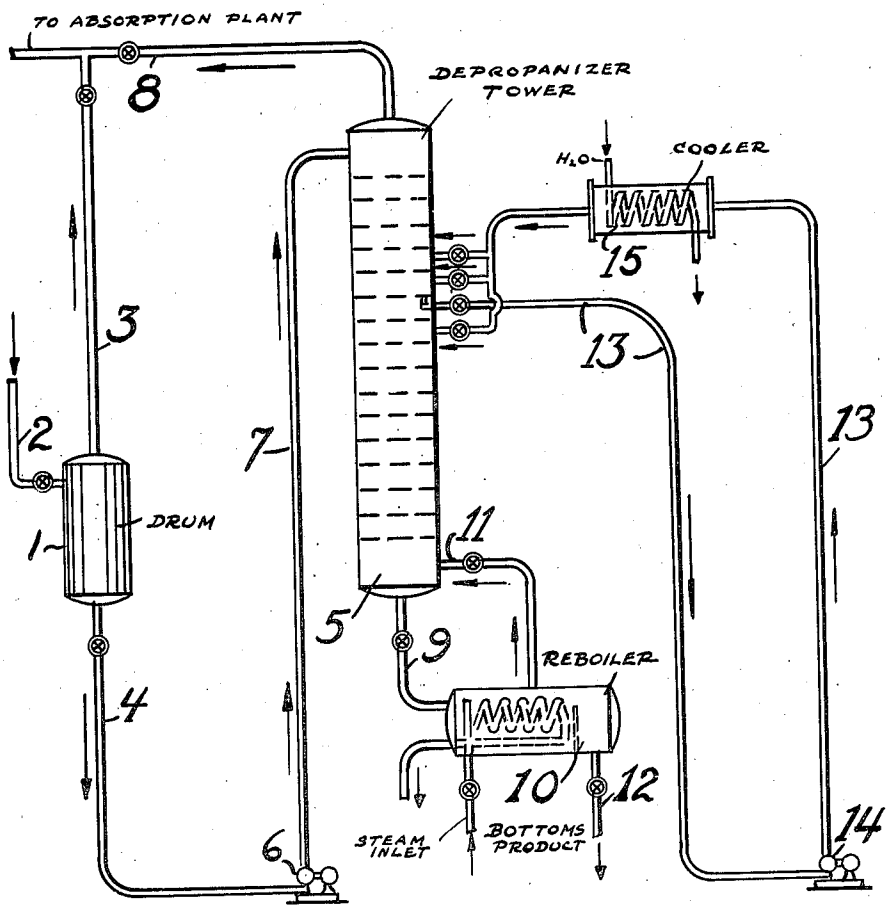
Nov. 10, 1942. J. B. MAXWELL ET AL 2,301,304

REFINING OF MINERAL OILS

Filed Nov. 30, 1940



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Patented Nov. 10, 1942

2,301,304

UNITED STATES PATENT OFFICE

2,301,304

REFINING OF MINERAL OILS

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Application November 30, 1940, Serial No. 368,000

5 Claims. (Cl. 196—11)

The present invention relates to the refining of mineral oils. The invention is more particularly concerned with an improved process for the removal of relatively low boiling hydrocarbon constituents from petroleum oils or fractions thereof containing the same in an efficient and economical manner. In accordance with the present operation, hydrocarbon feed oils containing objectionable amounts of relatively low boiling constituents are stabilized by passing the feed oils downwardly through a stripping zone in a manner in which the objectionable constituents are removed overhead and a stabilized product is removed as a bottoms. The operation is conducted in a manner that reflux is provided by withdrawing a portion of the downflowing feed oil from the system at at least one point, removing heat from the same, and returning the fraction to the system.

It is well known in the refining of mineral oils, particularly in the refining of petroleum oils, to stabilize the same by removing therefrom objectionable relatively low boiling constituents. One operation employed for securing these results is a conventional fractionating tower comprising a fractionating and stripping zone. The feed oil in this this type of operation is introduced into the fractionating tower at a point intermediate the respective zones and operating temperatures and pressures are adjusted to remove overhead a relatively low boiling fraction substantially free of undesirable relatively high boiling constituents and to remove as a bottoms product a relatively high boiling fraction substantially free of relatively low boiling constituents. In this type of operation reflux is provided by condensing the overhead and returning a portion of the condensed distillate to the top tray of the fractionating section.

However, in our operations it is sometimes uneconomical to separate relatively low boiling constituents from relatively high boiling constituents in this manner, particularly when the feed material contains a small amount of the relatively low boiling constituents and the final products desired are the relatively high boiling constituents free of the relatively low boiling constituents. When treating feed stocks of this character, it is the conventional practice to employ so-called stripping operations. In operations of thits character the feed oil is introduced into the top of the stripping zone and flows downwardly through the stripping zone under conditions in which the temperature of the feed is gradually increased. Sufficient reflux to accomplish the desired stripping can usually be secured by heating the bottoms product from the feed temperature to the temperature at the bottom of the tower which corresponds to the boiling point of the bottoms product at the operating pressure.

