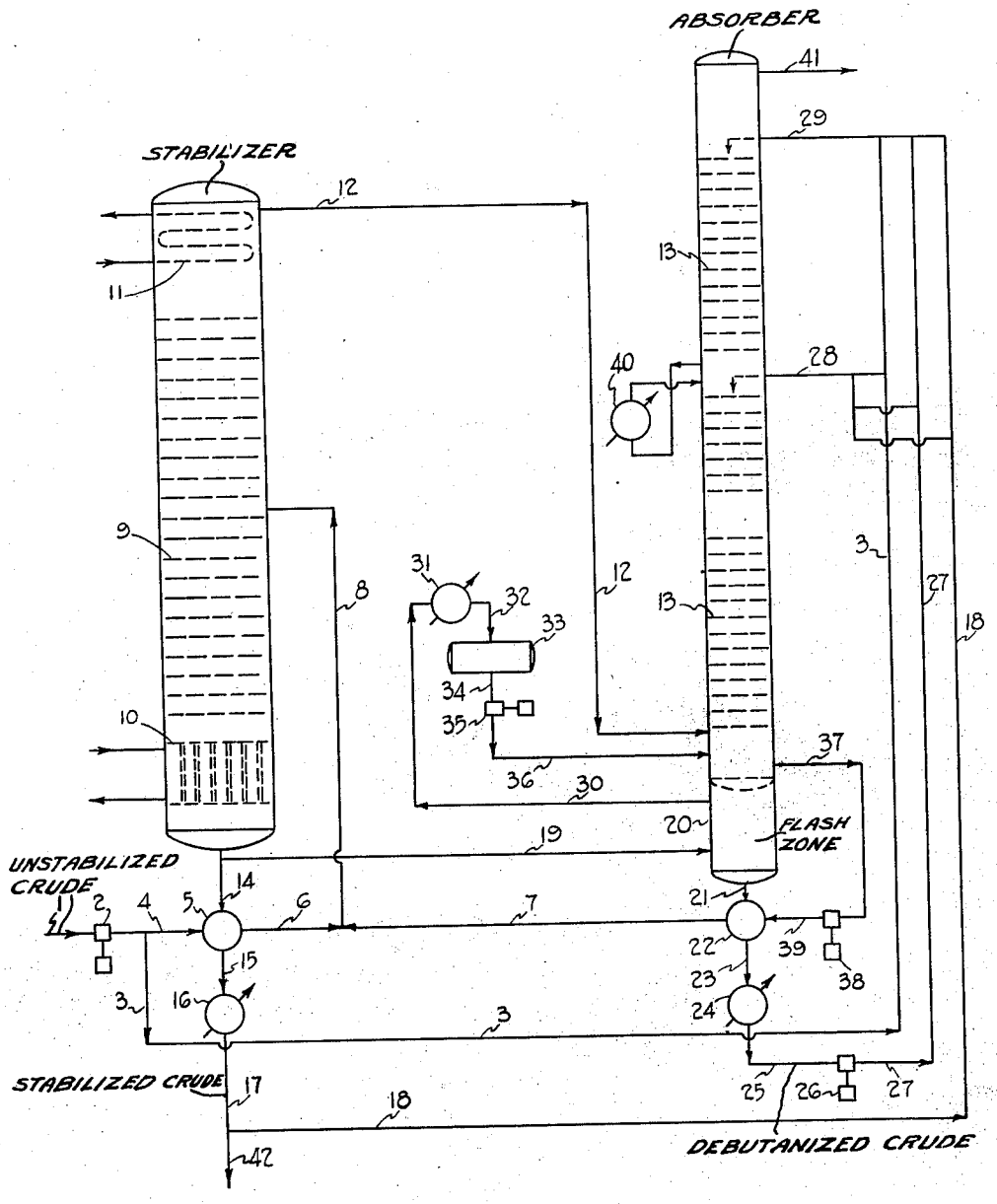
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METHOD OF STABILIZING CRUDE PETROLEUM

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METHOD OF STABILIZING CRUDE PETROLEUM

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This invention relates, in general, to the stabilization of crude petroleum for the removal therefrom by fractional distillation of dissolved, normally gaseous hydrocarbons, the presence of which causes excessive losses by evaporation during the storage and shipment of the crude.

