

UNITED STATES PATENT OFFICE

2,013,399

REFINEMENT OF CRACKED HYDRO-CARBON OIL

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No Drawing. Application October 5, 1931, Serial No. 567,138. Renewed January 25, 1934

3 Claims. (Cl. 196—40)

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 relatively high boiling hydrocarbon oils.

More specifically the invention contemplates the provision of a process whereby the quality of motor fuel fractions obtained by the conversion of such heavy hydrocarbon oils at elevated temperatures and pressures may be improved to a point consistent with commercial motor fuel requirements.

Certain undesirable properties are inherent in the raw motor fuel fractions resulting from the pyrolysis of heavy hydrocarbons, these being due to the presence of an excessive amount of unsaturated hydrocarbon compounds and also to the presence of sulfur derivatives of many types. While the unsaturated compounds, which include not only the olefinic but also the aromatic series, have greater value than the straight-chain paraffin hydrocarbons in reducing the knocking tendency of motor fuels, the compounds whose unsaturation is characterized by double and triple linkages are unstable and tend to polymerize and deposit gums and resins which render the fuel non-homogeneous on storage and develop color and odor to an undesirable extent.

While many types of treatment have been applied in attempts to remove the more unstable unsaturated compounds and retain the more stable mono olefins which contribute to the antiknock value of the fuel, relatively few have attained a commercial status because of factors such as cost of reagents, corrosion tendency and certain inherent difficulties of operation. The process comprised within the present invention offers a solution of the problem of selective removal of the more readily reactive gum-forming unsaturated hydrocarbons and possesses many advantages over treatments at present employed for the same purpose, such as cheapness and availability of materials and simplicity and flexibility of operation from a refinery standpoint.

In one specific embodiment the invention comprises treating cracked hydrocarbon distillates substantially in the liquid phase with sulfuric acid containing dissolved therein ferric chloride.

The process of the invention is particularly directed to the treatment of cracked hydrocarbon distillates of approximate gasoline boiling point range in the liquid phase, and in practice any suitable type of equipment may be employed which will insure good contact between the reagents and the distillates. The standardized

cone-bottomed agitator used extensively in all refineries is readily adaptable, the reagents characteristic of the invention being added gradually during circulation of the oil from the bottom of the cone back into the top until the desired amount has been added and the desired treating effect is produced. In such operations the combined reagent and oil will be taken by the circulating pump which is usually of the centrifugal type and intimately mixed, by the churning action of the impellers. Furthermore, the pump may discharge into a line containing baffling material such as a succession of orifices or perforated plates, etc. so that thorough mixing is assured.

Reagents may be added at selected points along the flow of oil through continuous treating plants, which consist in general of pumps, mixing devices for oil and treating materials, settlers, wash tanks, etc., the reagent being conveniently introduced on the suction side of a pump which discharges through mixers containing baffling material such as vanes or successive orifices.

While it is frequently possible to treat cracked distillates sufficiently at ordinary temperatures so that their re-running may produce a substantially finished gasoline except for neutralizing steps it is also within the scope of the invention to employ superatmospheric temperatures, with corresponding pressures necessary to maintain substantially liquid phase in the oils undergoing treatment. The treatments may also be conducted under refluxing conditions in lieu of the use of pressure.

While the treatments characteristic of the present invention are frequently sufficient for improving the quality of the oils to a marketable degree the process may be employed if desired as a step in combined treatments embodying other reagents such as the commonly used commercial sulfuric acid, caustic soda, fuller's earth, etc., the proportions of each type of reagent being adjusted to obtain the best results.

While the temperatures employed in the treatments may vary over a considerable range, unusually high temperatures are not generally contemplated and at the most, temperatures employed will be only moderately superatmospheric up to, for example, 200° F. which will cover most instances of operation unless excessive superatmospheric pressures such as obtain in some cracking processes are used.

Judging from the results of numerous treatments upon a variety of cracked distillates, the treating effects obtained are evidently to be ex-

plained upon the basis of selectively controlled polymerization although some effect has been noticed upon the total sulfur content. It has been found that the compound treating reagents produce effects greater than those possible by the use of the reagents singly or in combination.

While numerous examples might be given of improved results obtained by the treatment of cracked distillates, it will suffice for illustrative purposes to give two which are characteristic of the invention. The distillate treated in both cases was produced by the cracking of a heavy California charging stock, its properties being shown in the appended tabulation along with the properties of a gasoline distilled from it to make an approximately 410 end point gasoline. It will be seen that the effect of distillation upon the sulfur content was practically negligible, that the gums as determined by the copper dish method were practically the same as in the raw distillate, within the error of the method of the determination, and that while the color was improved it was still far below that required in commercial gasolines:

	Original	Steam distilled
I. B. P. ° F.	92	109
E. P. ° F.	480	411
Percent @ 410° F.	86	
Percent sulfur	0.45	0.43
Gum mgs./100 cc. (copper dish method)	253	236
Color	Red	-2

The distillate was treated with a mixture of ferric chloride in moderately dilute sulfuric acid at the rate of 1.93 pounds of anhydrous ferric chloride per barrel of oil and 1.87 pounds of sulfuric acid, the acid being diluted with 0.94 pound

of water. The gasoline produced by distilling the treated distillate had a color of plus 30 Saybolt and containing only 19 mgs. of gum per 100 cc.

Caustic washing was all that was required to render the distilled gasoline color stable when exposed to the sun in the standard four ounce sample bottle test for a period of four hours.

Increasing the temperature by heating the distillate under a relatively low superatmospheric pressure with the reagent, subsequently separating the sludge and the treated distillate, neutralizing and re-running the latter also gave good results.

While the foregoing description and example have served to describe and illustrate the process of the invention, it is not intended that the specification be construed in a limiting sense as the process is one of great flexibility and wide application.

We claim as our invention:

1. In the art of refining cracked hydrocarbon oil, the improvement which comprises subjecting said oil in substantially liquid condition to the refining action of sulphuric acid containing dissolved therein ferric chloride.

2. In the art of refining cracked hydrocarbon petroleum distillate, the improvement which comprises subjecting said distillate to treatment in the presence of sulphuric acid containing ferric chloride at an elevated temperature, and maintaining said distillate in substantially liquid condition.

3. In the refining of cracked hydrocarbon distillates, the step which comprises treating the distillate with sulphuric acid containing ferric chloride dissolved therein.

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