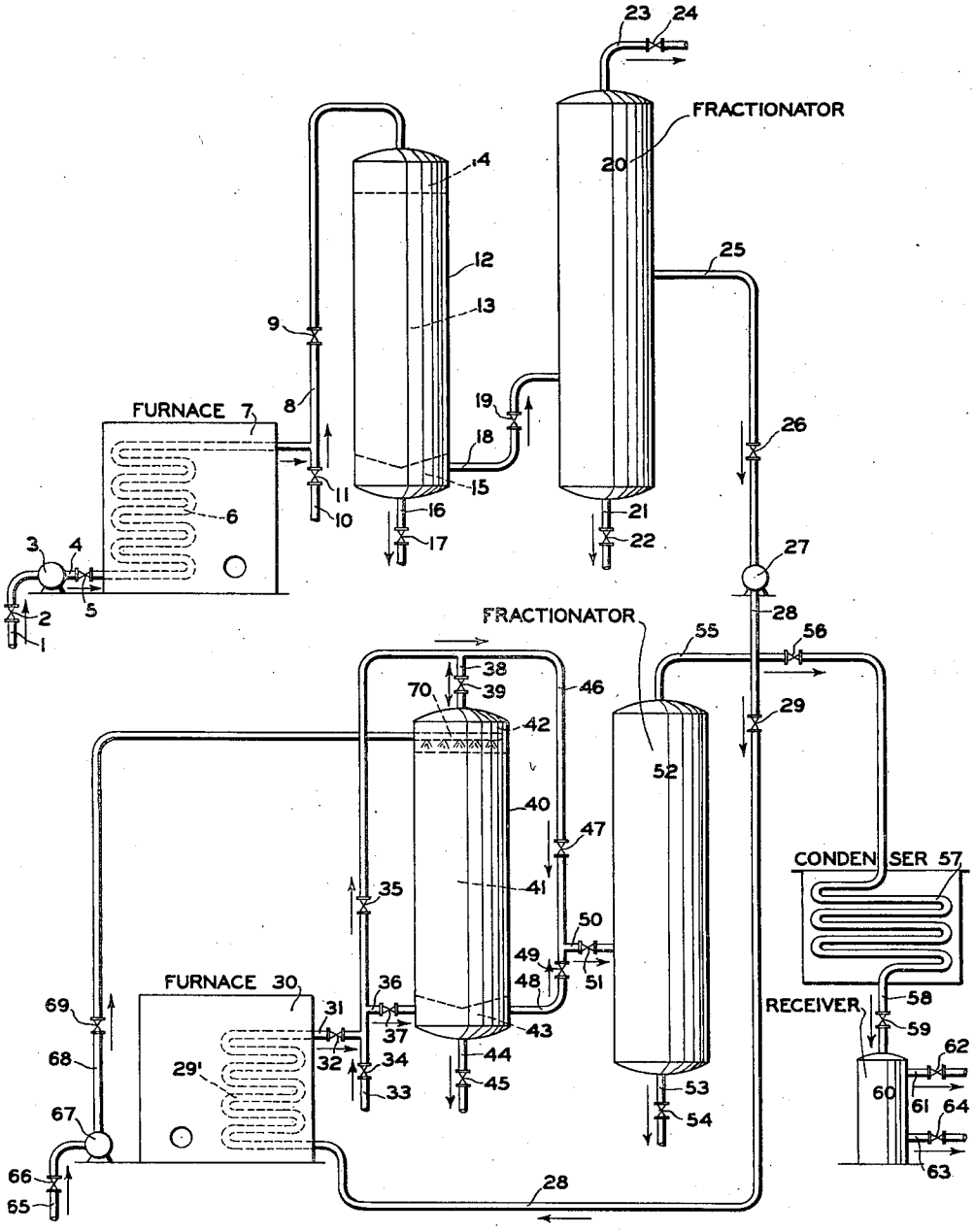
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention relates more particularly to the treatment of the lower boiling distillates produced in cracking heavy hydrocarbon oils for the production of gasoline, though it may also be applied to the treatment of corresponding straight run distillates which have a high sulphur content or which show a tendency to deteriorate on standing.

