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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 low boiling cracked distillates though similar distillates produced by the straight run or non-cracking distillation of crude petroleum may also be treated.

More specifically the invention contemplates treatment of low boiling hydrocarbon vapors by means adapted to controllably reduce their content of undesirable constituents such as the more highly unsaturated hydrocarbons which increase the gum-forming tendencies of the condensed distillate and some of the sulphur containing hydrocarbon derivatives which have a corrosive action upon metals either before or after their combustion when the distillates which contain them are burned in internal combustion engine cylinders.

The more generally used combination of steps employed to produce marketable gasoline by cracking the heavier and less desirable portions of crude petroleum consists in producing first a raw pressure distillate containing a high percentage of gasoline boiling point range fractions, treating this distillate with various chemical reagents such as caustic soda solutions, sulphuric acid of varying strength, sodium plumbite, etc., to reduce unsaturation and sulphur and then rerunning the treated distillate to produce a finished gasoline free from heavy polymerized and condensed reaction products which remain behind in the distillation. Obviously if the necessary chemical treatment could be done upon the vapors prior to their fractionation the treatment could be made continuous along with the operation of the cracking plant, the rerunning step eliminated and a considerable quantity of heat conserved which would add to the overall efficiency of the operation. Such treatments, however, have met with only partial success commercially owing to the fact that treatments must be conducted at the temperature of the vapors which is usually high enough to cause an undue increase in the reactivity of the vapors with the treating reagents employed. The present invention provides an improvement in vapor phase treating processes which if not always adequate in itself for a complete treatment, furnishes a step which is of great value in connection with other vapor phase chemical treatments.

In one specific embodiment the invention comprises treating hydrocarbon oil vapors, particularly cracked hydrocarbon oil vapors, with solutions of alkali hydroxides containing salts of oxidizing acids.

For economic reasons it is preferred to employ solutions of the commoner alkali hydroxides such as those of sodium and potassium and also to employ the more readily available oxidizing salts of sodium and potassium such as their chromates, dichromates, perchromates, manganates, permanganates, nitrates, etc. The use of the alkalis and salts mentioned in various combinations adapted to particular treatments will only be limited by their respective solubilities. However, it is preferred to use approximately saturated solutions since under the temperature and pressure conditions under which vapors are generally treated weaker solutions are rapidly concentrated on account of the evaporation of the solvent.

In conducting treatments within the scope of the invention upon vapors of approximate gasoline boiling point range arising from cracking operations the treating solution may be brought into contact with the vapors in a variety of ways, the simplest being to introduce the solution at the top of a baffled treating tower countercurrent to an ascending stream of vapors, the spent solution and reaction products being withdrawn from the bottom of the tower and the treated vapors further fractionated to produce distillates of the boiling point range desired in the finished gasoline. When the conditions of treatment are such that there is a separation of liquid hydrocarbon refluxes in the tower, these may be separately removed from the tower at a level above the level of the spent aqueous solution or the total liquid products may be withdrawn together and separated outside the tower.

Treatments may also be conducted by introducing the treating solutions into the cracked vapors which are passing downwardly over solid contact reagents such as those of the non-metallic or siliceous type or masses whose action is due essentially to their metallic content. Fuller's earth is an example of the siliceous adsorbent material and crushed rock or porcelain exemplifies any material which may be so used which has no distinctly adsorptive properties but merely acts as a distributing agent. Solutions may be injected into the vapors in such downflow treatments through atomizing devices such as sprays or nozzles to insure good contact therewith; the choice of downflow, concurrent treatment being determined to some extent by the amount of condensation which ensues and other factors.

Suitable treatment may also be effected by bubbling the vapors to be treated through stationary pools of solution, the vapors then passing to frac-

tionating equipment for the production of the final end-product gasoline.

As already stated in the preceding paragraph, treatment may be at times sufficient in itself in producing desired treating effects or it may be employed in conjunction with other treatments. For example, it may be applied before or after the use of sulphuric acid in case it is feasible to conduct sulphuric acid treatments by the use of dilute solutions of or solutions containing salts as spacing agents. Other treating steps that may be employed in conjunction with the process of the invention may be the use of adsorbent materials to remove polymers, metals or metal oxides to remove sulphur and the use of relatively inert filtering materials to remove entrained particles from the vapors.

To maintain the concentration of the solution at the optimum point steam may be introduced to lower the rate of evaporation of the solvent, and prevent separation of solids and the possibility of plugging up treating apparatus.

In general the effects produced upon hydrocarbon oil vapors by the use of alkali solutions containing oxidizing salts is to produce a polymerizing action upon the gum or resin-forming constituents of the vapors which removes substantially all of the highly unsaturated di and triolefins and also produces a limited desulphurizing effect, the extent of the latter action being determined by the type of sulphur compounds present in the vapors, the composition of the treating solution and the operating conditions. When the vapors contain relatively large amounts of hydrogen sulfide and mercaptans a large amount of desulphurizing may be effected, while if the sulphur content is due principally to sulphur ethers or thiophene compounds, lesser though very substantial effects upon the reduction of the sulphur content of the vapors may be noted. It may therefore be stated that the solutions used according to the process of the invention have a sweetening and desulphurizing action which is of value in the treatment of hydrocarbons generally as well as in special cases, such as in the treatment of the lower boiling vapors from stabilizing plants containing large percentages of propane, butane and isobutane.

As an example of results obtained by a treatment characteristic of the process of the invention vapors of approximate gasoline boiling point range arising from the final fractionator of a cracking plant operating upon a mixture of Mid-Continent residuum and heavy gas oil may be

passed upwardly through a treating tower countercurrent to a descending solution of potassium permanganate and caustic soda, the solution being substantially saturated with the alkali at the temperature of operation and containing approximately 5% by weight of potassium permanganate. A sufficient amount of steam may be introduced with the cracked vapors to inhibit the evaporation of water from the solution and prevent separation of solid salts. The amount of treating solution need not be large if proper recycling is practiced and may not exceed one to five percent by volume of gasoline condensed. The following tabulation shows a comparison of the properties of the gasoline which would be produced from the plant if no treatment were given the vapors and the gasoline produced by the treatment of the vapors in the manner just described. The loss in yield of gasoline may be less than 1% as a result of the treatment.

	Raw gasoline	Treated gasoline
Gravity, A. P. I.	55.0	55.4
End point, °F.	410	405
Color, Saybolt.	10	23
Color, after 4 hours in light.	Yellow	20
Gums, copper dish.	375	20
Total, sulphur, percent.	0.32	0.18
Reaction to doctor test.	Positive	Negative

A greater percentage reduction in sulphur may be noted with hydrocarbon mixtures containing higher sulphur contents such as cracked distillates or vapors from California, Venezuela and Mexican charging stocks.

The results just cited as typical of those obtainable by the use of the process upon cracked vapors will serve to indicate the value of the process but these results as well as the other descriptive material are only illustrative and the scope of the invention is not to be considered as limited thereto.

I claim as my invention:

1. A process for refining hydrocarbon vapors which comprises treating the vapors with a concentrated aqueous solution of an alkali metal hydroxide containing an alkali metal permanganate.
2. A process for refining hydrocarbon vapors which comprises treating the vapors with an aqueous solution substantially saturated with an alkali metal hydroxide and containing a relatively small amount of a permanganate of an alkali metal.

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