

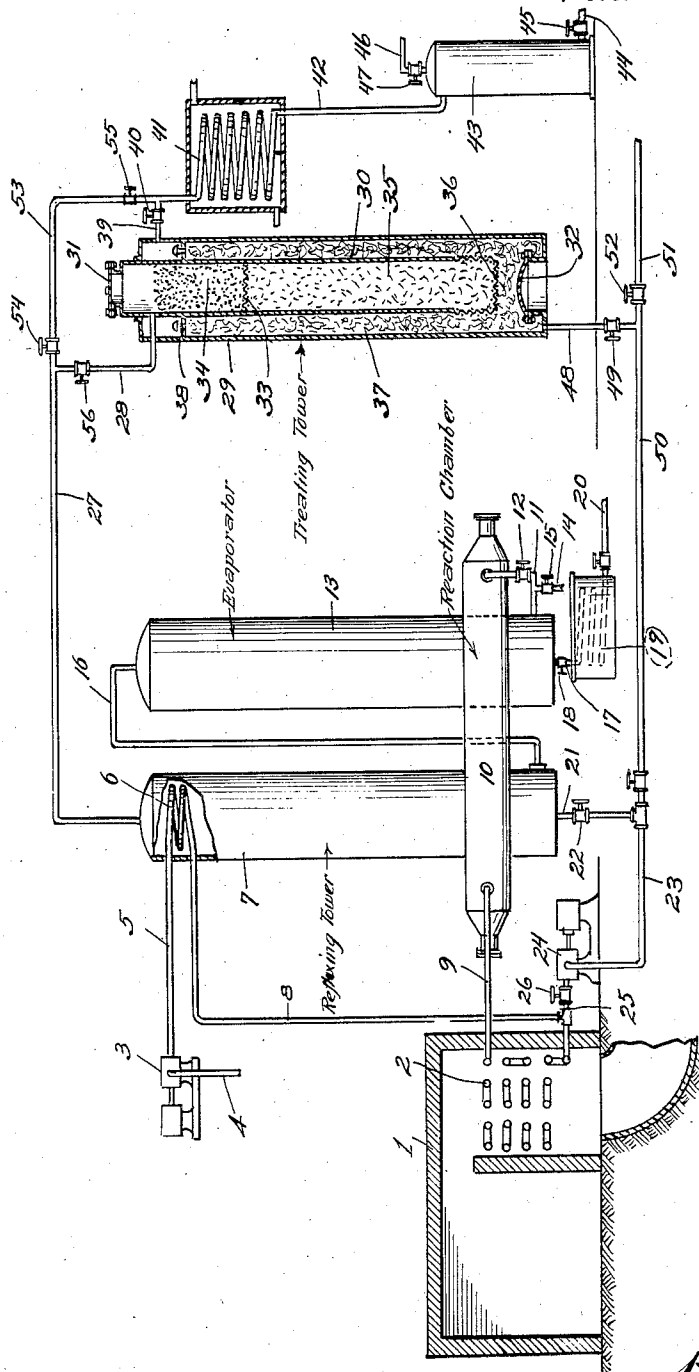
Jan. 5, 1932.

R. CROSS

1,840,158

METHOD OF TREATING HYDROCARBONS

Filed Oct. 22, 1925



Witness:

R. Hamilton

INVENTOR.
Ray Cross
BY *Thomas E. Scofield*
ATTORNEY.

UNITED STATES PATENT OFFICE

ROY CROSS, OF KANSAS CITY, MISSOURI, ASSIGNOR TO CROSS DEVELOPMENT CORPORATION, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

METHOD OF TREATING HYDROCARBONS

Application filed October 22, 1925. Serial No. 64,137.

This invention relates to improvements in a process for treating hydrocarbons, and refers more particularly to the decolorization, desulphurization and polymerization of the mixed hydrocarbons comprising gasoline together with those hydrocarbon constituents associated therewith in its manufacture.

The process, while not limited to such products, is particularly adapted to the treatment of light hydrocarbons produced by the cracking of relatively heavy hydrocarbons or of light hydrocarbons produced by the skimming of crude oils having a relatively high sulphur content. In this process the hydrocarbons are preferably treated in the vapor phase and at a temperature below the end boiling point of the oil being treated. Normally, the oil would comprise hydrocarbons having a boiling point of from below 0° F. up to 437° F. The treatment would be carried on at a temperature in which the oils exist substantially in the vapor phase although, in the case of heavier fractions, this temperature would be considerably below the boiling point temperature of these heavier fractions.

