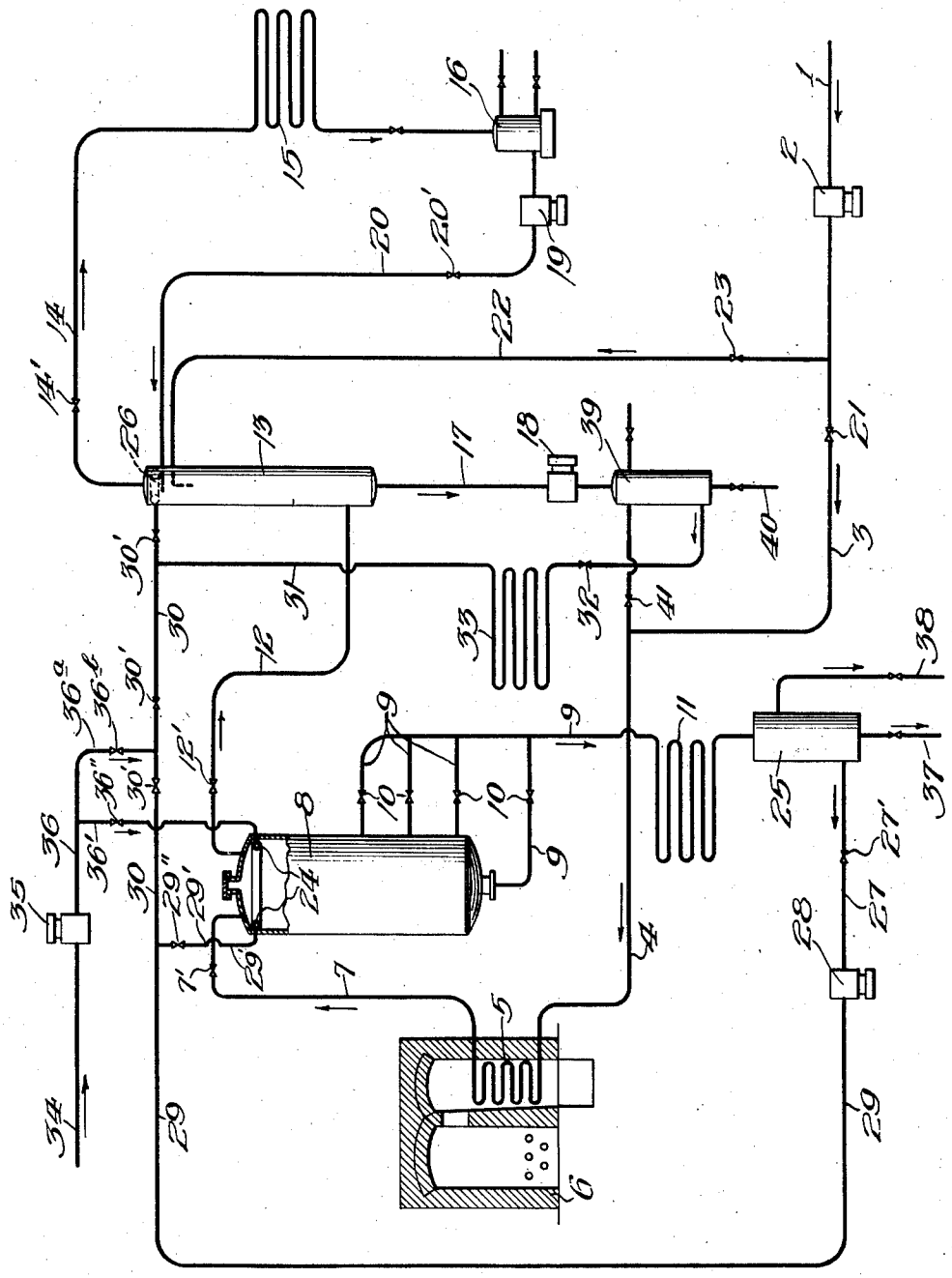
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HYDROCARBON OIL CONVERSION

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HYDROCARBON OIL CONVERSION

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This invention relates to improvements in the art of converting hydrocarbon oils into hydrocarbons of greater value, and will be fully understood from the following description. More specifically, it is directed to methods whereby the corrosion of the apparatus ordinarily taking place during such conversion may be prevented or greatly minimized.

