June 8, 1943. E. H. ATWOOD 2,321,540

METHOD FOR THE DISTILLATION OF CRUDE OILS CONTAINING ACIDIC SUBSTANCES

Filed Nov. 4, 1941

Fig. 1,

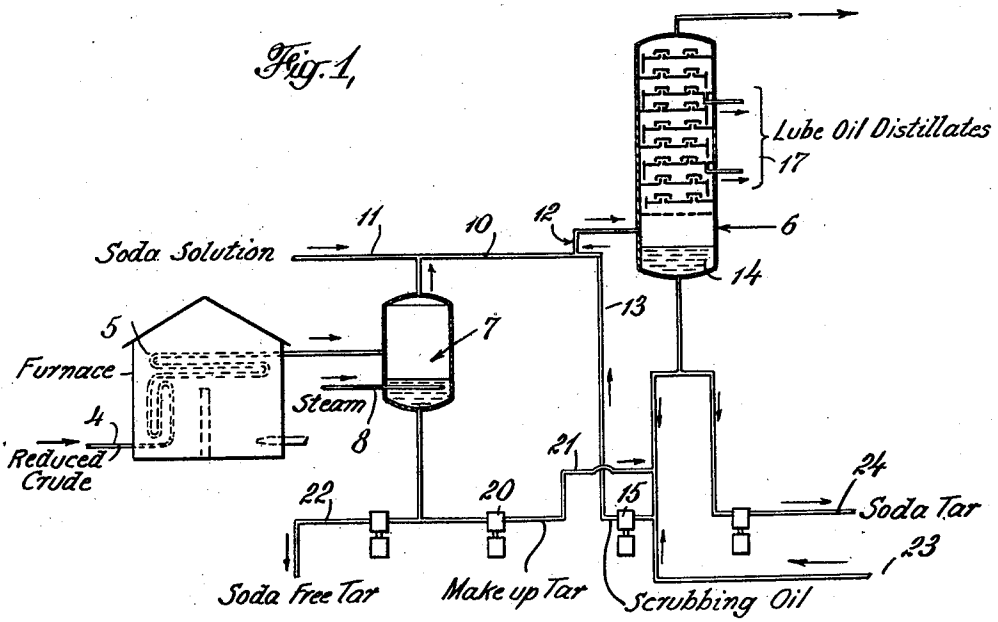
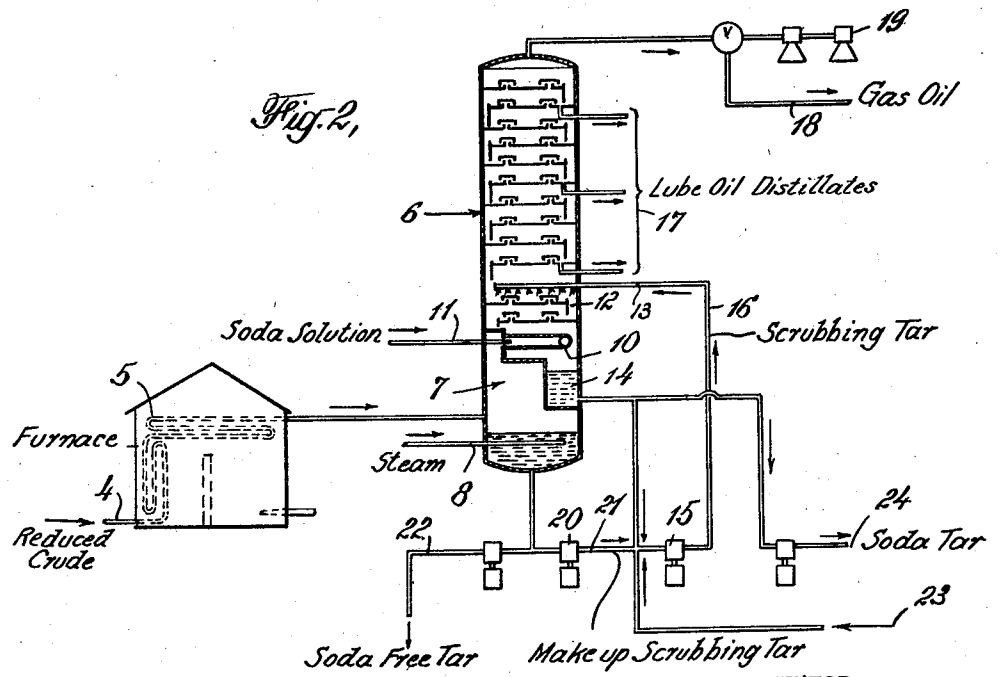


Fig. 2,



INVENTOR
EDWIN HAVENS ATWOOD
BY
ATTORNEY

Patented June 8, 1943 2,321,540

UNITED STATES PATENT OFFICE

2,321,540

METHOD FOR THE DISTILLATION OF CRUDE OILS CONTAINING ACIDIC SUBSTANCES

Edwin Havens Atwood, Woodbury, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

Application November 4, 1941, Serial No. 417,765

7 Claims. (Cl. 196—35)

This invention has to do with the distillation of crude oils and is particularly concerned with any distillation process where treating of portions is desired for the preparation of lubricating oil stocks from crude oils high in content of acidic matters such as naphthenic acids, for example, Coastal crudes.