In a more specific sense the invention is concerned with a process for both desulphurizing and stabilizing hydrocarbon distillates, particularly cracked distillates of approximate gasoline boiling range by a succession of closely cooperating steps, the over-all effect of which is to produce a stable finished product utilizable as motor fuel.

Low boiling cracked distillates containing gasoline boiling range fractions contain variable amounts of two classes of undesirable compounds. The first class includes sulphur compounds such as hydrogen sulphide, mercaptans, alkyl sulphides and heterocyclic sulphur compounds of the general character of thiophene or thiophanes. The presence of these sulphur compounds above a certain maximum value in sulphur content is undesirable on account of the tendency of many of them to corrode engine parts or produce sulphur oxides on combustion which corrode the crank cases or exhaust lines. The second class of compounds which is undesirable are the highly unsaturated olefinic hydrocarbons comprising conjugated diolefins which polymerize to form gums and resins in the presence of oxygen or sulphur, particularly when exposed to light in visible pumps.

Practically all methods of treatment proposed for refining cracked gasolines have as objects the substantially complete removal of the above classes of compounds. The oldest and most firmly established method of treatment which aims to selectively remove both classes of compounds is the sulphuric acid treatment in liquid phase although it is frequently necessary when the sulphur content is reduced to a value in the neighborhood of 0.01% to use quantities of acid which also remove and polymerize stable and valuable mono olefins as well as the gum-forming and more highly unsaturated compounds. Other methods involving the selective polymerization of diolefins by solid contact materials such as fuller's earth are used where the sulphur content of the distillates is not high enough to require special consideration. The state of the art in treating cracked distillates at the present time is not entirely satisfactory owing to the high costs of the more selective methods of treatment and the lack of selectivity in the cheaper processes. The present invention is a contribution to the art of treating cracked distillates and overcomes many of the disadvantages inherent in older processes.

In one specific embodiment the present invention comprises fractionating to produce fixed gases, desulphurized gasoline fractions and fractions boiling higher than gasoline desulphurizing cracked distillates by catalytic hydrogenation, stabilizing the resulting product by removing hydrogen sulphide and hydrocarbon gases and further treating the desulphurized gasoline distillates with polymerizing agents comprising either hydrochloric acid in contact with metals or with solutions of polymerizing salts. It is essential to stabilize the product because the hydrogen sulphide will interfere with the polymerizing step. Further as described below, the stabilized product returns some of its heat thus aiding in the subsequent step of treatment and rendering the process more economical.

The character of the invention thus briefly stated in the preceding paragraph may be further developed in connection with the description of the essential details of an operation as ordinarily conducted and for this purpose the attached drawing is provided which shows diagrammatically by the use of conventional figures in side elevation an arrangement of interconnected elements constituting a plant in which the process may be carried out.

Referring to the drawing and assuming the cracked distillates to be in liquid phase (although in some instances cracked vapors and gases may be treated directly as they are produced in the cracking plant), the distillates are fed through a line 1 containing control valve 2 to a charging pump 3 which in turn discharges through line 4 containing control valve 5 into and through tubular heating element 6 suitably arranged in a furnace 7. During passage through the heating element the distillates are vaporized and brought to temperatures within the approximate range of 600 to 700° F. The pressure to which they are raised will depend upon the need for more or less extensive reducing action but will seldom exceed 500 pounds per square inch, good results having been obtained on high sulphur distillates at 300 pounds per square inch.

Hydrogen (preheated if desired) is added to the vapors by way of line 10 containing control valve 11, the amount used varying with the percentage of total sulphur and the form of combination though the amount will seldom ex-

ceed 1 pound per barrel of oil for a total sulphur content of as high as 0.75%.