In one respect the invention relates, more particularly, to the stabilization of crudes containing potentially corrosive impurities.

A general requirement for satisfactory stabilization of crude petrolum is that propane and lighter hydrocarbons be removed substantially completely. The substantially complete removal of propane is normally attended by the removal of more or less of the butane content of the crude because of the closely related boiling points of these two compounds. For many purposes, it is highly desirable to retain a substantial proportion of the butane originally present in the crude, and this invention is particularly concerned with a stabilization process for accomplishing this result.

The known methods of stabilizing crude with substantial retention of butane employ a simple fractionating system, from which propane and lighter hydrocarbons are withdrawn as an overhead product. Some of the butane content is allowed to pass overhead also, as the retention of more than 90% of the butane in the crude makes for high equipment and operating costs, and is seldom economically justified. Stabilizer overhead vapors are passed to a water cooled condenser, and a relatively high pressure is maintained on the system to enable the condensation of a liquid for reflux consisting largely of propane at a temperature approaching that of the cooling water. At the same time the stabilizer bottoms are reboiled at a temperature high enough to drive out all the propane at the relatively high pressure maintained on the system.

Depending upon the quantities of light hydrocarbons present in the crude, previously proposed stabilizing systems have involved pressures of 200 pounds per square inch gauge and upwards, and bottom temperatures of about 550° to 650° F. It has been observed, however, that the stabilization of many crudes under these conditions is attended by serious corrosion problems, necessitating frequent replacement of expensive items of equipment. Such problems are especially serious since stabilization units are normally located near the source of crude, and hence frequently at remote distances from suitable repair and replacement facilities.

The tendency of certain crudes to attack the equipment in which they are stabilized has been found to be dependent upon the temperatures to which they are heated. The tubes of direct-fired external reboilers and the lower portions of fractionating columns are thus the most rapidly corroded, while the upper portions of the columns and the refluxing lines and condensers are practically immune. By correlating temperature with rate of corrosion, it has been found that little or no corrosion will occur in any part of a crude stabilizer providing the crude is not subjected to a temperature above about 540° F. Various theories have been advanced to account for this fact, one of which postulates the existence of non-corrosive sulfur compounds in the crude which decompose at elevated temperatures to produce corrosive ones. It is also known that many crudes contain emulsified brine which hydrolyzes at high temperatures to form hydrochloric acid.

One of the objects of my invention is the provision of a process for stabilizing crude at relatively low temperatures and pressures wherein the corrosion effects are obviated.

A further object of my invention is the provision of a process for stabilizing crude at relatively low temperature and pressure without excessive loss of the butane content of the crude. Various other objects, advantages and features of my invention will be apparent from the following detailed description thereof.

In proceeding in accordance with my invention, the crude to be stabilized is fractionally distilled at relatively low temperatures and pressure whereby corrosion tendencies are minimized and under such conditions that the substantially complete removal of propane and lighter hydrocarbons from the crude is effected without excessive loss of butane. These results are accomplished by admixing butane with the crude to provide sufficient reflux for the above fractionating requirements, recovering the butane thus added from the overhead vapors, and returning it to additional crude to be stabilized. A further feature of the invention is the recovery of the added butane by absorption in the crude undergoing stabilization or a portion thereof, or a portion of the crude which has been previously stabilized or substantially debutanized, and returning the butane to the fractionating zone in the absorbing oil.

In stabilizing crude petroleum by fractional distillation, pursuant to my invention, I preferably employ a reboiler temperature of about

425° to 475° F. Within this temperature range, little if any corrosion will be experienced when stabilizing the majority of crudes, but some may require that slightly lower temperatures be used, while others remain substantially non-corrosive up to as high as 540° F. I maintain a pressure on the system just high enough to permit the condensation of butane from the overhead vapors for use as reflux. This pressure is dependent upon the percentage of butane, propane, and lighter hydrocarbons in the crude, and upon the cooling water temperature. When the preferred reboiler temperature range is adhered to, a pressure of about 100 to 150 pounds per square inch will ordinarily be required. I preferably recover butane from the uncondensed stabilizer overhead vapors by absorption, using as a medium one or more oils derived from the crude itself.