However, the temperature difference between the feed and bottoms is sometimes insufficient to supply the required quantity of reflux. In this event it becomes necessary to introduce external cooling to increase the quantity of reflux. This may be accomplished by cooling the overhead vapors and returning liquid reflux to the feed plate. However, this is not particularly desirable due to the fact that an undesirable fractionation of constituents occurs when operating in this manner.

This is particularly the case when processing petroleum oil fractions boiling in the range below about 400° F., especially if the petroleum oil fraction boils in the range below about 250° F. For example, unstable light naphthas boiling in the range below about 250° F., containing fixed gases such as methane, ethane, propane, as well as butanes and higher boiling hydrocarbon constituents, cannot effectively be stabilized in a conventional manner due to the relatively small temperature differential between the feed temperature and the boiling point of the bottoms product. This is due in part to the fact that in commercial operations it is desirable, and in many cases essential, that the feed oils be introduced into the stabilization zone at temperatures in the range from about 70° F. to 80° F. Under these conditions the temperature differential between the boiling point of the bottoms product and the temperature at which the feed material is introduced into the zone may be relatively small and it is not possible to provide a sufficient quantity of reflux necessary to secure an efficient stripping operation. Furthermore as pointed out above, the problem cannot be readily solved by refluxing the feed oil due to the relatively high cost of operations of this character. Nor is it desirable to provide reflux for a stripping operation of this character by condensing and compressing the overhead product, since this type of operation tends to separate the lower boiling fractions more completely at the top of the tower than required, and results in a relatively large loss of intermediate boiling components.

We have now discovered a process by which feed stocks of this character may be readily and efficiently stabilized which comprises withdraw-

ing an intermediate stream at at least one point from the stripping zone, withdrawing heat from the separated stream and returning the stream to the tower, preferably at a point above the point at which it was withdrawn. The process of our invention may be readily understood by reference to the attached drawing illustrating modifications of the same. The feed oil, which for the purpose of description is taken to be a light naphtha boiling in the range below about 250° F., and containing fixed gases, methane, ethane, propanes, butanes, pentanes, and higher boiling hydrocarbons, is introduced into separation zone 1 by means of feed line 2. It is also assumed for purposes of illustration that it is desired to stabilize the product by removing therefrom hydrocarbon constituents boiling in the propane and lower hydrocarbon boiling range with a minimum loss of hydrocarbons containing four carbon atoms and higher in the molecule. Thus temperature and pressure conditions are adjusted in separation drum 1 to remove overhead by means of line 3 a gaseous product containing fixed gases, and hydrocarbon constituents having three and less carbon atoms in the molecule. These overhead gases are substantially free of hydrocarbon constituents containing four and higher carbon atoms in the molecule. The liquid product containing small quantities of propane and lower boiling constituents is withdrawn from separation zone 1 by means of line 4 and passed into the upper section of stabilization zone 5 by means of pump 6 and line 7. The liquid product flows downwardly through stabilization zone 5 under conditions in which the propane and lower boiling hydrocarbon constituents are separated and removed overhead from stabilization zone 5 by means of line 8. A stabilized product substantially completely free of undersirable relatively low boiling hydrocarbon constituents is withdrawn from the bottom of stabilization zone 5 by means of line 9 and passed into reboiler 10, from which heat is supplied to the bottom of stabilization zone 5 by recycling a portion of the bottoms by means of line 11. A final stabilized product, free of undesirable constituents, is withdrawn from the system by means of withdrawal line 12 and further handled and refined in any manner desirable. In accordance with the present modification of the invention, the feed stream is introduced into the stabilization zone 5 at a temperature in the range from about 70° F. to 100° F., and sufficient reflux is provided by withdrawing a portion of the downflowing liquid hydrocarbon stream by means of line 13 and pump 14. The withdrawn stream is passed through cooler 15 and then returned to the stabilization zone.

The process of the present invention may be widely varied. The invention essentially comprises withdrawing a stream at an intermediate point in a stripping zone, removing heat from the same, and returning the cooled stream to the tower in a manner to produce sufficient reflux for securing efficient stripping. Although the invention may be adapted for processing any feed oil, it is particularly useful in the stabilization of relatively low boiling fractions in which it is desired to introduce the feed oil into the stabilization zone at a temperature in the range from about 70° F. to 100° F. The invention is particularly adapted for the removal of relatively low hydrocarbon constituents from petroleum fractions boiling in the range below about 400° F., particularly in the range below about 250° F.

A very desirable feed stock which may be processed in accordance with the present operation is a light absorption plant naphtha, the constituents of which have been recovered from hydrocarbon vapors by means of an oil absorption operation. In these operations valuable hydrocarbon constituents are recovered from vaporous mixtures containing the same by absorption with various absorption oils. It was then the practice to remove the absorbed constituents from the absorption oil and to stabilize the segregated constituents in a subsequent distillation operation. In the stabilization of feed stocks of this character it has been suggested that the small amounts of undesirable relatively low boiling hydrocarbon constituents which are also absorbed, be removed from the absorption oil after removal of the absorption oil from the absorption zone prior to removing from the absorption oil the desired absorbed hydrocarbon constituents. This type of operation has not been entirely successful due to the fact that a sufficient quantity of reflux cannot be provided in an economical manner, which is not the case when employing the present process.

