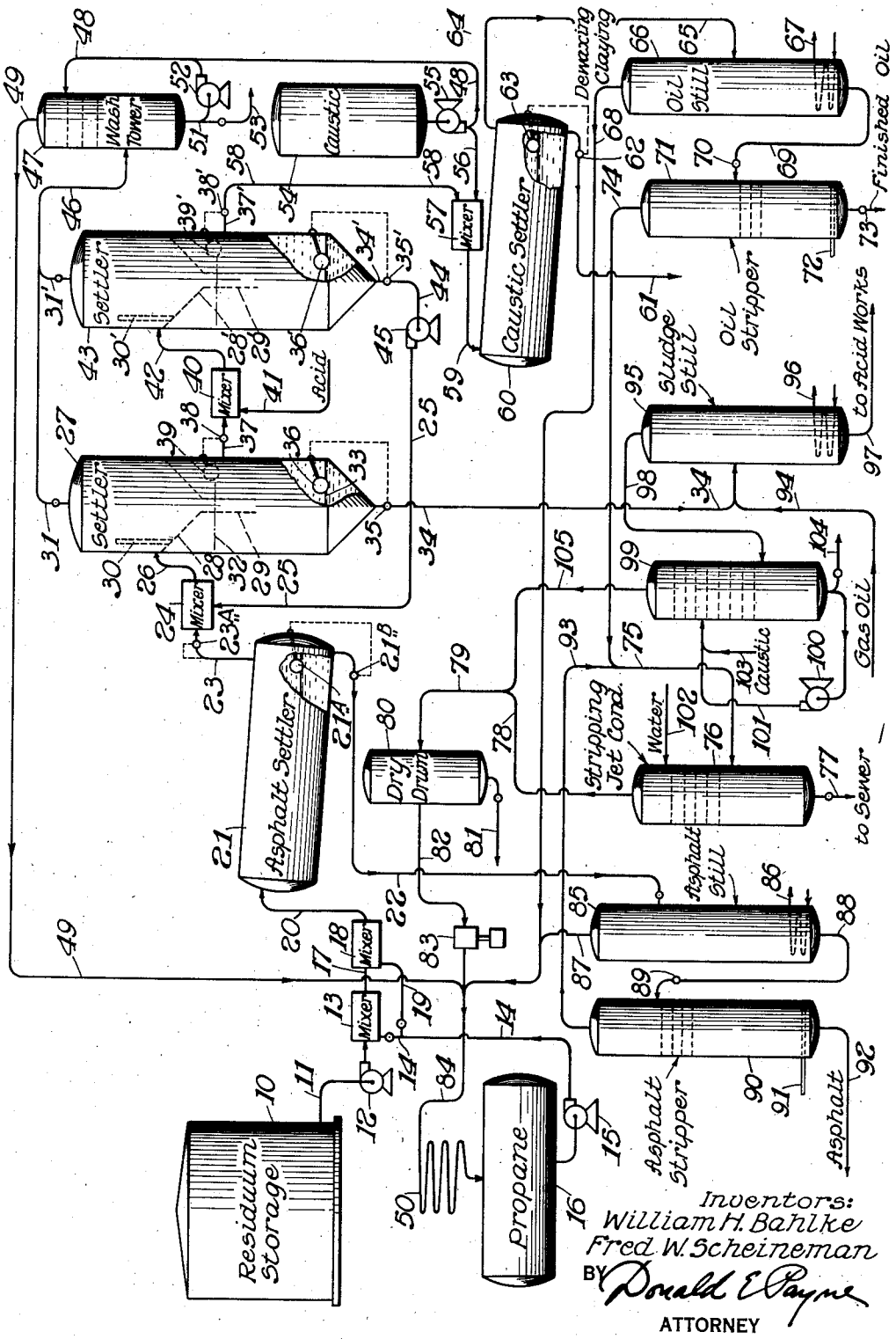
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OIL REFINING

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OIL REFINING

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This invention relates to an oil refining process and apparatus and it pertains more particularly to the preparation of heavy lubricating oils, bright stocks and/or cylinder stocks from residual petroleum oils or heavy petroleum distillates.

The object of the invention is to remove asphalt and sludge-forming materials from oils containing the same. A further object is to improve the process of "propane deasphalting" and to utilize propane or other normally gaseous hydrocarbon as a diluent liquid in the acid treating and neutralization of bright stocks or other lubricants.

