Feb. 3, 1942. F. R. RUSSELL 2,271,955

METHOD AND APPARATUS FOR PREVENTION OF FORMATIONS IN TRANSFER LINES

Filed June 17, 1939 2 Sheets-Sheet 1

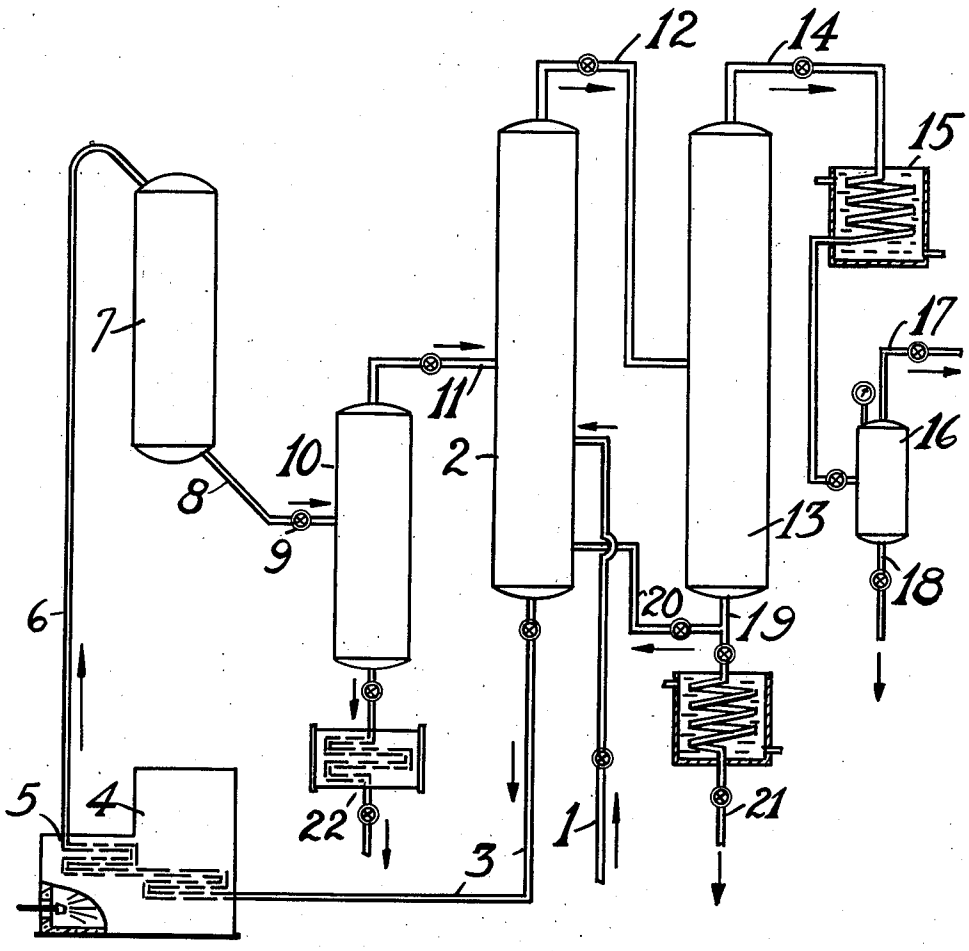


FIG. - 1

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METHOD AND APPARATUS FOR PREVENTION OF FORMATIONS IN TRANSFER LINES

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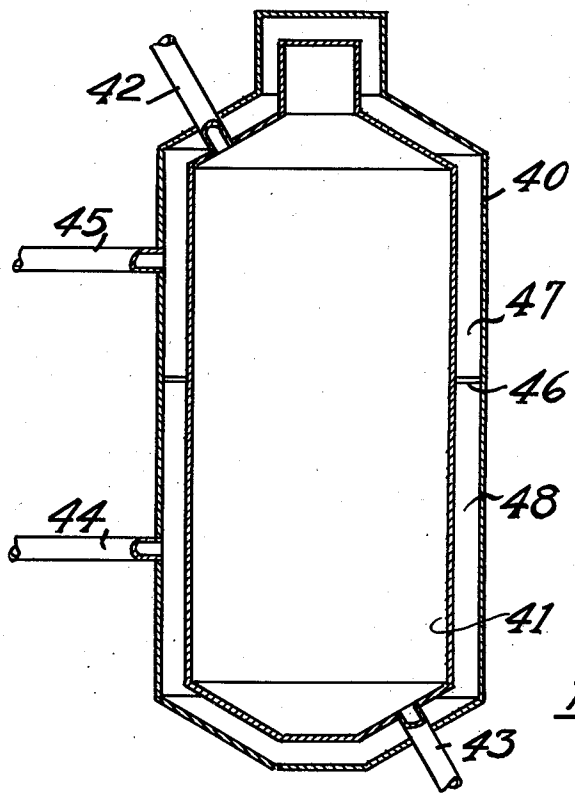


