate in vapor phase with a solution containing sufficient sulphuric acid to effect substantial refining of the vapors and to which has been added a sulfonated hydrocarbon in amount sufficient to dilute the sulphuric acid substantially.

2. In the refining of light petroleum distillates of the character of gasoline, the step which comprises treating the distillate in vapor phase with a solution containing sufficient sulphuric acid to effect substantial refining of the vapors and to which has been added a sulfonated aromatic hydrocarbon in amount sufficient to dilute the sulphuric acid substantially.

3. In the refining of light petroleum distillates of the character of gasoline, the step which comprises treating the distillate in vapor phase with a solution containing sufficient sulphuric acid to effect substantial refining of the vapors and to which has been added a sulfonated olefine hydrocarbon in amount sufficient to dilute the sulphuric acid substantially.

4. In the refining of light hydrocarbon distillates of the character of gasoline, the step which comprises treating the distillate in vapor phase with a solution containing sufficient sulphuric acid to effect substantial refining of the vapors and to which has been added benzene sulfonic acid in amount sufficient to dilute the sulphuric acid substantially.

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