

UNITED STATES PATENT OFFICE

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TREATMENT OF HYDROCARBON OILS

No Drawing.

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This invention relates to the treatment of hydro-carbon oils and refers more particularly to the treatment of relatively low boiling distillates produced in the straight run or non-cracking distillation of petroleum, and also to the corresponding distillates produced when the heavier portions of crude petroleum are subjected to cracking conditions under elevated temperatures and pressures.

More specifically the invention is concerned with the treatment of such distillates to improve the quality of the gasoline boiling range constituents which they contain, particularly in regard to sulphur content and gum-forming constituents in the finished gasoline, an improved treating process being disclosed which involves the utilization of new and novel means for producing the desired results.

The motor fuel fractions produced by the cracking of heavy petroleum or other hydrocarbon oils, and to a lesser extent fractions of similar boiling point range produced by straight run distillation petroleum, are characterized by the presence of varying, though usually minor amounts, of olefinic or unsaturated hydrocarbons and of sulphur compounds of different types. The olefinic constituents which contain more than one double bond between carbon atoms, such as the di- and tri-olefins, have a pronounced tendency to polymerize, particularly under the influence of air and light, to form gummy and resinous material which deposits upon feed lines, carbureters, valves, etc. when the fuel containing them is used in internal combustion engines and thus interferes with the proper operation thereof. Sulphur is present as free sulphur, as hydrogen sulfide in solution, and in combination in the several types of compounds such as mercaptans, sulphur ethers, thiophenes, thiophanes, etc., the reduction of the sulphur content being necessitated by the fact that it and many of its compounds are corrosive as such and that the products of its combustion are acidic and cause further crank case corrosion.

The problem of reducing the unsaturate content to a point where the gasoline possesses sufficient stability of storage has been

attacked from two standpoints, the first being to selectively remove the more unstable compounds and the second to hydrogenate them to saturated compounds which are of a stable nature. The success of the first type of treatment is contingent upon the use of accurately controlled amounts of reagents only sufficient to remove the more reactive compounds without removing the mono-olefins, thus preserving the majority of the unsaturates for the antiknock value, and minimizing treating losses. These types of treatment which commonly employ selected strengths of sulphuric acid are practically the only ones that have thus far obtained a commercial status, though some processes involving a limited oxidation and/or polymerization have met with some success.

In the matter of sulphur reduction there has been little departure up to the present time from the use of sulphuric acid and sodium plumbite, though it has been recognized that an efficient desulphurizing catalyst would be of great value.

In one specific embodiment the present invention comprises the use of metal chromites, particularly copper chromites, as catalysts in oxidation and reduction reactions upon hydrocarbon oils.

Chromites may be considered as salts of the hypothetical chromous acid, which may be designated by the formula H_2CrO_2 . Chromites of the following metals have been prepared: lithium, sodium, potassium, copper, calcium, barium, beryllium, magnesium, zinc, cadmium, aluminum, cerium, lead, antimony, bismuth, tungsten, manganese, iron, nickel and cobalt. They may be prepared by several general methods, such as calcination of the corresponding chromates, reduction of chromates, or the fusion of chromous oxide with the oxide or hydroxide of another metal.

Catalysts of the chromite type are generally characterized by the combination of superior catalytic power in both reducing and oxidizing reactions and by exceptional resistance to the poisoning influences of such elements as sulphur, selenium, arsenic, etc. The chromites of the heavy metals such as copper, zinc, cadmium, aluminum, iron, etc.

are especially adaptable to use in reactions involving the reduction or oxidation of hydrocarbons.

Catalysts of this type, particularly cuprous chromite CuCrO_2 and cupric chromite $\text{Cu}(\text{CrO}_2)_2$ are especially well adapted to treatments of hydrocarbon oil vapors when the object of the treatment is to induce a limited degree of polymerization to remove gum-forming constituents. In such treatments the chromite catalyst may be supported on or admixed with inert spacing materials such as crushed fire brick, sand, pumice, etc. and the mass may act as filler in the treating apparatus or may be supported upon regularly spaced trays in a vertical tower. In the case of cracked vapors of approximate gasoline boiling point range, they may be mixed with a limited amount of air or other oxygen-containing gas and pass upwardly over the catalyst, the vapors then being passed if necessary through filtering or adsorbent material to remove the heavy polymers formed and finally being subjected to fractionation to produce an end point product.

In the case of the reducing reactions in which the chromite catalysts may be employed they may be divided generally into two types, the first type involving operations in vapor phase at substantially atmospheric pressure or only slightly elevated pressure, and the second involving the use of high super-atmospheric pressures up to such pressures as 2000 lbs. per square inch.