FIG. -3

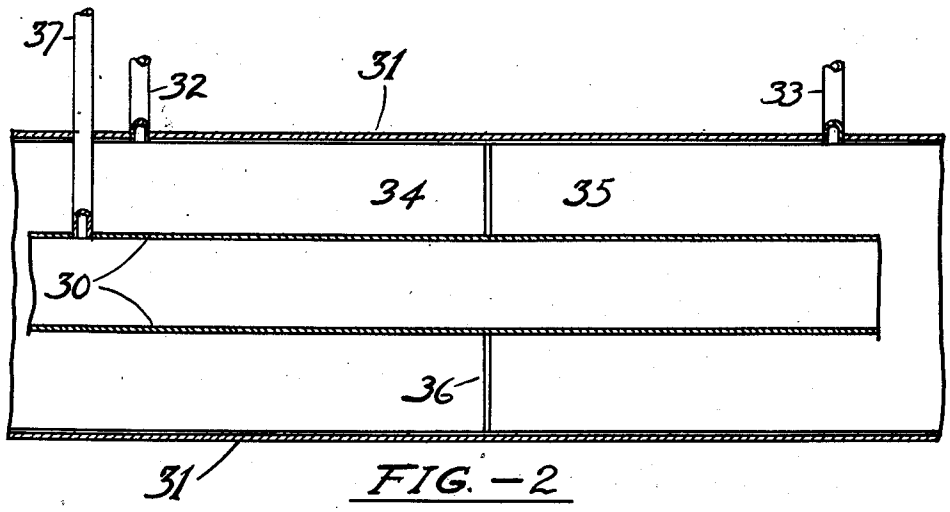


FIG. -2

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UNITED STATES PATENT OFFICE

2,271,955

METHOD AND APPARATUS FOR PREVENTION OF FORMATIONS IN TRANSFER LINES

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Application June 17, 1939, Serial No. 279,636

6 Claims. (Cl. 196—47)

The present invention relates to the prevention of formations in transfer lines and the like. The invention is directed to the reduction and elimination of deleterious coke and tar formations in petroleum oil transfer lines, heating tubes, and reaction vessels. The invention comprises processing oils in a metallic vessel concentrically disposed within a hydrogen filled metallic jacket. The invention further comprises a hydrogen filled jacket surrounding any or all of the tubes and vessels containing the reaction products which for any reason are subject to the deposition of coke or tarry materials upon their surfaces. The invention is particularly directed to transferring, heating or reacting petroleum hydrocarbons in concentrically disposed lines or in concentrically disposed reaction vessels in which hydrogen gas is maintained in an area segregated from said petroleum hydrocarbons. The concentrically disposed tubes or vessels comprise a hydrogen permeable metallic vessel disposed preferably within a hydrogen filled copper-lined metallic jacket.

The present invention is particularly applicable in processes in which petroleum oils are subjected to elevated temperatures and pressures, as for example, in the conversion of petroleum oils into relatively higher boiling and into relatively lower boiling stocks. In these oil cracking processes, the feed material is subjected to various temperature and pressure conditions for various time periods which are usually measured in terms of yield per unit throughput, hereinafter termed "conversion per pass." These various variable factors are optimumly adjusted and, to a large extent, are functions of the particular feed material being processed and upon the yields and quality of the products desired. It has been found that the capacity, yields and operating conditions of petroleum oil cracking operations are limited by the tendency of the oil being treated to form deleterious coke and tarry formations. The formation of the coke and tar usually occurs upon the surfaces of the reaction chambers and in the tubes in which the oil is heated to the desired temperatures, as well as in the tubes carrying the oil through the cracking unit. Various processes and equipment have been employed in an effort to eliminate and reduce coke formations. For instance, it has been suggested that the oil being treated be passed through a porous air or oxygen permeable treating tube or vessel disposed concentrically within a steel outer tube or vessel and that air or oxygen be maintained in the area between the respective tubes or vessels under sufficient pressure to cause the air or oxygen to permeate through the porous wall of the inner tube or vessel. The gas thus may form substantially a gas wall between the liquid being treated and the wall of the inner tube or vessel, or may serve to oxidize any coke which forms. Processes of this character have not been entirely successful due to the inherent difficulties in the manufacture of satisfactory air and oxygen permeable porous tubes or vessels having necessary strengths and wearing qualities.

I have now discovered a process and apparatus for carrying it out by which these difficulties are overcome, resulting in improved operating efficiencies and greater yields of higher quality products. The process of my invention may be readily understood by reference to the attached drawings illustrating one modification of the same. For purposes of illustration I have applied my invention to a conventional petroleum oil cracking unit.