Heretofore the acid sludge from heavy lubricating oils has been extremely difficult to handle, so that its reuse was practically impossible. An object of our invention is to obtain fluid sludge from heavy oil acid treating, so that this sludge may be reused for giving another batch of oil a preliminary acid treatment. Heretofore continuous acid treating processes have only been applicable to gasoline and very light oils; an object of our invention is to make possible the continuous countercurrent acid treating of very heavy oils. A further object is to provide improved apparatus for effecting such continuous countercurrent acid treating.

When liquefied, normally gaseous hydrocarbons are used in processes which result in the formation of corrosive gases, these gases may do serious injury to the propane compressors, condensers, etc. A further object of the invention is to provide a method and means for eliminating corrosive gases from the propane before it is returned for recompression.

A further object is to provide means for removing propane from acid sludge without unduly impairing the consistency of said sludge and the ease of handling.

A further object is to provide an improved system for removing moisture which is introduced into the system as stripping steam or as neutralizing solution.

A further object is to provide a process which will minimize acid requirements, clay requirements, and requirements as to the quality of the original lubricating oil stock undergoing treatment.

Other objects will be apparent from the detailed description of the invention.

In practicing the invention, we mix propane or the like, preferably in a plurality of stages, with a residual lubricating oil stock, preferably from Mid-Continent crude. We pass this stock with about 2 to 8 volumes of propane through a continuous asphalt settler at a temperature of about 110–195° F. and at a pressure of about 250 to 650 pounds per square inch, removing the asphalt from the lowermost point of the settler and removing the propane-soluble material from the topmost point thereof. We then, preferably after reducing the pressure on the propane solution, mix it with a heavy oil-acid sludge from a later stage. An important feature of the invention is the use of an efficient system for this countercurrent acid treatment of the heavy oil stock. Propane from the acid treating system is neutralized before being returned to the compressor so that corrosion is minimized. Sour oil, preferably in propane solution, is then neutralized with caustic and is finally depropanized, the dewaxing and claying being effected either before or after the removal of propane from the oil.

The invention will be more clearly understood by reference to the accompanying drawing, which is a conventional flow diagram of the improved system.

We will describe the invention as applied to a twenty-five per cent Mid-Continent residual stock, i. e., a Mid-Continent crude from which seventy-five per cent of the oil has been distilled under non-cracking conditions by the use of steam and/or vacuum distillation. It should be understood, however, that the invention is equally applicable to other viscous oil stocks containing asphaltic, tarry and/or resinous materials or containing other impurities which are removable by the process hereinafter described. The invention is applicable to heavy distillate stocks such as overhead bright stocks and it is applicable to Pennsylvania, Coastal, and other crudes as well as Mid-Continent crudes.

In practicing the invention, we prefer to use propane as the asphalt-precipitating medium and as the diluent and fluxing material in the acid treating step. This propane should not contain a large amount of unsaturates such as propylene, ethylene, etc., but it may contain considerable amounts of ethane, butane and the like. It should be understood that ethane, butane, etc. may be

used instead of propane, provided that the temperature and pressure conditions are suitably adjusted. The invention may be broadly described as improvements in the apparatus and process of manufacturing bright stock by the use of liquefied, normally gaseous hydrocarbons.

The twenty-five per cent Mid-Continent residual stock is withdrawn from storage tank 10 by means of a suitable discharge heater. It is forced through pipe 11 by pump 12 into mixer 13 wherein it is admixed with propane from line 14. This propane may be forced through line 14 by pump 15 from propane storage tank 16, but it should be understood that if storage tank 16 is maintained at sufficiently high pressures the pump may be dispensed with.

We prefer to use a plurality of mixers so that the oil is mixed with a little propane at a time to avoid agglomeration of asphaltic particles and to provide a solution of the residuum in the propane before enough propane is added to cause precipitation of the asphaltic matter. Thus the material from mixer 13 is passed by line 17 to mixer 18 into which are introduced further amounts of propane through line 19. The total amount of propane which is mixed with the stock will depend to a considerable extent on the nature of the stock and the nature of the desired end products; in the present case 2 to 8 volumes of liquid propane are employed per volume of residual stock, about 1 part of propane being introduced into mixer 13 and 1 to 7 parts being introduced into mixer 18. The temperature of the propane and the lube stock is preferably about 135° to 160° F. and the present commercial installation is designed to handle about 1,000 barrels of charging stock per day, which means that about 35 gallons of oil stock per minute are charged.