As a feature of this invention, a liquid film is interposed between the hot reacting substances and the walls of the apparatus used, such film serving as a protective non-corrosive coating for the surfaces usually attacked, and greatly prolonging the life of the apparatus.

As a further feature of the invention, the liquids employed to form the protective film may comprise products of the cracking process, or may be entirely foreign substances of suitable characteristics. In either case, they may be separated and recovered for further use after passage over the surfaces to be protected.

In the operation of cracking processes, a source of expense and danger is the eating away of the apparatus at the high temperatures employed. This corrosion has been found to take place to some extent with all oils and with most oils, especially those of high sulphur content, is of considerable magnitude. Moreover, it has been noted that this eating away takes place within the apparatus to a much greater extent on those portions of the surface exposed to the oil vapors than on those remaining covered with liquid oil. Why this should be the case is not known, but the phenomenon is commonly observed. It may be that the greater molecular freedom of motion in the vapors is responsible for the disparity, or that the most corrosive constituents of the oils are very volatile and are not usually retained in the non-vaporized oil.

Whatever be the real cause of this corrosion where walls are exposed to hydrocarbon vapors the results necessitate premature abandonment of the apparatus so exposed because of the thinning and weakening of portions of the walls. As replacement of the heavy metal and piping used in cracking operations is very expensive, it is most desirable to prevent or minimize this corrosion which may otherwise render the equipment unsafe to use in a relatively short time.

With the present tendency towards increased cracking in the vapor phase, this problem has become more acute. I propose, therefore, to protect the walls of cracking apparatus subject to corrosion by maintaining immediately adjacent the exposed surface, a liquid film whereby the corrosive vapors are prevented from attacking the surface. The liquid film may be of any suitable substance relatively non-volatile at the temperatures employed and may, in addition to its corrosion inhibiting features, possess other desirable characteristics such as catalytically promoting the cracking reaction.

The invention may be more fully understood by reference to the attached drawing, which is in no wise to scale and entirely diagrammatic. In the drawing, raw oil to be treated may be introduced through line 1 to pump 2 which delivers it through lines 3 and 4 to the oil heating coil 5 mounted in any suitable furnace 6 wherein the oil is raised to the desired cracking temperature and passed through transfer line 7, in which may be interposed valve 7', to separating or reaction chamber 8. There vapors separate from the unvaporized products which later are withdrawn through one or more of the lines 9, controlled by valves 10, and sent through a cooler 11 to storage or subjected to further treatment as desired.

The vapors evolved in chamber 8 pass out overhead through vapor line 12, in which may be interposed valve 12', to dephlegmator 13, where they are fractionated and/or dephlegmated, the sufficiently converted material passing off through line 14, in which may be interposed valve 14', to condenser 15 and receiver 16 of any conventional design. Insufficiently converted material entering dephlegmator 13 may be condensed and returned through line 17 and hot oil pump 18 to the heating coil 5 for retreatment. Regulated quantities of the pressure distillate from receiver 16 may be returned to the top of dephlegmator 13, by means of pump 19, in which may be interposed valve 20', and line 20, to regulate the temperature therein. Further regulation of dephlegmator 13 may be secured by diverting all or a portion of the raw charging stock from line 3 by means of valve 21, and passing it through line 22, controlled by valve 23, into dephlegmator 13 where it condenses a portion of the ascending vapors and passes to the heating coil with the reflux condensate.

Within chamber 8 may be positioned adjacent the sides at the top of the wall thereof a perforated ring or annular trough 24, adapted to distribute liquid against the walls of the chamber in such manner that it will flow downward maintaining said walls covered with a thin film of the liquid. The protecting liquid may be drawn off at the bottom of the chamber 8, with the non-vaporized oil and separated therefrom in tank 25, if desired. A similar perforated annular ring

or trough 26 may be positioned in the top of dephlegmator 13, functioning in a like manner to distribute a liquid film over the sides of the dephlegmator.