The mixture of oil vapors and hydrogen passes through a line 8 containing control valve 9 and enters a hydrogenating treater 12 containing an effective catalytic mass in central zone 13, the catalyst dividing the chamber into upper vapor space 14 and lower vapor space 15. The types of catalyst which it is preferred to employ in the primary or hydrogenating steps of the process are those which have been found generally to posses a sufficient activity along with the maintenance of this activity over extended periods of time even in the presence of sulphur compounds and the hydrogen sulphide produced by their reaction with hydrogen. Usually the most effective catalysts are the oxides and sulphides of the metals of the 6th group comprising chromium, molybdenum and tungsten, though other oxides and sulphides such as those of the iron group may be employed alone or in admixture, and promoting substances may also be included such as, for example, aluminum and zinc oxides and alkali aluminates. The composition and activity of the catalyst chosen for any particular case will be determined by the usual considerations of efficiency, availability and cost, and the use of any particular catalyst is not a special feature of the present invention. Each catalyst or catalyst mixture which may be used alternatively will exert its own peculiar action upon the reactions involved which will not be exactly equivalent to the other similarly acting materials.

Any unvaporized hydrocarbons accumulating in lower space 15 of treater 12 may be withdrawn therefrom through line 16 containing control valve 17 and either retreated with fresh charging stock or blended with oils to be cracked. The vapors and gaseous reaction products from chamber 12 then pass through line 18 containing control valve 19 to a stabilizer or fractionator 20 whose function in the process is to produce gasoline boiling range fractions free on the one hand from fixed gases including hydrogen sulphide, hydrogen, methane, ethane, ethylene, propane, propylene, and the necessary percentages of 4 carbon atom hydrocarbons, and on the other hand from constituents boiling higher than the desired end point in the finished gasoline. The removal of hydrogen sulphide at this point increases the efficiency of the second treating step to be presently described in that no fixation of sulphur occurs during the polymerization and condensation reactions to form mercaptans and other organic sulphur derivatives. The removal of the other gases such as hydrogen and the lighter hydrocarbons mentioned reduces appreciably the vapor volume passing through the treater of the secondary stage and hence increases the contact time of the vapors in any plant of given capacity. The removal of hydrogen sulphide further eliminates the possibility of depreciating the metallic catalysts by the formation of sulphides.

According to the present scheme of operations, therefore, fractionator 20 acts as a stabilizer from which fixed gases are removed through upper line 23 containing control valve 24 to storage or reuse in the hydrogenating step, line 25 containing control valve 26 serves for the removal of stabilized gasoline fractions as side cuts (line 25 represents any single line or multiple lines at different levels which may be employed) and line 21 containing control valve 22 a bottom draw line for the removal of fractions heavier than gasoline. These last named products may be somewhat similar in character to those removed through line 16 containing control valve 17 and may be disposed of similarly.

If the hydrogen sulphide and sulphur compounds are removed from the gas vented through line 23 and valve 24 by any suitable method, it may sometimes be returned for further use in the hydrogenating step until a point is reached where the accumulation of hydrocarbons renders its use impractical and other methods of hydrogen recovery must be resorted to.

Regarding the conditions of operation in stabilizer 20, current practice ordinarily dictates the use of temperatures of from 100 to 150° F., at the top of the tower and temperatures of approximately 300 to 350° F., at the bottom of the tower when using pressures of from 100 to 150 pounds per square inch. The necessary temperature gradient through such a tower is commonly attained by the use of both overhead reflux and reboiling coils in the bottom sections of the tower. In the present set up owing to the presence of considerable quantities of hydrogen in the gas-vapor mixture entering the stabilizer, these conditions may be somewhat modified to the extent of using a high reflux ratio at the top of the tower and a somewhat higher temperature gradient.

The gasoline fractions from the first stage of the process are conducted through line 25 containing control valve 26 to a pump 27 which discharges through line 28 containing control valve 29 to a heating element 29' positioned in the furnace setting 30 in which the oil is again vaporized prior to the second stage treatment. Obviously by the use of suitable heat exchange devices the secondary furnace could be eliminated with a corresponding conservation in heat units though the simpler but less effective method of revaporizing by direct heating is shown in the drawing. The temperatures and pressures employed in the second stage treatment are as a rule both somewhat lower than in the first stage and the temperatures employed are usually no higher than the critical temperature necessary to insure substantially complete vaporization. Thus, for example, pressures up to about 200 pounds per square inch may be employed and temperatures of from 300 to 500° F., depending upon the need for the stabilization of the oils and the particular combination of catalyst and reagents chosen for this purpose.

