Sept. 8, 1942. H. G. VESTERDAL 2,295,065

SEPARATION OF SOAPS FROM OIL

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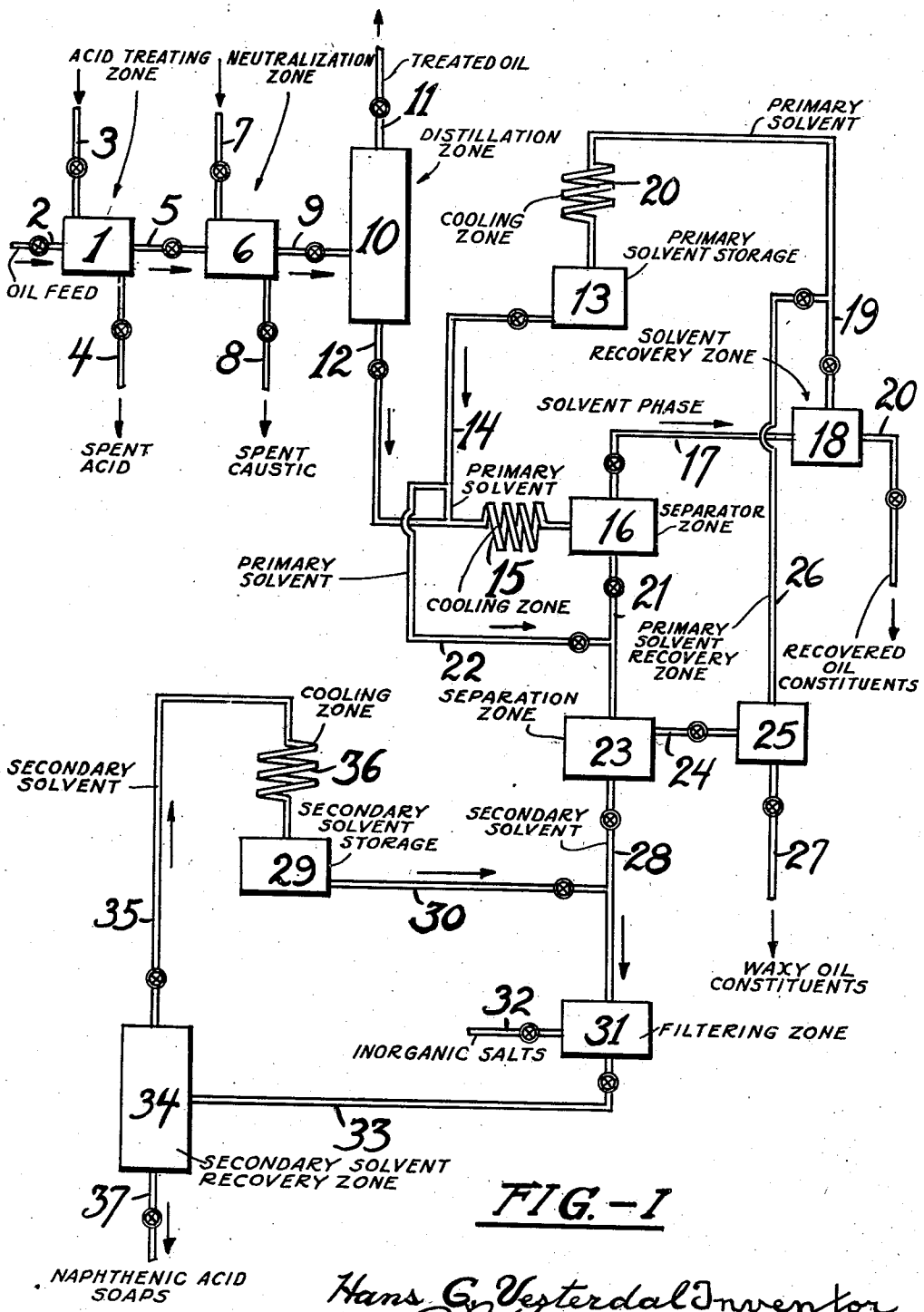