The novelty of the invention lies primarily in the treatment of relatively light hydrocarbons in successive and separate stages, the first stage comprising a treat with a metallic substance having an affinity for the sulphur compounds in the oil, and the second treating stage comprising a treat with adsorptive material such as the highly adsorbent clays found through the Western States, particularly in California, Nevada and Montana, and commercially known as "Bentonite".

Further advantages and novelty in the treatment lie in the fact that the treatment is carried on while the oil is hot but preferably at a temperature substantially below the end point boiling temperature of the oil undergoing treatment. Pressure may be required and the hydrocarbons may be in either the liquid or vapor phase or both. An additional novelty and advantage in the present process lies in the fact that the oil fractions, after polymerization or after the successive treatments with a metallic substance and an adsorptive material, are subjected to reflux-

ing and fractionation before being finally condensed.

The single figure is a diagrammatic side elevational view of the apparatus with parts in section and parts eliminated to simplify the drawing and explanation.

Referring to the drawing, at 1 is shown a furnace in which are mounted the heating tubes 2. Oil is supplied to the heating tubes by means of a pump 3 receiving the charging stock from any convenient suitable source through the pipe 4. This oil is discharged from the pump through the line 5 which is connected with a preheating coil 6 mounted in the refluxing tower 7. The oil, on discharge from the preheating coil, is directed to the heating coils through the pipe 8 where it is rapidly brought to a cracking temperature and circulated at sufficient velocity through the tubes to prevent any substantial cracking in the heating coil. The oil, on being discharged from the coil, passes through the transfer line 9 to a reaction chamber 10 which is preferably fabricated by forging from a single ingot of steel. This chamber is highly insulated to prevent loss of heat from radiation. The oil is maintained in a body in the chamber for a sufficient length of time to consummate the cracking which is initiated in the heating coil. It is also maintained at temperature and pressure conditions controlled to prevent any substantial vaporization during its passage through the chamber. It is discharged from the reaction chamber in the form of a synthetic crude which has been brought to a condition which is termed as an "equilibrium" through the discharge line 11 controlled by a valve 12. At the reduction valve 12 the pressure is reduced and the synthetic crude vaporized off in an evaporating tower 13. Steam or a cooler hydrocarbon may be introduced through a pipe 14 controlled by a valve 15.

There is sufficient contained heat in the oil during its evaporation to carry over from the top of the tower through the line 16 a considerable portion of the synthetic crude in the form of vapors. The unvaporized bottoms, which consists primarily of the heavier residual bottoms or fuel oil content of the

synthetic crude, are driven off from the bottom of the evaporator through the pipe 17 regulated by a valve 18 and, after cooling in the cooling coil 19, are discharged to storage through the pipe 20.

The overhead material passing through the line 16 is directed into the bottom of a refluxing tower which is preferably of bubble tower construction adapted to separate out the high boiling point hydrocarbons. These fractions are separated by partial condensation and gravitated to the bottom of the refluxing tower where they are drawn off through the pipe 21 regulated by a valve 22 and may be recirculated to the heating coil through the line 23 which communicates with the suction side of the pump 24 which, in turn, discharges the recycle stock through a connecting line 25 communicating with the charging line 8. A valve 26 is interposed in this line for the purpose of control. The vapors uncondensed in the refluxing tower pass over through the line 27 which has a connection 28 with the treating tower 29.

The process, up to this point, is nothing more than the high pressure cracking system such as is utilized for the treatment of petroleum hydrocarbons according to the cross cracking process. The passage of the oil vapors from the top of the refluxing tower until they have completed their travel through the treating tower comprises the invention herein involved and the connection shown between the cracking system and this method of treatment is disclosed primarily for the purpose of showing the adaptability of this type of equipment to a cracking unit and furthermore to disclose at what part of the system the treating is most advantageously interposed.

The treating tower 29 consists primarily of an outer casing in which is positioned a treating cylinder 30. This treating cylinder has an upper removable manhole plate 31, while the outer casing is closed by a lower manhole plate 32. The cylinder is divided vertically into two sections by means of a screen 33. This screen supports, in the upper part of the tower, a metallic substance designated as 34 which has an avidity for the sulphur compounds in the oil vapors. A material adapted to this purpose is copper, iron, manganese and other metallic substances having a marked affinity for the sulphur compounds. These metals may be used either in metallic form or in the form of a compound such as an oxide, carbonate, sulphide, sulphate, or in any other form that they may be handled to effectively remove the undesirable sulphur compounds from the oil vapors. Below the screen 33 is supported a column of adsorptive material 35 by means of a lower screen 36. This adsorptive material is preferably a highly adsorptive clay, such as bauxite, fuller's earth, floridin, or any

hydrous aluminum silicate having the characteristics of the highly adsorptive clays found throughout the Western States and commercially known as Bentonite. In addition to the adsorptive clays and hydrous aluminum silicates, adsorptive carbon, chemically prepared silica or any other adsorptive earthy materials may be used. These materials are capable of selectively polymerizing the objectionable, unstable, unsaturated hydrocarbons present in cracked gasoline to convert the same into compounds of higher boiling point, and the phrase "solid adsorbent polymerizing agent" used in the claims is intended to cover only such materials as have this characteristic.