The volatility of these oils is a measure of their efficiency in absorbing butane, and, in accordance with my method I may control the volatility of these oils over a relatively wide range, suiting their properties to the degree of recovery desired and to the quantity of gas to be contacted. Specifically, my absorber oils are made up of one or more of the following materials arranged in the order of decreasing volatility because of relative freedom from butane and lighter hydrocarbons and hence increasing efficiency in absorbing butane, the proportions of each employed depending upon the properties desired:

1. Unstabilized crude.
2. Stabilized crude.
3. Stabilized crude after flashing at a reduced pressure suitable for debutanization.

After the absorber oils have been contacted with stabilizer overhead vapors and have absorbed butane therefrom, they are returned to the stabilizer, whereby the provision of an additional apparatus for stripping purposes is obviated. The effect of returning absorber rich oil to the stabilizer is to recycle or circulate constantly through the stabilizing zone a sufficient quantity of butane to provide reflux at the top of the stabilizer, whereby additional butane entering in the fresh crude is largely retained in the stabilizer bottoms and withdrawn with the stabilized crude.

When the butane to be recovered by absorption has a relatively low value, so that a high percentage recovery is not demanded, I prefer to use unstabilized crude alone as the absorber oil. With this material some butane will naturally be lost by vaporization on the top tray of the absorber, yet an overall retention of better than 75% of the butane fraction can usually be obtained, and the heat load on the system is minimized.

When a higher butane retention is desired, I prefer to use stabilized crude as the absorbing medium in the upper portion of the absorber tower, augmenting it, when desired, with a stream of unstabilized crude introduced near the center. When the utmost yield of butane is required, I divert a stream of hot stabilized crude from the bottom of the stabilizer to a flash zone maintained at a pressure somewhat below the pressure on the main system; at the lowered pressure, substantially complete removal of butane from the stream, that is, debutanization, can be effected, and the debutanized oil is then passed to the top of the absorber to scavenge the last traces of butane unabsorbed by more volatile absorbing medium introduced at a lower point in the absorber. The vapors flashed from the stabilized crude to obtain clean-up oil are condensed and pumped to the base of the absorber, where they reunite with the crude from which they came.

It will be understood that an infinite variety of absorber oils can be made from the three components available, so as to satisfy to a nicety any required butane retention.

Referring now to the annexed drawing which illustrates one form of my invention, fresh unstabilized crude is withdrawn from any suitable source through line 1 by pump 2 and all or a portion thereof is passed through line 4 to heat exchanger 5 where heat is transferred to it from hot stabilizer bottoms. In the event economic considerations permit, a portion of the unstabilized crude may be diverted through line 3 for use as an absorbing medium, as will be hereinafter described.

Preheated unstabilized crude from exchanger 5 passes through line 6 and is joined by a stream of enriched absorber oil from line 7. After joining, the two streams pass through line 8 to the center portion of the stabilizer 9 which is fitted with a plurality of vapor-liquid contacting elements such as conventional bubble trays. Heat is supplied to the base of the stabilizer 9 by means of a reboiler 10 through which is passed a heating medium. Since it is important that no portion of the crude be heated above the chosen safe reboiler temperature, I prefer to use high pressure steam as the heating medium in reboiler 10, since it is thereby possible to avoid excessive temperatures in the oil film immediately adjacent to the external heat transferring surface. By utilizing the latent heat of condensation of the steam, reboiler duty can be supplied at a precisely controlled constant temperature, which is not the case when direct-fire reboilers are used.

In passing down over the trays in the stabilizer, the crude is substantially freed of propane and lighter hydrocarbons, which pass upwardly together with other volatile constituents such as butane. A portion of the vapors reaching the top of the tower are condensed and return to the top tray as reflux, as for example, by means of the internal cooling coil 11 through which a stream of cooling water is passed. The temperature and pressure at the top of the stabilizer are such that all of the propane and lighter hydrocarbons present in the unstabilized crude remain uncondensed and pass overhead through line 12, together with a constant quantity of butane which is recycled to the stabilizer in the enriched absorber oil. Sufficient reflux is maintained by the removal of heat to cooling coil 11 as to prevent the escape of more than the desired percentage of butane present in the unstabilized crude. The remaining butane is carried back down through the stabilizer as reflux condensate, and remains in the stabilized crude withdrawn from the bottom. Stabilizer overhead vapors pass through line 12 to the base of an absorber 13 which is also fitted with bubble trays or the like.