Figure 1 shows a diagrammatic flow plan of a normal cracking operation. Figure 2 is a sketch illustrating a suitable tube construction in accordance with my invention, while Figure 3 illustrates a reaction chamber or soaking drum constructed in accordance with the present invention.

Referring specifically to Figure 1, it is assumed that the feed oil is a petroleum gas oil fraction boiling in the range from about 400° F. to 700° F. The fresh feed oil is introduced by means of feed line 1 into the bottom of primary bubble tower 2. The feed, together with cycle oil, is withdrawn from the bottom of primary bubble tower 2 and introduced into furnace 4 by means of line 3. Furnace 4 is designed to secure optimum heat transfer as the feed stock flows through tubes 5 in the respective sections and to bring the oil up to the desired temperatures. The total feed is withdrawn from furnace 4 by means of line 6 and passed into soaking drum or reaction chamber 7 in which the oil is held for an additional time under cracking conditions. The cracked oil is withdrawn from reaction drum 7 by means of line 8 and passed through pressure release valve 9 into evaporator 10. The flashed vapors pass overhead from evaporator 10 through line 11 into primary bubble tower 2, while tar or fuel oil of the desired gravity is removed as a bottoms from evaporator 10 by means of line 22. Cycle stock accumulates in the bottom of primary bubble tower 2, while vapors pass overhead by means of line 12 into

secondary bubble tower 13. The temperature at the top of tower 13 is controlled so as to produce an overhead distillate of the desired end point which is removed by line 14 and condensed in cooler 15. Fixed gas and uncondensed hydrocarbon vapors are separated from the condensate in distillate drum 16 and removed by means of line 17, while the condensed distillate is removed by means of line 18. Heating oil may be withdrawn from the bottom of tower 13 by means of line 19 and may be recycled, if desired, through line 20 or withdrawn by means of line 21.

Figure 2 illustrates in detail the tubes or transfer lines of the present invention as applied to tubes and lines 3, 5, 6, and 8 of Figure 1. It is to be assumed that any number of tubes may be employed and arranged in any desirable manner.

All of the tubes, vessels, and transfer lines may be of the type of the invention. In general, however, the tubes, vessels, and transfer lines of the present invention are employed only where coking difficulties are critical. The tube of the present invention as illustrated in detail in Figure 2 comprises a hydrogen permeable main tube 30 and a concentrically disposed jacket tube 31. Jacket tube 31 preferably comprises a copper tube or a copper-lined steel tube. Tube 30 preferably comprises a copper and aluminum-free metallic tube, preferably a steel tube. Suitable means are employed for maintaining hydrogen at any desirable pressure in the area between the jacket tube 31 and the main tube 30. Hydrogen is injected into this area by means of hydrogen inlets 32 and 33. The area between tubes 30 and 31 may be divided into numerous sections. As illustrated in Figure 2, the area between the respective tubes is divided into sections 34 and 35 by means of baffle 36. The hydrogen pressure may be adjusted in the respective areas to give the necessary or desirable rate of hydrogen penetration. The hydrogen within these areas is held under sufficient pressure to cause the hydrogen to permeate through the hydrogen permeable metallic tube 30 into the oil being processed. If desired, heating may be secured by direct combustion by the introduction of air or nitrogen-containing gas into tube 30 by means of line 37.

Figure 3 illustrates in detail a reaction chamber or soaking drum constructed in accordance with the present invention. This chamber comprises a jacket vessel 40 and a main hydrogen permeable vessel 41. The oil being processed is introduced into reaction vessel 41 by means of line 42 and withdrawn by means of line 43. The inner reaction vessel 41 comprises preferably a copper and aluminum-free metallic vessel and is preferably a steel vessel. Outer vessel 40 comprises a metallic vessel, preferably a copper-lined, steel vessel. Means 44 and 45 are provided for introducing hydrogen at the desired pressure into the area between the vessels 40 and 41. The area between vessels 40 and 41 may be subdivided into various sections. As illustrated, the area between the vessels is divided into areas 47 and 48 by means of baffle 46. The hydrogen pressure may be adjusted in the respective areas to give the necessary or desirable rate of hydrogen penetration through the wall of vessel 41 in each subdivision.

The process of the present invention may be widely modified. It is to be understood that it may readily be applied to processes other than petroleum oil cracking operations.

The pressure maintained on the hydrogen within the area between the respective concentric lines or vessels will vary widely and will be a function of temperature, the wall thickness of the inner metallic vessel, the pressure of the oil within said vessel, and the amount of hydrogen desired to permeate into the oil within said vessel.

In general, when using inner steel vessels having a wall thickness of from three-eights to five-eighths inches, it is preferred to maintain the hydrogen at a pressure of from one to ten atmospheres above the pressure of the material in the inner tube. However, if only a relatively small amount of hydrogen is desired to permeate into the inner tube, the hydrogen pressure may be equivalent to, or even somewhat lower than the pressure within the inner tube.