Crude oils of the Coastal type, containing a very considerable amount of materials of the nature of naphthenic acid, and the like, boiling within the lubricating oil boiling range, are normally so processed as to prevent the presence of those acids in the distillates. The usual method of processing is to add to the crude oil, either before any distillation or after it has been topped part way through gas oil, usually the latter, enough of a base, such as caustic soda, to combine with the acids remaining in the crude oil, and then subject the oil to distillation to recover desired lubricating oil distillates. This method of operation leaves the soda salts of the naphthenic acids in the undistilled residue of the crude. This "soda tar," due to the presence of alkali is reduced in value as fuel oil or as a base for asphalts, and the net result is that a very material percentage of the crude oil, usually as much as 12 per cent, and in some crudes as much as 25 per cent, is reduced to a value less than that normally obtainable for heavy fuel oil of the same grade and gravity.

In the above usual method of operation, the soda added not only contacts the lubricating fractions which it is desired to treat, but also is in contact with the tar. As this tar usually also contains a considerable amount of naphthenic acids, these acids also react with the soda and make it necessary to use larger quantities of soda than would be required if it were not necessary to have the soda solution contact the tar. If it were possible to avoid the inclusion of soda, etc., in the residue, that residue would be capable of being worked up into asphalts, etc., and to other materials, and would frequently be able to command a better price than corresponding heavy fuel oil, and as only that soda necessary to treat the lubricating fractions would be required, the cost of soda treatment would be materially reduced.

This invention has for its object the provision of a process whereby the inclusion of soda or similar alkali in the total residue from the distillation of such crudes is avoided, and wherein increased recoveries of usable products of higher values than heretofore available can be made. A second object of this invention is the reduction of the amount of soda now required to neutralize the acids in the lubricating fractions of crude oil during its distillation.

In order to understand this invention more completely, reference is made to the drawing attached hereto, the two figures of which show, in diagram form, ways in which the process disclosed herein may be accomplished.

Since the two figures of the drawing are alike in process, merely differing in apparatus arrangements for accomplishing certain process steps, they will be described together.

In these figures an oil such as Coastal crude which has been subjected to the conventional atmospheric distillation to remove lighter materials of gasoline and kerosene boiling range, and so much of the gas oil as it is desired to remove before passing the reduced crude to vacuum distillation for the recovery of lubricating oil distillates is treated. The residue or reduced crude from this conventional operation is taken through pipe 4 and heated in coil 5 for delivery into the second stage vaporizer and fractionator wherein the process of this invention is brought into play.

The reduced crude, heated to a degree sufficient to accomplish the desired vaporization is introduced into the vaporizing space 7 and therein allowed to vaporize, leaving the desired amount of residue unvaporized. Vaporizer space 7 may be a separate vessel as in Figure 1, or may be a space in the main lube oil fractionator as in Figure 2. Steam stripping of this residue may be practiced, if desired, as indicated at 8. No soda or other alkali having been added to the reduced crude during heating or vaporization, this residue, constituting the total residue produced from the crude oil, is wholly soda-free and constitutes a wholly desirable fuel oil, or if desired, from proper crudes such as Coastal, may even be finished to asphalts. Heretofore in prior processes, the whole of such stock has been soda-tar. The vapors from the vaporizer section 7, now free from tar, pass to the soda (treating) section 10, in which they are intimately contacted with a fine spray of caustic soda solution or of other appropriate alkali, introduced through pipe 11. This soda contacting section may be a pipe connecting space 7 and fractionator 6 as in Figure 1, or may be a tube or passage in the main fractionator as in Figure 2. Continuing from the soda contacting space, the vapors, which are now substantially freed from acidic materials but which usually may contain some entrained caustic, other al-

kali or reaction products, pass through scrubbing section 12 in which they are scrubbed by a heavy oil introduced through pipe 13. This scrubbing oil removes the caustic or other alkali or reaction products from the vapors. This scrubbing may be done by intimately contacting the lubricating oil vapors and the scrubbing oil in any of the conventional manners, such as passing the vapors through a finely divided spray of scrubbing oil (as indicated in Figure 1), or by passing the vapors up through bubble plates on which the scrubbing oil is delivered (as shown in Figure 2). In the case of use of spray contacting, the vapors then pass through suitable mist extractors, bubble plates or other devices to separate entrained scrubbing oil from the lubricating oil vapors. The scrubbing oil is then collected in space 14 and is recirculated therefrom for reuse by pump 15 and pipes 13 or 16. After passing the heavy oil scrubbing, the distillate vapors, now free of acidic and alkaline material, continue upwardly to encounter conventional fractionation and recovery, indicated in diagram at 17, 18, 19.