It is frequently possible to sufficiently desulphurize cracked hydrocarbon vapors by passing them alone or with small amounts of hydrogen or hydrogen-containing gases over selected chromite catalysts, the net reactions resulting in the evolution of hydrogen sulfide with the fixation of very minor amounts of sulphur in high boiling organic derivatives of the heterocyclic type, such as thiophene derivatives. With a sufficient excess of hydrogen, the sulphur content may be reduced to a practical minimum with attendant hydrogenation of some of the olefinic constituents.

When hydrogenation reactions are conducted at high pressure, such as the 2000 lb. per square inch already mentioned, chromite catalysts again serve as the means of speeding up the reactions to a point commensurate with commercial needs and great increase in capacity of the apparatus. In such treatments sulphur is completely removed as hydrogen sulfide, oxygen as water, and the character of the charging oil undergoes extensive alteration with the development of more desirable characteristics in all hydrocarbon fractions.

Examples of results obtainable by the use of catalysts characteristic of the process of the invention might be multiplied considerably but it will suffice to give a few characteristic sets of results.

In one example the vapors from a cracking plant operating upon a mixture of Mid-continent fuel oil and heavy gas oil may be mixed with 10 percent by volume of hydrogen and passed through a small treating tower containing cupric chromite mixed with crushed rock in the ratio of one part of oxide to five parts of rock. After this treatment the vapors may be fractionated to produce a finished gasoline which is condensed, treated with caustic soda to remove dissolved hydrogen sulfide, and stabilized to remove propane and major percentages of butanes. In such an operation the effectiveness of the catalytic mass may persist until an equivalent of 5000 barrels of condensed gasoline has passed over the mass in vapor form. The temperature of the vapors inside the treater may be 375 to 400°F. , and the pressure 65 to 70 lbs. per square inch. Under these conditions of operation it may be possible to produce a finished gasoline of 410°F. endpoint with a sulphur content of 0.07%, whereas a similar gasoline produced without the use of the catalytic chamber may have a sulphur content of 0.33%.

As an example of the use of cupric chromite in catalyzing polymerization reactions for the removal of di- and tri-olefins where the sulphur content of the vapors is low enough to be a minor consideration, the case of the treatment of cracked vapors produced from a Pennsylvania gas oil charging stock may be given. By mixing these vapors with approximately 5% by volume of air, passing the air-oil vapor mixture through a similarly proportioned catalytic mass as that in the first example it may be possible to produce a 390°F. endpoint gasoline having a gum content as low as 10 mgs. if the catalytic treatment is followed by passage of the vapors through fuller's earth and subsequent fractionation to produce gasoline as an overhead fraction. Without the use of the catalytic oxidizing chamber it may be found that by the use of fuller's earth alone that yields of only 500 barrels per ton of clay, are possible when this low gum content product is produced, whereas by the use of the catalytic chamber in conjunction with the clay yields as high as from 4000 to 6000 barrels per ton of clay are possible.

As an example of the use of this type of catalyst in high pressure hydrogenation operations, a California cracked distillate containing approximately 75% of gasoline boiling range constituents may be treated in a pressure vessel at 2000 lbs. per square inch hydrogen pressure in the presence of recirculated hydrogen, the general method of operation being similar to that employed in present day commercial hydrogenation processes. To compare the overall efficiency of cupric chromite as a catalyst in this work with, for example, such catalysts as nickel oxide or

molybdenic oxide it may be stated that the life of the chromite catalyst may be found to be approximately 20% longer when used under equivalent conditions.

5 It will be evident that the foregoing specification has disclosed a process which may be advantageously applied to treatment of miscellaneous petroleum products, the examples given indicating the commercial advantages thereof. However, the process is of broader
10 scope than that given in the specifications and examples, and these are not to be construed as imposing limitations upon the scope of the invention.

15 I claim as my invention:

1. A process for refining hydrocarbon oils which consists in subjecting the oil in heated vaporous condition to the action of hydrogen while in contact with a chromite of a metal
20 for the purpose of desulphurizing such oil.

2. A process for refining hydrocarbon oils while in a heated vaporous condition which consists in passing said vapors through copper chromite while in the presence of a hydrogen containing gas.
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3. A process of refining hydrocarbon oils which consists in passing such oils while in a heated vaporous condition through comminuted cadmium chromite in the presence of hydrogen whereby the sulphur content of the
30 vapors being treated is materially reduced.

In testimony whereof I affix my signature.

MARVIN SMITH.

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