In one embodiment of this invention, the material introduced into chamber 8 to form the liquid film may be a part or all of the residual oil withdrawn from chamber 8 through line 9 and cooler 11, which may be diverted from tank 25 through line 27, valve 27', and pump 28 which returns it through line 29 and branch 29', controlled by valve 29'', to annular ring 24 in chamber 8 and/or through line 30 and valves 30' to ring 26 in dephlegmator 13. This residual oil when introduced at the top of the elements 8 and 13, readily flows down the sides, forming a film over the walls which blankets and protects said walls from the corrosive action of the highly heated vapors to which they are otherwise exposed. In addition to lessening corrosion by preventing most of the vapors from coming in contact with the steel surfaces, the residual oil also acts to prevent corrosion by maintaining the walls at a lower temperature than that of the vapors thereby further lessening the corrosion rate. Since residual oil consists usually of hydrocarbons of high boiling point, vaporization in its passage down the walls of the chamber will be small. If, however, as is frequently the case, some lower boiling fractions have been entrained within the residual oil drawn off through line 9, these lower boiling fractions may be liberated from the film by vaporization and passed to dephlegmator 13.

In a similar manner, a portion of the reflux condensate from pump 18 may be introduced through line 31, valve 32 and cooler 33 into spreader ring 26 in dephlegmator 13 and flowed down the walls thereof to prevent the contact and consequent corrosive effect of the oil vapors undergoing fractionation and/or dephlegmation therein.

In another embodiment of my invention, an extraneous high boiling liquid of a stable non-corrosive character at the temperatures within the cracking apparatus, may be introduced through line 34, pump 35, line 36, branch 36' and valve 36'' to the spreader ring 24, whereby it is distributed over the chamber walls in a manner similar to that when residual oil from the system is used. This liquid material, after flowing down over the walls of chamber 8 may be withdrawn with the unvaporized oil through lines 9 and cooler 11 to the tank 25. There it may be separated by gravity from the residual oil and returned through line 27, pump 28 and line 29, as described for the return of residuum. Or, the extraneous liquid may be separated from the residual oil in tank 25 and be withdrawn from the system through line 37. The residual oil may be drawn off through line 38. It is obvious that the relative positions of the lines 27, 37 and 38 may be varied depending upon the extraneous material used and the residual oil produced.

A branch 36*a* of line 36, controlled by valve 36*b*, may also feed the extraneous liquid through line 30 to the spreader ring 26 when it is desired to use an extraneous liquid in the dephlegmator. In this case, the liquid may be removed from the reflux condensate leaving dephlegmator 13 through line 17 in a separator 39 and withdrawn through line 40, or returned to spreader ring 26 through line 31, valve 32 and cooler 33. If desired, the separator 39 may be dispensed with and the extraneous material pumped through the heating coil 5 with the body of oil undergoing treatment and removed at separator 25 along with the anti-corrosion liquid introduced into chamber 8.

Or, the liquid introduced may comprise a molten metal or salt or any similar refractory material of high boiling point. This corrosion-preventing-fluid may also be chosen to secure other benefits such as a catalytic effect within the chamber. One substance known to give that effect is aluminum chloride. The use of a catalytic material to make up this film may further decrease the rate of corrosion by lowering the temperature necessary to secure a given degree of reaction with the system.

Additional advantages other than those dependent purely on the cracking reaction may follow from the use of a suitable film of liquid in this invention. For example, with the addition of suitable heating means and the use of molten lead or lead compounds as the film-forming liquid very desirable anti-knock characteristics may be imparted to the motor fuel produced through the formation of small quantities of organic lead derivatives. Such a film may also produce a marked desulphurizing effect in the vessel in which it is used, decreasing the extent of corrosion in the balance of the system and lessening the refining and treating subsequently required on the products of the system.

It will be noted that in addition to preventing corrosion and its other benefits, this invention has the further advantage of maintaining the walls of the cracking apparatus at a somewhat lower temperature than would be possible except for the insulating effect of the interposition of this film. Since the strength of steel decreases with increase of temperature and very rapidly at the higher temperatures, the use of a non-corrosive film increases the resistance and tensile strength of the walls, and, therefore, safety of operation.