The hot mixture of propane and oil stock is then introduced through line 20 into asphalt settler 21, which may be an 8′ x 30′ pressure vessel mounted in a substantially horizontal position, or with the outlet end slightly lower than the inlet end. With the present stock and operating conditions, this settler sustains a pressure of about 650 pounds per square inch and it is, of course, equipped with suitable pressure and temperature gauges and with a loaded pressure release valve which discharges into a gas line in case the pressure becomes dangerously high.

An interface liquid level is usually maintained within this settler, preferably about one-fourth to one-third of the distance from the bottom to the top and when the nature of the precipitate asphalt permits, this liquid level is maintained by a float 21A which controls valve 21B in asphalt drawoff line 22, which is placed at the lowermost point of the settler.

It should be understood that instead of using a horizontal pressure drum for effecting this deasphalting step we may use a vertical countercurrent baffled tower, in which case we will introduce the hot residuum at the top of the tower and introduce the propane at the bottom of the tower; this will not only serve to give a gradual mixing of the propane with the residuum, but it will give excellent countercurrent deasphalting and it will result in the elimination of an extremely dry asphalt from which substantially all of the desirable lubricating oil has been removed.

The propane solution of deasphalted oil is discharged from the settler through line 23 through release valve 23A into mixer 24 wherein it is admixed with acid sludge from line 25. Heretofore it has been impossible to employ countercurrent acid treating processes for extremely heavy oils because the character of the acid sludge has been such that handling and mixing with incoming stock was impossible. We have discovered that in our propane process the sludge is sufficiently mobile and fluid that it may be readily pumped through line 25 to mixer 24 and it may be utilized to remove a large amount of the impurities from the oil stock before said stock is treated with fresh acid. It should be noted that the release of pressure immediately preceding mixer 24 causes a violent and turbulent flow through said mixer and thus facilitates and insures a thorough mixture of the oil with the sludge. The reduction of pressure also causes a cooling effect due to the vaporization of a portion of the propane. This cooling effect, or "self-refrigeration", is of importance as better efficiency of acid treatment is obtained on some oils when the temperature is reduced.

This oil sludge mixture is introduced by pipe 26 into the upper part of settler 27, which operates at a temperature of about 110° F. and a pressure of about 200 pounds per square inch and which may be a vertical pressure vessel about 6′ in diameter and 20′ high. The lowered pressure causes an extremely turbulent condition in the settler and, in order to prevent this turbulent condition from interfering with quiescent settling, we provide a funnel-shaped baffle 28 terminating in a central downwardly extending pipe 29 which extends into the body of acid treated oil. A vent pipe 30 is provided for releasing gases which accumulate between the liquid level in the settler and the under side of the conical or funnel-like baffle 28. Propane is removed from the top of the settler through pipe 31.

In the base of settler 27 we maintain a quiescent body of sour oil and sludge,—more specifically, an oil level 32 and a sludge level 33. Sludge is withdrawn from the base of the settler through line 34 in amounts regulated by valve 35, which is controlled by float 36 or by other suitable liquid level control apparatus. Sour oil is withdrawn through line 37 in amounts regulated by valve 38 which is controlled by float 39 or other suitable liquid level control apparatus. The sour oil is introduced into mixer 40 wherein it is intimately mixed with fresh acid from line 41, preferably about ½–¾ pound of 93% sulfuric acid per gallon of oil (although various quantities and concentrations will be required for various other oil stocks, as is well known to those skilled in the field of petroleum refining).

The mixture of oil with fresh acid is introduced through line 42 into settler 43, which is identical in structure with settler 27. It should be noted that any heat evolved by the chemical reaction of the acid with certain constituents in the oil does not cause an appreciable increase in the temperature of the oil, as sufficient propane will vaporize to keep the temperature practically constant. By proper control of pressure in settler 43 it will be possible to carry out the acid treatment at any desired temperature not exceeding that of the oil entering mixer 40. The sludge from the base of settler 43 is passed by line 44 and pump 45 to line 25 for admixture with the propane-oil solution in mixer 24, as hereinabove described. This reuse of acid sludge for treating further amounts of oil is unique in the treating

of bright stock and is attributable to the remarkable effect of the propane as a fluxing medium. Heretofore acid sludge from such heavy oils has been so nonfluid and contaminated with coke and tarry matter that its reuse has been impossible. It is needless to point out that this countercurrent acid treating of bright stocks results in the saving of large quantities of both acid and clay.