The heavy oil used for scrubbing may be, and usually is, the soda free residue produced in the preceding vaporizing operation, a portion of which is withdrawn by pump 20 and passed to the circulation scrubbing system by pipe 21, the major production of soda free tar being withdrawn from the distillation by pipe 22. If desired, other heavy oil from any extraneous source may be introduced by pipe 23. To avoid undue concentration of soda and reaction products in the circulating heavy scrubbing oil, a portion of it may be withdrawn, intermittently or continuously, by pipe 24, this being the entire production of soda tar of the system, and being much less in amount than that formerly produced by prior processes at 22. Since the amount is small and its disposal it not an imperative problem, the concentration reached before withdrawal may be quite high. Makeup of circulating scrubbing oil by pipe 21 or pipe 23 is of course properly balanced against withdrawals through pipe 24.

While the above operation is described in connection with an operation of combined atmospheric-vacuum distillation, it is, of course, obvious that it is not restricted thereto, but may be practiced in connection with any distillation setup properly adapted to the oil being processed. For example, tower 6, wherein the second distillation step is practiced, could be operated at atmospheric pressure. Or again, under circumstances wherein it is appropriate to distill the crude in a single flash distillation operation, the entire crude could be vaporized in chamber 7 and appropriate arrangements could be made for separation of lube oil distillate cuts, gas oil cuts, kerosene cuts, and gasoline cuts, above scrubbing section 12, either in a single tower or in multiple towers, as is well known in the art.

Illustrative of the capability of the operation here disclosed, it may be contrasted with conventional operation.

In conventional operation, a 23° A. P. I. Coastal crude mixture was reduced to 60% bottoms, by atmospheric distillation. The 60% of reduced crude was then distilled under vacuum. .302 pound per barrel crude of caustic soda was added as a 25° Bé. solution at the crude charge pump. Upon vaporization and distillation in the fractionating systems, there were recovered 37.72% of gas oil, 46.60% of lube oil distillates, and 14.02% of soda tar.

In the improved operation a similar 23° A. P. I. Coastal crude mixture was reduced to 60% bottoms by atmospheric distillation which was then separated, under vacuum distillation according to the process herein disclosed, using a portion of the soda free residue as scrubbing oil. These distillations recovered 39.85% of gas oil, 43.44% of lube oil distillates, 13.2% of soda-free residuum, and 2.18% of soda tar. In this operation .187 pound of caustic soda per barrel of crude, in the form of an 18° Bé. solution, were utilized in the vapor treating operation.

I claim:

1. That method for the distillation of mineral oil containing acidic substances to produce distillates substantially free of acidic substances comprising heating the oil to a temperature sufficient to distill the desired fractions therefrom, separating vapors from residue, passing the vapors through a contact zone and therein contacting them with an alkaline reacting material, passing the alkali contacted vapors through a scrubbing zone wherein they are scrubbed by contact with a heavy oil fraction to remove alkaline material and reaction products therefrom, subsequently fractionating the vapors to desired product, and removing the scrubbing oil from the system while preventing its admixture with the main residual product of the distillation.

2. That method for the distillation of mineral oils containing acidic substances to produce distillates substantially free of acidic materials and a residue free of alkali and alkaline reaction products of acidic materials which comprises heating the oil to a temperature sufficient to distill the desired fractions therefrom, separating vapors from residue, passing the vapors through a contact zone and therein contacting them with an alkaline reacting material, passing the alkali contacted vapors through a scrubbing zone wherein they are scrubbed by contact with a heavy oil fraction to remove alkaline material and reaction products therefrom, subsequently fractionating the vapors to desired product, and removing the scrubbing oil from the system while preventing its admixture with the main residual product of the distillation.

3. That method for the distillation of crude oils containing acidic substances to produce high boiling distillates substantially free from acidic substances and a residue free from alkali and alkaline reaction products of acidic substances which comprises the steps of first distilling the crude oil to remove therefrom a substantial portion of products lighter than the desired high boiling products, heating the reduced crude so formed to a temperature sufficient to distill desired heavy products therefrom and separating it into a vapor and a residue, withdrawing the residue from the system, passing the vapors into a contact zone and therein contacting them with a medium comprising an alkaline reacting substance, passing the vapors thence through a scrubbing zone wherein they are scrubbed by contact with a heavy oil, then fractionating the vapors to recover desired distillate products in substantially acid-free, alkali-free condition, removing the heavy oil from the system, and preventing admixture of contaminated scrubbing oil with distillation residue.