The three types of absorber oil which may be availed of for the purpose of recovering and recycling butane, are proportioned in accordance with the allowable loss of butane from the crude, and may be prepared and utilized as follows: Unstabilized crude is diverted from the charging stock stream through line 3 and passed to the absorber directly. Stabilized crude is diverted from the main product stream leaving the process, and passed through line 18 to the absorber. Flashed stabilized or debutanized crude is ob-

tained by taking a portion of the hot stabilizer bottoms through line 19 to a low pressure zone 20 where a vaporous fraction is separated from it. The material remaining unvaporized at the reduced pressure is withdrawn through line 21 and cooled, for example, by heat exchange with enriched absorber oil in exchanger 22. It then passes through line 23 to additional cooler 24, and thence through line 25 to pump 26 which delivers it through line 27 to the absorber. For the sake of simplicity, the low pressure separator 20 has been shown as constructed integrally with the absorber 13. Obviously, however, a separate vessel could be used. The distillate flashed from the stabilized crude in the separator 20 is withdrawn therefrom through line 30 to condenser 31 and line 32 to accumulator 33 whence it is withdrawn through line 34 by pump 35 and delivered through line 36 to the base of the absorber.

Lines 3, 27, and 18 carrying the three absorber oils are suitably manifolded, as shown, so that all or a portion of any one of them may be delivered through lines 28 and 29 to either the middle or the top of the absorber respectively. The points of introduction of the various oils are determined as hereinbefore explained by the requirements as to butane retention which must be met. One or more intercoolers may be provided to remove heat from the absorber oil as it flows downwardly through the absorber, as exemplified by the intercooler 40.

In passing upwardly through the absorber 13, the stabilizer overhead vapors entering through line 12 are stripped to a relatively low butane content so that the gases leaving the top of the absorber through line 41 contain, in most instances, not more than approximately 5 to 25% of the butane originally present in the unstabilized crude, according to the loss permitted by economic considerations. Enriched absorber oil containing butane to be recycled is withdrawn from the base of the absorber 13 through line 37 together with condensed distillate from separator 20. This stream is passed by pump 38 through line 39 to exchanger 22 against flashed stabilized crude and thence through line 7 to join line 6, re-entering the stabilizer through line 8.

Stabilized crude not set to the separator 20 for flashing is passed through line 14 to heat exchanger 5 against incoming fresh crude and thence through line 15 to a final cooler 16. Continuing through line 17 a portion is diverted through line 18 for absorption purposes while the remainder is passed to storage or shipment through line 42.

It is to be understood that the arrangement of exchangers, coolers, condensers, and refluxing means, shown in the drawing, is by way of example only, for numerous other arrangements could be employed without departing from the essentials of the invention. For example, the cooling coil 11 could be replaced by an external condenser and separator interposed in the vapor line 12, with reflux return to the top tray of the stabilizer from the separator by means of a pump; also, the reboiler 10 could be supplied with the vapors of any substance having a suitable boiling point, or even with a liquid heating medium such as hot gas oil provided means for precise control of temperature were used.

The following example will illustrate further the manner in which my invention may be practiced:

A 43° A. P. I. crude petroleum was to be stabilized for the retention of approximately 90 percent of its butane content, and was known to become corrosive when heated above about 470° F. These circumstances, coupled with a summer cooling water temperature of 100° F., made it desirable to use flashed stabilized crude as the absorbing medium in the top of the absorber, augmented by a stream of unstabilized crude introduced at a somewhat lower point.

The stabilizer tower, containing 25 bubble trays, was operated at a pressure of 120 pounds per square inch, a bottom temperature of 435° F., and a top temperature of 105° F. The reboiler in the bottom of the stabilizer was heated with high pressure steam. About 121 mols of butane entered the system per hour with the fresh crude, and 108 mols per hour left the system in the stabilized crude, leaving 13 mols per hour as loss in the absorber tail gas. In contrast with these quantities, approximately, 630 mols per hour of butane left the stabilizer as overhead vapors, to be returned thereto in the enriched absorber oil.