Propane from settlers 27 and 43 may contain sulfur dioxide or other corrosive gases and we therefore pass them through line 46 to wash tower 47 and scrub them with caustic from line 48 before passing them through line 49 to condenser 50. The wash tower may be a 3' x 9' baffled pressure vessel and it may be provided with a circulating line 51 and pump 52 for recirculating the caustic,—also with line 53 for withdrawing used caustic. In apparatus operated at lower pressures it may be necessary to compress the propane gases before passing them to the propane condensers and in such cases it is especially important that sulfur dioxide and other corrosive gases be removed from the propane.

The caustic used in wash tower 47 may be obtained from caustic storage tank 54 and caustic from this tank may be introduced through pump 55 and line 56 to mixer 57 for intimate admixture with sour oil from settler 43 and line 58. This mixture of neutralized diluted oil is then passed through line 59 to caustic settler 60, which may be a horizontal 6' x 30' drum mounted in a slightly inclined position as described in connection with asphalt settler 21. The caustic wash liquor is withdrawn through line 61 in amounts regulated by valve 62, which is operated by float 63. The neutralized oil is withdrawn from the opposite and upper end of the settler through line 64, from which it may be introduced into suitable dewaxing means or clay treating means (not shown). The propane with which the oil is diluted may be utilized both as a diluent and as a refrigerant in the dewaxing step and/or it may be used as a diluent in the clay percolation step. In the dewaxing process the propane has been found to greatly improve filtering and settling rates and in the clay treating processes it has been found to greatly improve the clay yields. Both of these processes per se are old and they will therefore not be described in detail in this case.

Finally, the finished oil which is still in propane solution is introduced through line 65 to oil still 66, which may be heated by closed steam coils 67. The propane may be removed through line 68 directly to condenser 50 because still 66 is preferably maintained at a pressure of about 200 pounds per square inch and the temperature in the base of this still is preferably about 250° F. Hot oil from the base of the still may be passed through line 69 in reducing valve 70 to stripper 71 at about 35 pounds pressure and the last traces of propane may be removed by the introduction of stripping gas such as steam through line 72. The finished oil may be withdrawn through line 73 to storage.

Propane and steam from stripper 71 may be passed through line 74 and line 75 to stripping jet condenser 76 wherein the stripping steam is condensed and separated from the propane, the former passing through line 77 to the sewer and the latter passing through line 78 and line 79 to dry drum 80 which acts as a water trapout, any remaining water being withdrawn therefrom through line 81. Propane from dry drum 80 is passed through line 82 to compressor 83 and thence through line 84 to propane condenser 50.

Asphalt from settler 21 is withdrawn through line 22 to asphalt still 85, which is provided with steam heater coil 86 and which is likewise maintained at a pressure of about 200 pounds. Propane from the top of this still is passed by line 87 directly to propane condenser 50. Asphalt from the bottom of still 85 is passed through line 88 and reducing valve 89 to stripper 90, open steam being introduced through line 91 and finished asphalt being withdrawn through line 92. The propane and steam from the top of stripper 90 is introduced through line 93 and line 75 to stripping jet condenser 76, from which the propane follows the course hereinabove described.

If the acid sludge from line 34 were depropanized in the conventional manner, the sludge would be converted into a viscous, coky mass which would be almost impossible to handle. We have discovered, however, that by mixing gas oil from line 94 with this acid sludge from line 34 and introducing the mixture of gas oil and acid sludge into sludge still 95, we may drive off practically all of the propane by means of closed coils 96 and we may then withdraw the gas oil-sludge mixture to the acid works through line 97. Propane is removed from sludge still 95 through line 98 to neutralizing condenser 99 through which we prefer to circulate an aqueous caustic solution by means of pump 100 and line 101. Water is introduced into stripping jet condenser through line 102 and fresh caustic is introduced into the neutralizing condenser through line 103, the used caustic being withdrawn through line 104. Propane from the neutralizing condenser is withdrawn through line 105 and passed through line 79 to dry drum 80, from which the propane is passed to the compressor and condenser as hereinabove described.

In the above process we have described a deasphalting temperature of 160° F., but it should be understood that we may employ other temperatures, depending upon the nature of the oil undergoing the deasphalting treatment, the nature of the desired end products, the amount of propane employed, etc. As a general rule, we may operate at any temperature between about 100° F. and the critical temperature of the liquefied, normally gaseous hydrocarbon. In the case of propane, we may use any temperature between 100° F. and 200° F., but we prefer, as hereinabove described, to operate at about 150–170° F.