Between the outer shell of the tower and the outside surface of the inner treating cylinder the tower is packed with a broken up material such as an inert packing 37 consisting of tile, metal lath or other suitable material, the purpose being to fractionate or separate out any oil existing in a liquid condition. Near the top of the tower, in the annular space between the outer shell and the inert treating cylinder, is one or more bubble trays shown diagrammatically at 38 which serve to further separate out any mechanically entrained liquid and fractionate the oil prior to its being directed to the final condensing stage.

The oil vapors are introduced to the inner cylinder through the line 28 and follow a course downwardly through the metallic compound wherein they are purified to the extent that the sulphur compounds are eliminated. After passing through the bed of metallic material and through the screen 33, they are percolated through a column of adsorptive material which decolorizes and further purifies the hydrocarbon vapors. On passing through the bottom screen, they rise in the annular space about the outside of the inner cylinder and are fractionated by being passed through a zone of packing and through the bubble tower arrangement near the top of the tower.

After this treatment they pass off through the line 39, controlled by a valve 40 to the final condensing coil 41 and thence through the line 42 to the receiving tank 43. This receiving tank is equipped with a liquid draw-off line 44 controlled by a valve 45 and a gas relief line 46 regulated by a valve 47. By means of the valves on the receiving tank, a pressure may be maintained upon the treating tower if so desired. Any liquid material separated from the vapors in the treating tower collect in the annular space at the bottom of the tower and is drawn off through the pipe 48 controlled by valve 49 and may be returned through the line 50 communicating with the pipe 23 to the heating coil in the cracking stage for recirculation through the system or it may be eliminated from the system by the line 51 controlled by the valve 52.

The treatment, of course, is continuous and two towers may be connected up with a cracking unit in order that one may be cut out of the system to be cleaned and the material regenerated while the other treating tower unit is cut in. A by-pass line 53, controlled by valves 54 and 55, serve to by-pass the tower in case the vapors passing off from the top of the refluxing tower are not to be subjected to a refined treatment such as that described. In order to cut out the tower and pass these vapors through the by-pass line, the valve 56 in the line 28 and the valve 39 in the line 40 are closed and the valves 54 and 55 in the line 53 are opened.

As a typical instance the end boiling point of the gasoline passing off from the top of the bubble tower is approximately 437° F. and these hydrocarbon vapors constitute a combination of oil fractions having a boiling range from approximately -250° F. to 437° F. All of these hydrocarbons will, however, exist together in vapor phase at the equilibrium distillation temperature, which, in this instance may range from 300° F. to 350° F. dependent upon pressure conditions on the system despite the fact that some of the heavier hydrocarbons have a boiling point above the equilibrium distillation temperature. This is due to the partial vapor pressure of these heavier hydrocarbons and the predominating proportion of the lower boiling point hydrocarbons which exert a normal vapor pressure greater than the pressure existing on the system and thereby act as carriers of the vapor having the higher boiling points,—the latter higher boiling point hydrocarbons exerting only a fractional portion of such pressure.

With reference to the particular metals available and adaptable for this purpose, copper is perhaps as cheap and as effective as any. A very useful form of copper is the copper scale as obtained from copper rolling mills. When first used this will be largely in metallic form, but on regeneration for removal of sulphur, it will be in the form of copper oxide. The particular form in which the metallic material is used does not seem to be of any great importance provided it is active in its avidity for sulphur,—therefore, it must be substantially free from sulphur compounds. When the vapor of the hydrocarbons is passed through copper or its compounds alone that gasoline is completely deodorized, largely desulphurized and passing the "doctor" and "copper corrosion" tests and is considerably improved as to its gumming properties. However, it does not have a suitable color,—being ordinarily a greenish yellow or yellow. If, now, the oil vapors are treated with a sufficient amount of clay the hydrocarbon distillate is completely bleached to a clear water-white product. It has been found, however, that if clay is first used for