For the sake of brevity the treater of the second stage designated by number 40 is shown equipped to treat the vapors either with solutions of polymerizing salts such as zinc chloride, stannic chloride, etc., or with hydrochloric acid in the presence of metals. In the latter case connections are shown for either up or down flow through the treater though as a rule upward flows are preferred when solutions are employed for the treatment and down flows when the vapors are mixed with hydrochloric acid and contacted with metals.

To follow the course of the vapors when they are treated with hydrochloric acid and metals, they pass through line 31 containing control valve 32 and receive an addition of a small amount of hydrochloric acid by way of line 33 containing control valve 34. The acid is usually added as

an aqueous solution, since a certain amount of water is essential to the success of the treatment. Alternatively dry hydrochloric acid gas and water or steam may be added separately in regulated proportions. The mixture of oil vapors, hydrochloric acid and steam then passes through line 33 and valve 35 and enters vapor space 42 at the top of the treater by way of line 38 containing control valve 39. Preferably the central portion of the treating tower is filled with granular metal particles such as, for example, brass turnings in space 41. During the passage of the vapors and hydrochloric acid through the metal contact mass a polymerizing effect is exerted which results in the removal of substances which give gum and color-forming properties to the distillates. It is not known exactly why such compounds should exist in hydrogenated distillates but it is probable that they remain owing to the limited character of the hydrogenated reactions which affect both the sulphur content and the olefins in varying degree. Secondary reactions may also produce unsaturated sulphur compounds which tend to polymerize and affect the stability of the final product. Whatever may be the exact chemical reasons, it has been uniformly observed that the present type of treatment effects a stabilization of properties of the finished product.

The metal contact masses employed with hydrochloric acid may consist of single metals, alloys or mechanical mixtures thereof, either alone or mixed with relatively inert and preferably siliceous material such as for example, fuller's earth, clays, silica and porcelain fragments, etc. Brass turnings were mentioned in the above paragraph as an example of an alloy containing zinc representing metals above hydrogen in the electromotive series and copper as a metal below hydrogen, since favorable results have been obtained with alloys of this character. The various alternatives will each exert their own particular action on the treating reactions which will not be exactly equivalent, though similar to the actions of the other alternatively used materials.

Any liquid material including polymerized hydrocarbons and sludge reaction products from the metallic contact masses which may accumulate in lower space 43 of the treater may be withdrawn through line 44 containing control valve 45. The material still vaporous at this point, which is usually over 99% of the ingoing material, may be passed through a line 48 containing control valve 49 and through the fractionator inlet line 50 containing control valve 51, receiving additions of ammonia or alkali solutions to neutralize the hydrochloric acid and prevent corrosion of the fractionator. Fractionator 52 functions to produce an end point product and remove all traces of material boiling higher than the end point desired in the finished gasoline, such heavy liquids being withdrawn through line 53 containing control valve 54. The vapors from the fractionator pass through line 55 containing control valve 56 and are condensed during passage through a condenser coil 57 after which they flow through run down line 58 containing control valve 59 to a final receiver 60 provided with a fixed gas release line 61 containing a control valve 62 and a liquid draw line 63 containing control valve 64.

In the alternative operation using solutions of polymerizing salts such as, for example, zinc chloride, the solution is admitted to a pump 67 by way of line 65 containing control valve 66 and discharged through a line 68 containing control valve 69 to a spraying or atomizing device 70 positioned in the upper vapor space of the treater. In such cases the filling material in space 41 may comprise either granulated metals (as mentioned above in connection with the use of hydrochloric acid) or inert substances such as silica fragments, Raschig rings, etc., to break up the streams of solution and insure their intimate contact with the countercurrently ascending gases.

The vapors enter the treater through line 36 containing control valve 37, valve 35 being closed, rise against the descending solution and leave the treater by way of line 38 containing control valve 39, thence following line 46 containing control valve 47 to line 50. In these treatments hydrochloric acid and steam may also be admitted through line 33 as before in order to maintain the concentration of the treating solutions and prevent the deposition of oxychlorides.