Stabilized crude was flashed at 400° F. and 40 pounds absolute pressure to provide a 38° A. P. I. lean or debutanized oil which contained less than 1.0 mol percent butane. 4600 gallons per hour of this oil, supplied at the top of the absorber, plus 11,400 gallons per hour of unstabilized crude, supplied to the middle of the absorber, were sufficient to recover the recycled butane. Two intercoolers were used and the absorber was fitted with 48 bubble trays.

From the foregoing it will be apparent that the process therein described accomplishes the objects of my invention of providing a process for the stabilization of crude with substantially complete removal of propane and lighter hydrocarbons at relatively low temperatures and pressure whereby corrosion effects are minimized and at the same time excessive loss of butane from the crude is obviated.

What I claim is:

1. A process for stabilizing crude petroleum by removal of propane and lighter hydrocarbons at relatively low temperatures and pressures for the minimization of corrosion and without excessive loss of butane, which comprises enriching the butane content of a portion of said crude by contacting it with a mixture of hydrocarbon vapors including butane and lighter hydrocarbons under suitable conditions whereby the butane is largely absorbed in the crude and the lighter hydrocarbons separated, fractionating said butane-enriched crude into a bottoms product, constituting the desired stabilized crude, said product being substantially free of propane and containing butane in amount constituting a substantial proportion of the butane-content originally present in the crude, and an overhead vaporous product consisting of a mixture of hydrocarbon vapors including butane and lighter hydrocarbons, the quantity of butane therein being not less than that absorbed by the crude from said mixture of hydrocarbon vapors, enriching the butane-content of an additional portion of crude to be stabilized by contacting said portion with said overhead vaporous product under suitable conditions whereby the butane is largely absorbed in said portion and the lighter hydrocarbons separated, and continuously repeating said cycle of steps.

2. A process for stabilizing crude petroleum by removal of propane and lighter hydrocarbons at relatively low temperatures and pres-

sures for the minimization of corrosion and without excessive loss of butane, which comprises enriching the butane content of a portion of said crude by contacting said portion with a mixture of hydrocarbon vapors including butane and lighter hydrocarbons under suitable conditions whereby the butane is largely absorbed in said portion and the lighter hydrocarbons separated, mixing said butane-enriched portion with a second portion of said crude and fractionating said mixture into a bottoms product, constituting the desired stabilized crude, said product being substantially free of propane and containing butane in amount constituting a substantial proportion of the butane content originally present in the crude, and an overhead vaporous product consisting of a mixture of hydrocarbon vapors including butane and lighter hydrocarbons, the quantity of butane therein being not less than that absorbed by said first mentioned portion of crude from said mixture of hydrocarbon vapors, enriching the butane content of an additional portion of crude to be stabilized by contacting said portion with said overhead vaporous product under suitable conditions whereby the butane content of said product is largely absorbed in said portion and its lighter hydrocarbons separated, and continuously repeating said cycle of steps.

3. A method of stabilizing potentially corrosive sulfur-bearing crude petroleum including the steps of introducing said crude and recycled butane into a fractionating column, operating said column at a relatively low bottom temperature and under such a pressure that butane in amount equivalent to said recycled butane and a minor proportion of the butane originally present in said crude, and substantially all hydrocarbons lighter than butane will distill off as vapors, partially condensing said vapors and refluxing said column with the condensate, recovering butane from the uncondensed portion of said vapors, and recycling it to said column as aforesaid, whereby said crude is stabilized without the employment of corrosion-promoting temperatures and with retention therein of a major proportion of the original butane content thereof.

4. A method as in claim 3 including the steps of recovering butane from said uncondensed vapors by absorbing it in crude petroleum to be stabilized, and recycling recovered butane by introducing the thus-enriched crude petroleum into said fractionating column.

5. A method as in claim 3 including the steps of recovering butane from said uncondensed gases by absorbing it in stabilized crude petroleum, and recycling recovered butane by introducing the thus-enriched stabilized crude into said fractionating column.

6. A method as in claim 3 including the steps of recovering butane from said uncondensed gases by absorbing it in debutanized crude petroleum, and recycling butane by introducing the thus-enriched absorbent medium into said fractionating column.

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