For a clearer understanding of the effect of propane-to-oil ratios and operating temperatures on Mid-Continent residual oil stock, we will describe results obtained from the systematic investigation made with a 300 viscosity M. C. residual stock. In this investigation the propane-to-oil ratio was varied from 2.3 to 9.0 volumes of propane per volume of oil at temperatures of 100° F., 165° F., and 190° F. At 100° F. the yield of deasphalted oil decreased with increasing propane ratio and as the yield decreased the viscosity of the recovered oil decreased, while the color of the oil was improved. At 165° F. the yield of oil recovered was much lower than that at 100° F., but the yield increased with increasing propane concentration. Moreover, at 165° F. the viscosity of the recovered oil remained substantially constant with increasing propane ratio, but the color of the oil was very markedly improved by larger propane ratios. At 190° F. the general compara-

tive effect was the same as at 165° F. The results of our experiments may be tabulated as follows:

Propane to oil ratio	Temperatures		
	100°		
	Percent yield	Color No.	Viscosity at 210°
2.33	94	1/8	226
4.0	87	3/8	180
9.0	80	1	165
Propane to oil ratio	165°		
	Percent yield	Color No.	Viscosity at 210°
2.33	16	7/8	120
4.0	36	2 1/2	107
9.0	58	4 1/2	107
Propane to oil ratio	190°		
	Percent yield	Color No.	Viscosity at 210°
2.33	3	3	85
4.0	19	6	80
9.0	33	9+	80

Note: All color units are Tag Robinson — R (Diluted).

These results should be sufficient to teach one skilled in the art the general trends to be expected in propane deasphalting and the particular operating conditions in any case must be based on preliminary experiments with the oil to be treated.

While we have described in detail a preferred embodiment of our invention, it should be understood that we do not limit ourselves to any of the details hereinabove set forth except as defined by the following claims which should be construed as broadly as the prior art will permit.

We claim:

1. The method of refining a heavy lubricating oil stock containing asphaltic material to form bright stocks which comprises mixing said stock with liquefied propane in a plurality of stages, fractionating said stock at a pressure of about 250 to 650 pounds per square inch and at a temperature of about 110–200° F. in a high pressure settling zone, separately withdrawing asphalt and propane-oil solution from said settling zone, reducing the pressure of the propane-oil solution, treating the said solution with acid at a lower pressure than that used in the asphalt separation step using less than ¾ pound of 93% sulfuric acid per gallon of oil, neutralizing the acid treated oil, and removing propane from the neutralized oil.

2. The method of preparing bright stocks from heavy viscous lubricating oil stocks containing asphaltic material, which comprises mixing said oil stock with a saturated liquefied normally gaseous hydrocarbon of two to four carbon atoms, subjecting said mixture to a temperature within 100° F. of the critical temperature of the normally gaseous hydrocarbon and at a pressure sufficient to maintain it in liquid state, separating precipitated asphalt from the solution of oil and said hydrocarbon, admixing said solution with a solution of acid sludge in a liquefied normally gaseous hydrocarbon, separating the resulting sludge from the resulting sour oil solution, admixing fresh acid with said sour oil solution using less than ¾ pound of 93% sulfuric acid per gallon of oil, separating this second sludge and returning it to said first named mixing step, neutralizing the sour oil from the second acid treating step, and removing the liquefied normally gaseous hydrocarbon from the neutralized oil.

3. The method of claim 2 wherein the saturated liquefied normally gaseous hydrocarbon consists chiefly of propane, wherein the separation of precipitated asphalt from the solution is effected at a temperature of about 110° F., and wherein the ratio of propane-to-oil stock charged is greater than 2:1 but less than 8:1.

4. The method of refining a heavy residual petroleum oil having about the viscosity of a 25% Mid-Continent reduced crude which comprises mixing said oil with a small amount of propane to prevent agglomeration of asphaltic particles and to provide a solution of the residual oil in the propane, adding further amounts of propane to this solution to increase the propane to oil ratio to about 2:1 to 8:1, allowing the resulting mixture to stratify to two liquid layers at a temperature of about 100 to 200° F. at a pressure of about 250 to 650 pounds per square inch, withdrawing the lower layer and removing propane therefrom, removing the upper layer of propane soluble material from the stratification zone, reducing the pressure of the removed propane soluble fraction to about 200 pounds per square inch and treating it with a sulfuric acid in amounts of about ½ pound of 93% acid per gallon of oil treated, withdrawing and depropanizing the sludge from the acid-treating step, separately withdrawing and neutralizing the acid treated propane solution and removing propane from the neutralized solution.

5. The method of claim 4 wherein the propane removal from the separated materials is effected at a pressure of about 200 pounds per square inch and at a temperature of at least about 250° F. in one stage and at substantially atmospheric pressure in another stage.

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