This invention will be found to have especially marked advantages in operations carried on in the vapor phase, or of the so-called low level type where only a small portion of the apparatus is in contact with liquid oil and a relatively large portion exposed to the action of the vapors.

A further advantage may be found, particularly in the reaction chamber, in that the downward flow of the non-corrosive film exerts a washing action, lessening the tendency of sufficiently converted hydrocarbon particles to adhere to the sides of the chamber and thereby remain at the elevated cracking temperature too long with resultant conversion into excess coke and sludge. Further, if any such particles do adhere to the walls of the chamber, the lower temperature of the walls will greatly retard this polymerization and excessive coke formation.

The liquid introduced into dephlegmator 13 will, to some extent, control the end temperature therein and may enable the recirculation of less pressure distillate. It may also act as a shock absorber between the temperature within the dephlegmator and that of the surrounding atmosphere, decreasing the intensity with which quick variations of the latter may affect the inner temperature.

By controlling the temperatures of the cooling coils 11 and 33, and by regulating the pre-heating of the extraneous liquid, if such be used, the cooling effect exerted within the system by the use of the non-corrosive film, may be varied as desired. The rate of introduction and hence the velocity

of flow of the film may also be regulated by control of the pumps 28 and 35 and the valves 32 and 41.

Although the illustrations given have only shown the introduction of a film-forming liquid into two conventional units of a cracking process, i. e., the reaction or separating chamber and the dephlegmator, the formation of such a film is contemplated wherever corrosion from vapors is particularly marked, or where the apparatus is especially expensive to replace. From the foregoing description methods of forming such a corrosion inhibiting film will be apparent to those skilled in the art and the use of such a film in any apparatus is well within the scope of this invention.

It will be apparent that this invention provides a simple means for preventing the corrosion ordinarily incident to cracking and that by the choice of a proper agent to compose the film, the cracking reaction may at the same time be assisted, and other valuable results obtained.

The liquid introduced through lines 34 and 29 may be cold (atmospheric temperature or below) or may be preheated, but it is preferably below the temperature existing in the part of the apparatus to which it is introduced.

I have illustrated and described the element 13 as being a fractionating column or dephlegmator. It is to be understood that the illustration is diagrammatic. The element 13 may be a dephlegmator, fractionating tower, bubble tower, reflux condenser or similar vessel. I have also illustrated the ring 26 as being disposed immediately adjacent the upper end of the element 13. Where the element 13 is provided with pans, baffles or the like, the ring may be dropped down to a point below the lower pan or baffle if desired. In practical use and operation, a great deal of corrosion takes place in the lower half of the element 13.

I claim as my invention:

1. A process which comprises subjecting hydrocarbon oil to heat in a tube, discharging said heated oil into an enlarged chamber where separation of vapors from non-vaporous products of reaction occurs, introducing to said enlarged chamber a liquid substantially non-volatile at the temperatures prevailing therein and causing same to flow downwardly as a continuous film interposed between said vapors and the wall of said enlarged chamber with which the vapors normally contact, said film being formed of a liquid other than the oil being charged to the process.

2. A process which comprises subjecting hydrocarbon oil to heat in a tube, discharging said heated oil into an enlarged chamber where separation of vapors from non-vaporous products of reaction occurs, introducing to said enlarged chamber a liquid substantially non-volatile at the temperatures prevailing therein and causing same to flow downwardly as a continuous film interposed between said vapors and the wall of said enlarged chamber with which the vapors normally contact, said liquid being introduced at a temperature below the temperature existing within said enlarged chamber at the point of introduction of said liquid and comprising a material other than the oil being charged to the process.

3. A process which comprises subjecting hydrocarbon oil to heat in a tube, discharging said heated oil into an enlarged chamber where separation of vapors from non-vaporous products of reaction occurs, introducing a liquid to said enlarged chamber and causing same to flow downwardly as a continuous film interposed between said vapors and the wall of said enlarged chamber with which the vapors normally contact, said liquid comprising a hydrocarbon oil other than the one being charged to the process and which is substantially non-volatile at the temperatures existing in the enlarged chamber at the point at which it is introduced.

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