4. That method for the distillation of crude oils containing acidic substances to produce high boiling distillates substantially free from acidic substances and a residue free from alkali and alkaline reaction products of acidic substances,

which comprises the steps of first distilling the crude to remove therefrom a substantial portion of products lighter than the desired high boiling products, heating the reduced crude so formed to a temperature sufficient to distill desired heavy products therefrom and separating it into a vapor and a residue, withdrawing the residue from the system, passing the vapors into a contact zone and therein contacting them with a medium comprising an alkaline reacting substance, passing the vapors thence through a scrubbing with a heavy oil, then fractionating the vapors to recover desired distillate products in substantially acid-free, alkali-free condition, passing the heavy oil used for vapor scrubbing zone wherein they are scrubbed by contact through the alkali scrubbing operation countercurrent to the vapors passing therethrough to remove reaction products of alkali treatment, collecting the used scrubbing oil and recirculating it for reuse while preventing admixture of contaminated scrubbing oil with distillation residue.

5. That method for the distillation of crude oils containing acidic substances to produce high boiling distillates substantially free from acidic substances and a residue free from alkali and alkaline reaction products of acidic substances, which comprises the steps of first distilling the crude to remove therefrom a substantial portion of products lighter than the desired high boiling products, heating the reduced crude so formed to a temperature sufficient to distill desired heavy products therefrom and separating it into a vapor and a residue, withdrawing the residue from the system, passing the vapors into a contact zone and therein contacting them with a medium comprising an alkaline reacting substance, passing the vapors thence through a scrubbing zone wherein they are scrubbed by contact with a heavy oil, then fractionating the vapors to recover desired distillate products in substantially acid-free, alkaline-free condition, collecting the used scrubbing oil and recirculating it for re-use while preventing admixture of contaminated scrubbing oil with distillation residue and withdrawing contaminated scrubbing oil from the system as the total production of alkali tar therefrom.

6. That method for the distillation of crude oils containing acidic substances to produce high boiling distillates substantially free from acidic substances and a residue free from alkali and alkaline reaction products of acidic substances, which comprises the steps of first distilling the crude to remove therefrom a substantial portion of products lighter than the desired high boiling products, heating the reduced crude so formed to a temperature sufficient to distill desired heavy products therefrom and separating it into a vapor and a residue, withdrawing the residue from the system, passing the vapors into a contact zone and therein contacting them with a medium comprising an alkaline reacting substance, passing the vapors thence through a scrubbing zone wherein they are scrubbed by contact with a heavy oil, then fractionating the vapors to recover desired distillate products in substantially acid-free, alkali-free condition, passing the heavy oil used for vapor scrubbing through the alkali scrubbing operation countercurrent to the vapors passing therethrough to remove reaction products of alkali treatment, collecting the used scrubbing oil and recirculating it for re-use while preventing admixture of contaminated scrubbing oil with distillation residue, supplying a portion of the distillation residue to the oil scrubbing step for makeup therein, and withdrawing contaminated scrubbing oil from the system as the total production of alkali tar therefrom.

7. That method for the distillation of crude oils containing acidic substances to produce high boiling distillates substantially free from acidic substances and a residue free from alkali and alkaline reaction products of acidic substances, which comprises the steps of first distilling the crude to remove therefrom a substantial portion of products lighter than the desired high boiling products, heating the reduced crude so formed to a temperature sufficient to distill desired heavy products therefrom and separating it into a vapor and a residue, withdrawing the residue from the system, passing the vapors into a contact zone and therein contacting them with a medium comprising an alkaline reacting substance, passing the vapors thence through a scrubbing zone wherein they are scrubbed by contact with a heavy oil, then fractionating the vapors to recover desired distillate products in substantially acid-free, alkali-free condition, collecting the used scrubbing oil and recirculating it for re-use while preventing admixture of contaminated scrubbing oil with distillation residue, supplying a portion of the distillation residue to the oil scrubbing step for makeup therein, and withdrawing contaminated scrubbing oil from the system as the total production of alkali tar therefrom.

EDWIN HAVENS ATWOOD.

BEST AVAILABLE COPY

CERTIFICATE OF CORRECTION.

Patent No. 2,321,540. June 8, 1943.

EDWIN HAVENS ATWOOD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 16, claim 4, strike out the words "zone wherein they are scrubbed by contact" and insert the same in line 12, after "scrubbing"; line 43, for "alkaline-free" read --alkali-free--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of August, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.