bleaching followed by the metal treatment, the color is again produced. If, as described in the process herein explained, the metal or metallic compound is first used to remove sulphur and to sweeten and this treat immediately followed by a treatment of adsorptive clay, the resulting distillate is completely refined as to color, odor, sweetness and gumming properties and permanence of color in sunlight. In some cases it is advantageous to treat first with a mixture of metal compound and clay containing a large portion of metallic compound and then with a clay and fuller's earth containing a small proportion of metal compound. Treatment also may be accomplished by one composition of metal compound and clay having less than ten per cent (10%) of the metal. The disadvantage of this is that there is a limit to the number of times that the clay may be rejuvenated while there is no limit to the times the copper may be revived. Therefore, in practice it is desirable to allow the hydrocarbons to be treated first with the metal compound followed by the clay in a separate treat. This metal compound may then be roasted for example at a temperature of from 900° F. to 1500° F. to remove the sulphur. Such roasting may be accomplished in any suitable apparatus used for desulphurizing ore. A typical apparatus for this purpose is the Wedge furnace built by the Bethlehem Foundry Company, of Bethlehem, Pennsylvania.

The copper or other metal compound is the most expensive part of the treatment and therefore the cost of operation is greatly reduced by indefinitely regenerating the copper. The clay, however, is relatively inexpensive and is required in large quantities so that, while it may be regenerated as many as twenty times due to the fact that it gradually loses its activity on regeneration, it is not practical to regenerate through as many cycles. When the metallic compounds are combined with the clay, they are lost when the clay has lost its usefulness;—therefore, the need of the separate stages of treatment.

This process of refining may be applied to any type of petroleum distillate, being particularly adapted to the cross cracking process in which gasoline of the proper distilling range is made direct from the plant. In this case both the metal compound and the clay exert a polymerizing action, which results in the formation of some of the heavier fractions of the gasoline being converted into fractions too heavy to be classified as gasoline. At the same time, the treatment results in the conversion of some of the gaseous products into materials having the distilling range of gasoline. This polymerization also effectively eliminates the objectionable gum forming compounds.

While it is ordinarily most convenient to

treat these hydrocarbons in the vapor phase, the treatment is as effective in the liquid phase, using the proper sequence of metal compound following by the adsorptive clay treat and finally a stage of redistillation. The highly colored polymers and objectionable materials are removed by distillation after action by the metal compound and the clay where the treatment is effected in the liquid phase.

In the typical operation mentioned, the mixed vapor enters the tower at a temperature of approximately 330° F. so that the treatment in the tower, although in the vapor phase, is well below the end boiling point of the heavier fractions. The treatment is preferably carried on at substantially the equilibrium distillation temperature of the vaporous fractions, unless under considerable pressure. Generally, it can be said that the temperature of the mixed hydrocarbons approximates 100° F. below the end boiling point of the product desired. Furthermore, the process covers hot treatment of the oil under pressure whether in the vapor or in the liquid phase.

In actual practice it will probably be advisable to have two separate towers,—one containing the metallic material and the other the adsorptive products, as treatment in a single tower where vapors and liquid are passing from the copper to clay would tend to contaminate the adsorptive clay material with the fine particles of the metal which would defeat, to a great extent, the very purpose of the separation of the treating materials. Furthermore, it has been found that the effect of one of the treating materials may be exhausted much more rapidly than in the other and, in such case, it would be more advisable to have them in separate treating containers, with alternate receptacles of each material, in order that these alternate units could be cut in when materials become exhausted. In other words, there would be double adsorptive clay treaters connected up in series with double tower units containing the metal treating substance.

I claim as my invention:

1. The method of refining hydrocarbons, which consists in passing the same in vapor phase at substantially the equilibrium distillation temperature through a treating material comprising a metallic compound having high affinity for sulphur compounds and through a subsequent zone in which the vapors are subjected to a different treating material comprising a solid adsorbent polymerizing agent.

2. The method of refining hydrocarbons, which comprises the steps of passing the same in vapor phase through successive stages of treatment, subjecting the vapors substantially at the equilibrium distillation temperature in the initial stage to a treating

material comprising a metallic compound which has high affinity for sulphur compounds and subjecting the vapors at substantially the same temperature in a subsequent stage to a different treating material comprising a highly adsorbent inorganic polymerizing agent.

3. The method of refining hydrocarbons, which comprises the steps of passing the same in vapor phase at a temperature substantially below the highest boiling point temperature of the desired product successively through a desulphurizing stage in which a copper compound is utilized to relieve the vapors of their objectionable sulphur content and a separate polymerizing stage in which the vapors are subjected to treatment with a highly adsorptive inorganic material having polymerizing qualities.

4. The method of refining cracked hydrocarbons which comprises passing the same in vapor phase at a temperature substantially below the highest boiling point temperature of the desired product through successive treating zones of different treating materials, the material of the initial zone comprising a bed of metallic compound and the material of the second zone comprising a bed of a solid adsorbent polymerizing agent.