The point at which the intermediate stream is withdrawn from the stripping zone will depend to some extent upon the character of the feed oil being stabilized and upon general operating conditions. In general at least one intermediate stream is withdrawn from the stabilization zone at about the center section of the stabilization zone, preferably from the upper middle quarter section.

The number of intermediate streams withdrawn likewise may vary considerably depending upon the feed stock being stabilized and general operating conditions. Usually the number of intermediate streams withdrawn should not exceed three and preferably be from one to two. Although the cooled liquid may be returned to the tower over a relatively wide range, in general it is preferred that the stream be returned to a point in the stabilization zone above and adjacent the point from which it was withdrawn.

In order to further illustrate our invention, the following examples are given which should not be construed as limiting the same in any manner whatsoever.

Example 1

The designations C_1 to C_7 represent compounds containing from one to seven carbon atoms in the molecule. In operations employing top reflux and the reflux added as in the present invention, the composition of the overhead vapors are as follows:

Feed mols	Overhead vapors	
	Top reflux mols—Operation A	Recirculating reflux mols—Operation B
$2C_1$	$2.0C_1$	$2.0C_1$
$6C_2$	$6.0C_2$	$6.0C_2$
$12C_3$	$12.0C_3$	$12.0C_3$
$10C_4$	$10.0C_4$	$5.0C_4$
$10C_5$	$5.0C_5$	$2.0C_5$
$10C_6$	$0.5C_6$	$1.0C_6$
$50C_7+$		$.5C_7$
100	35.5	28.5

From the above it is apparent that distinct

advantages are to be secured by the present process. Although both processes stabilize the feed by completely removing from the bottoms product all constituents having three and less carbon atoms in the molecule, the process of the present invention, as shown in operation "B," resulted in a considerably less loss of desirable hydrocarbon constituents. This is evident by the fact that 15½ mols of desirable hydrocarbon constituents were lost with the overhead vapors when employing top reflux, whereas only 8½ mols of desirable constituents were lost in the overhead vapors when employing side stream reflux. This is due to the fact that the vapors leaving the top of the stripping zone are saturated in equilibrium with the liquid at the operating temperature and pressure. Thus when employing top reflux the overhead vapors will contain considerably more butane and pentane fractions in the above described operation, due to the fact that these vapors do not contain any of the relatively less volatile hydrocarbon constituents having, for example, seven carbon atoms in the molecule. When employing side stream reflux in the above operation, a small amount of hydrocarbon constituents having seven carbon atoms in the molecule is removed overhead and thus has the same saturating effect as many times this quantity of butane and pentane hydrocarbon constituents. In these operations 0.5% hexane constituents +0.5% heptane are equivalent to 5.0% butane constituents +3.0% pentane constituents. Thus the net reduction in butane and higher boiling constituents when using the recirculating reflux of the present invention is 7%. Furthermore, the recovery of the heavier constituents in an absorption system is considerably less when processing overhead vapors containing therein a small quantity of relatively high boiling constituents.

The advantages of the present invention are that the quantity of the desirable relatively higher boiling constituents lost in the overhead vapors is appreciably less; that a stripping zone may be operated at a considerably lower pressure for any set of fixed conditions; that it is possible to remove relatively low boiling constituents such as depropanizing very light feed stocks without employing excessive operating pressures; that when removing relatively low boiling constituents such as depropanizing at lower pressure, the heat loss in the bottoms product is appreciably less when cooling the bottoms product after removal from the stripping zone with water.

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 insofar as the prior art permits.

We claim:

1. A process for removing undesirable relatively low boiling hydrocarbon constituents from mineral oils containing the same which comprises introducing the feed oil in the liquid state into the top of a stabilization zone, passing the feed oil downwardly through the stabilization zone under conditions that the temperature increases in the direction of flow of the feed oil, and providing reflux within said stabilization zone by withdrawing at least one intermediate stream, cooling and returning the same to the stabilization zone.

2. A process as defined by claim 1 in which the feed mineral oil contains a relatively small concentration of undesirable relatively low boiling hydrocarbon constituents.

3. A process as defined by claim 1 in which the feed mineral oil contains a relatively small concentration of undesirable relatively low boiling hydrocarbon constituents, and in which said feed oil boils in the range below about 250° F.

4. A process for the removal of hydrocarbon constituents having three and less carbon atoms in the molecule from petroleum feed oils boiling in the range below about 250° F. which comprises introducing the feed oil in the liquid state into the top of a stabilization zone, passing the feed oil downwardly through the stabilization zone under conditions in which the temperature increases in the direction of flow of the feed oil, providing reflux within said stabilization zone by withdrawing at least one intermediate stream, cooling and returning the same to the stabilization zone, removing said hydrocarbon constituents containing three and less carbon atoms in the molecule overhead and providing heat to said stabilization zone by withdrawing a bottoms stream, heating and returning the same to the stabilization zone.

5. A process as defined by claim 4 in which said intermediate stream is withdrawn from the upper middle quarter of the stabilization zone and returned to said stabilization zone above and adjacent the point from which it is withdrawn.

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