The outer jacket is preferably a cupreous-lined steel tube or vessel. However, other metals having the property of being impermeable to hydrogen may be used, as for example, aluminum. The cupreous lining may be of relatively small thickness, as for example, one-sixteenth to one-eighth inch. The thickness of the copper-lined jacket steel tube or vessel is sufficient to safely withstand operating conditions and pressures. For the sake of economy, the elimination of the copper lining in certain operations might be permissible.

In order to illustrate the present invention, the following data are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

The following data clearly illustrate the advantage of the applicant's invention with respect to the control of the permeation of hydrogen:

Hydrogen in ccs. per square centimeter per second for 1 mm. thickness at 1 atmosphere of pressure

Metal	0° C.	500° C.	1000° C.
Iron	6×10^{-6}	1×10^{-4}	1×10^{-3}
Copper	4×10^{-15}	1×10^{-6}	1×10^{-4}
Aluminum	2×10^{-23}	2×10^{-7}	Melts at 659° C.

Example 2

Petroleum oil when passed under cracking conditions through steel heating tubes, transfer lines, and reaction chambers of 0.5 inch in thickness, said tubes, transfer lines and reaction chambers being jacketed with cupreous lined steel tubes will absorb the following amount of hydrogen from the area between the respective vessels under the following conditions:

Temp., ° F.	Differential pressure	Inner steel wall thick.	Hydrogen cc./min./sq. ft. surface	
			To oil	To atmos.
	Atmosphere			
1,000° C.	1	.5	4.40	0
500° C.	1	.5	0.44	0
500° C.	50	.5	3.10	0

The process of the present invention is not to be limited by any theory or mode of operation, but only by the following claims in which

it is desired to claim all novelty in so far as the prior art permits.

I claim:

1. A process for maintaining hydrocarbons under conditions of temperature and pressure which normally cause deposition of carbonaceous material, which comprises passing the hydrocarbons through an inner zone having an imperforate hydrogen-permeable wall, supplying heat to the hydrocarbons, and maintaining hydrogen under sufficient pressure in an outer zone spaced from the inner zone by said wall to cause substantial flow of hydrogen through said hydrogen-permeable wall of said inner zone into the hydrocarbons passing through said inner zone to substantially eliminate the deposition of carbonaceous material therein.

2. A process for maintaining hydrocarbons under conditions of temperature and pressure which normally cause deposition of carbonaceous material, which comprises passing the hydrocarbons through an inner zone having an imperforate hydrogen-permeable wall substantially free of aluminum and copper, maintaining hydrogen under sufficient pressure in an outer zone spaced from said inner zone by said hydrogen-permeable wall and having a substantially hydrogen-impermeable outer wall to prevent passage of hydrogen therethrough to cause substantial flow of hydrogen through said hydrogen-permeable wall of said inner zone into the hydrocarbons passing through said inner zone to substantially eliminate the deposition of carbonaceous material therein.

3. A process in accordance with claim 2 in which said outer zone is lined with a substantially hydrogen-impermeable metal selected from the group consisting of aluminum and copper.

4. A process for converting petroleum hydrocarbons into relatively lower boiling and into relatively higher boiling constituents under conditions which normally cause deposition of carbonaceous material in the heating and conveying means, comprising passing said hydrocarbons through an inner zone having an imperforate hydrogen-permeable wall and substantially free of metals of the class consisting of copper and aluminum under temperature and pressure conditions to effect cracking of the hydrocarbons, maintaining hydrogen under sufficient pressure in an outer zone spaced from and surrounding said inner zone and having a lining substantially hydrogen-impermeable, said hydrogen being under sufficient pressure to cause the hydrogen to pass through said hydrogen-permeable wall and pass into said hydrocarbons being converted in said inner zone to substantially eliminate carbonaceous deposition therein.

5. A process in accordance with claim 4 in which said outer zone is lined with a metal selected from the group consisting of aluminum and copper.

6. Apparatus adapted for use with hydrocarbons heated to elevated temperatures including a tubular metallic vessel concentrically disposed within and spaced from an outer tubular jacket vessel, said inner metallic vessel having an imperforate hydrogen-permeable steel wall, means for maintaining hydrogen under sufficient pressure in the space between said metallic vessel and said jacket vessel to effect passage of hydrogen through said permeable wall and into said metallic vessel to substantially eliminate carbonaceous deposition in said metallic vessel when heating hydrocarbons to elevated temperatures, said outer jacket vessel being lined with a metal selected from the class consisting of copper and aluminum to prevent passage of hydrogen therethrough.

FRANCIS R. RUSSELL.