5. The method of refining cracked hydrocarbons, which comprises passing the same in vapor phase at a temperature substantially below the highest boiling point temperature of the desired product through successive zones of different treating materials, the material of the initial zone comprising a bed of metallic compound having high affinity for sulphur compounds and the treating material of the second zone comprising a bed of a solid adsorbent polymerizing agent, the respective treating stages being maintained at a temperature approximately 100° F. less than the end boiling point of the final product.

6. The method of refining hydrocarbons which comprises passing the same in vapor phase substantially at the equilibrium distillation temperature through successive zones of different treating materials, the material of the initial zone comprising a bed of metallic compound and the material of the second zone comprising a bed of a solid adsorbent polymerizing agent.

7. The method of refining hydrocarbons which comprises passing the same in vapor phase at substantially the equilibrium distillation temperature through successive zones of different treating materials, the material of the initial zone comprising a metallic compound having high affinity for sulphur compounds and the material of the second zone comprising a solid adsorbent polymerizing agent, and fractionating the vapors thus treated.

8. The method of refining hydrocarbons which comprises passing the same in vapor

phase at substantially the equilibrium distillation temperature through successive zones of different treating materials, the material of the initial zone comprising a metallic compound having high affinity for sulphur compounds and the material of the second zone comprising a solid adsorbent polymerizing agent, and scrubbing the vapors thus treated.

9. The method of refining hydrocarbons which consists in passing the same in vapor phase at substantially the equilibrium distillation temperature through successive zones of different treating materials, the treating material of the first zone comprising a copper compound and the treating material of the second zone comprising fuller's earth.

10. The method of refining hydrocarbons which consists in passing the same in vapor phase at substantially the equilibrium distillation temperature through successive zones of different treating materials, the treating material of the first zone comprising a copper compound and the treating material of the second zone comprising fuller's earth, and fractionating the vapors thus treated.

11. The method of refining hydrocarbons which consists in passing the same in vapor phase at substantially the equilibrium distillation temperature through successive zones of different treating materials, the treating material of the first zone comprising a copper compound and the treating material of the second zone comprising fuller's earth, and scrubbing the vapors thus treated.

12. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at a temperature approximately 100° F. below the end boiling point thereof under the pressure conditions maintained, through successive zones of treating materials, the treating material of the first zone comprising a metallic compound having high affinity for sulphur compounds and the material of the second zone comprising a solid adsorbent polymerizing agent.

13. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at a temperature approximately 100° F. below the end boiling point thereof under the pressure conditions maintained, through successive zones of different treating materials, the treating material of the first zone comprising a copper compound and the treating material of the second zone comprising fuller's earth.

14. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at a temperature approximately 100° F. below the end boiling point thereof under the pressure conditions

maintained, through successive zones of treating material, the treating material of the first zone comprising a metallic compound having high affinity for sulphur compounds and the material of the second zone comprising a solid adsorbent polymerizing agent, and fractionating the hydrocarbons thus treated.

15. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at a temperature approximately 100° F. below the end boiling point thereof under the pressure conditions maintained, through successive zones of treating materials, the material of the first zone comprising a copper compound and the material of the second zone comprising fuller's earth, and fractionating the hydrocarbons thus treated.

16. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at temperatures between 300° and 350° F., through successive zones of different treating materials, the treating material of the initial zone comprising a metallic compound having affinity for sulphur compound and the material of the second zone comprising a solid adsorbent polymerizing agent.

17. The method of refining hydrocarbons of gasoline boiling range which comprises passing the same in vapor phase under super-atmospheric pressure and at temperatures ranging from 300° to 350° F., through successive zones of different treating materials, the treating material of the initial zone comprising a copper compound and the treating material of the subsequent zone comprising fuller's earth.

18. The method of refining hydrocarbons of gasoline boiling range which consists in passing the same in vapor phase under super-atmospheric pressure and at temperatures between 300° and 350° F. through successive zones of different treating materials, the treating material of the initial zone comprising a metallic compound having affinity for sulphur compounds and the material of the second zone comprising a solid adsorbent polymerizing agent, and fractionating the hydrocarbons thus treated.

19. The method of refining hydrocarbons of gasoline boiling range which comprises passing the same in vapor phase under super-atmospheric pressure and at temperatures ranging from 300° to 350° F., through successive zones of different treating materials, the treating material of the initial zone comprising a copper compound and the treating material of the subsequent zone comprising fuller's earth, and fractionating the hydrocarbons thus treated.

ROY CROSS.