Treatments with zinc chloride may also be conducted in substantially liquid or mixed phase by utilizing higher pressures in treater 40. Thus central space 41 may be filled with composite catalytic material such as pumice or fuller's earth mixed or saturated with zinc chloride in which case the liquid or partially liquid distillate is pumped downwardly therethrough and the total products are discharged into fractionator 52. The use of this alternative procedure will be determined by the extent of treatment found necessary to properly treat and stabilize the distillates from the first stage.

As an example of the results obtainable by the operation of the process in practice the following example is given.

A cracked naphtha produced from a California residuum and having an end boiling point of 475° F., and a sulphur content of 0.70% was subjected to the treatment of the process. The primary hydrogenating step was effected at a temperature of 700° F., and a pressure of 300 pounds per square inch using a catalyst of the following composition.

	Per cent
Molybdic acid (MoO_3'')	37.8
Nickelous oxide (NiO)	50.1
Sodium aluminate ($NaAlO_2$)	12.1

Hydrogen was added to the vapors at the rate of 1.5 pounds per barrel of liquid distillate, the consumption being approximately half of that admitted.

The gasoline-boiling range distillate produced after the first stage had a reddish color which turned to a light yellow on standing, the gum content being approximately 50 mg. by the copper dish method. The sulphur content was reduced to 0.18%.

The distillate was revaporized after a light caustic wash and subjected to a treatment with hydrochloric acid and steam at the rate of about 1 pound of 40% acid per barrel of liquid in the presence of brass turnings. The temperature employed was 350° F. and the pressure 200 pounds per square inch. After final fractionation it was found that the gasoline had a water white color which was stable under storage conditions and that the gum content had been reduced to 15 mg. The sulphur content was slightly reduced to 0.15%.

The character of the invention and the type of results obtainable by its use will be seen from a consideration of the preceding specification and single instance of results obtained, but neither

should act in a limiting sense upon its generally broad scope.

I claim as my invention:

1. A process for the treatment of hydrocarbon oil containing gasoline to refine and more particularly to desulphurize the same, which comprises subjecting said hydrocarbon oil in vapor phase to the action of hydrogen in the presence of a catalyst whereby to remove objectionable sulphur compounds, fractionating the resulting vaporous product to separate the desulphurized gasoline from the hydrogen, hydrogen sulphide, hydrocarbon gases and hydrocarbons heavier than gasoline, thereafter subjecting the separated gasoline to the action of a polymerizing agent comprising hydrochloric acid in contact with a metal to remove objectionable color and gum compounds, and recovering the thus refined gasoline as the product of the process.

2. A process for the treatment of hydrocarbon oil to refine and more particularly to desulphurize the same, which comprises subjecting said hydrocarbon oil at elevated temperature to the action of hydrogen in the presence of a catalyst whereby to remove objectionable sulphur compounds, stabilizing the resulting hydrocarbon product to separate and remove hydrogen sulphide and hydrocarbon gases, and thereafter subjecting the thus treated hydrocarbon to the action of a heavy metal salt having polymerizing properties to remove objectionable color and gum compounds.

3. A process for the treatment of hydrocarbon oil to refine and more particularly to desulphurize the same, which comprises subjecting said hydrocarbon oil at elevated temperature to the action of hydrogen in the presence of a catalyst whereby to remove objectionable sulphur compounds, stabilizing the resulting hydrocarbon product to separate and remove hydrogen sulphide and hydrocarbon gases, and thereafter subjecting the thus treated hydrocarbon to the action of a salt having polymerizing properties to remove objectionable color and gum compounds, comprising zinc chloride.

4. A process for refining hydrocarbon oil containing gasoline which comprises desulphurizing the oil by treatment thereof in vapor phase with hydrogen under conditions such as to convert sulphur compounds contained therein into hydrogen sulphide, fractionating the resulting vaporous product to separate the gasoline from the hydrogen sulphide, hydrogen, hydrocarbon gases and hydrocarbons heavier than gasoline, then eliminating gum and color forming substances from the separated gasoline by treatment with polymerizing material selected from the group consisting of hydrochloric acid in contact with metal and heavy metal salts having polymerizing properties, and recovering the thus refined gasoline as the product of the process.

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