FIG.-1

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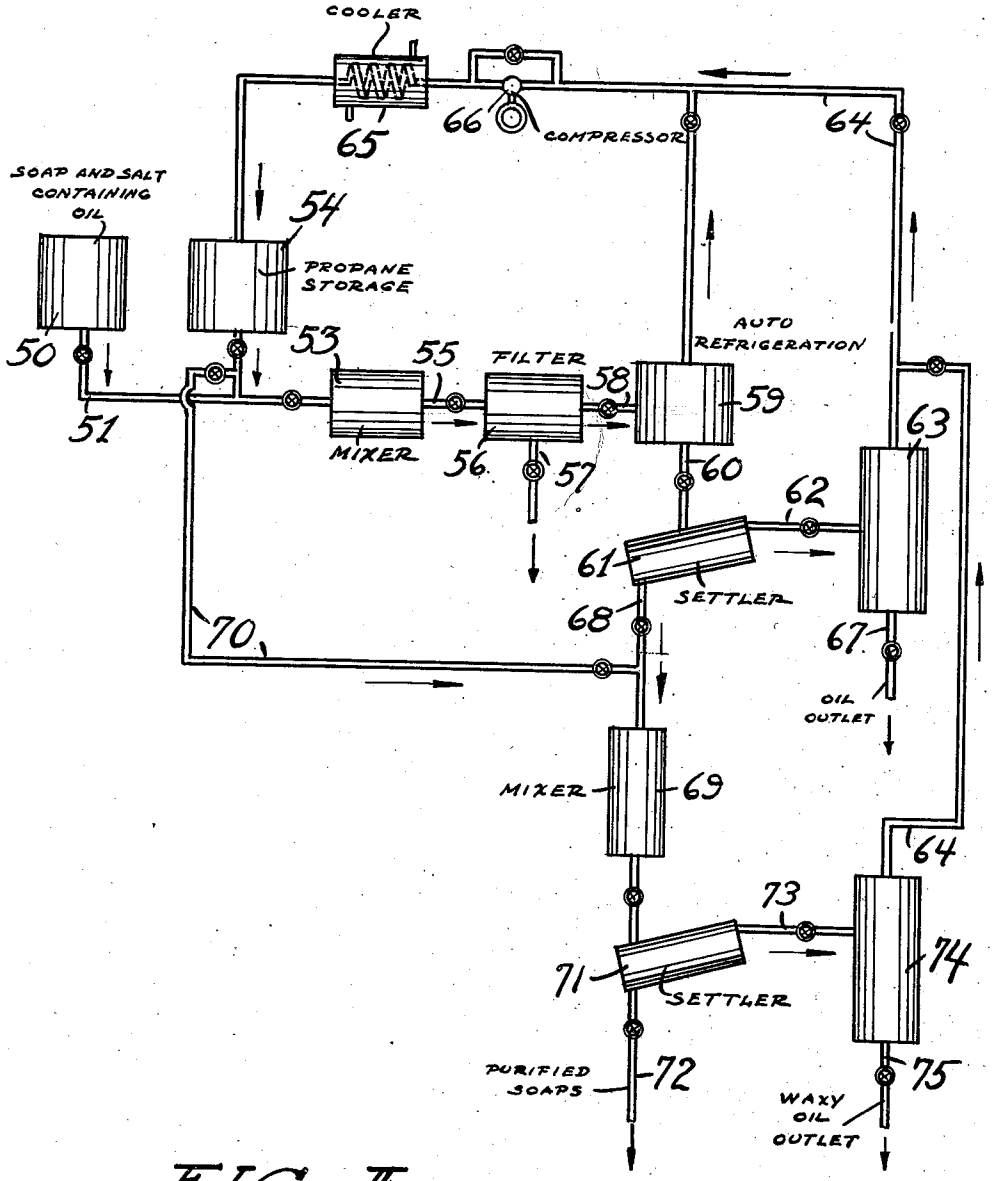


FIG.-II

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Patented Sept. 8, 1942

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UNITED STATES PATENT OFFICE

2,295,065

SEPARATION OF SOAPS FROM OIL

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Application October 1, 1940, Serial No. 359,194

6 Claims. (Cl. 196—13)

The present invention relates to the refining of mineral oils and is more particularly concerned with an improved process for segregating valuable naturally occurring naphthenic type constituents from petroleum oils containing the same. In accordance with the present invention petroleum oil fractions comprising petroleum oil constituents and naphthenic acid constituents are treated with a liquefied normally gaseous hydrocarbon solvent in a particular sequence of stages, whereby valuable petroleum oil constituents and naphthenic acid type constituents are produced.

It is well known in the refining of petroleum oils, particularly in the production of various heating oil and petroleum lubricating oil products, to treat the feed oil in a manner to remove objectionable constituents therefrom. In these refining operations a conventional procedure is to contact the feed petroleum oil fraction with a mineral acid such as sulfuric acid and to neutralize the acid oil after removal of the spent acid with a suitable alkali such as sodium hydroxide. The neutralized oil is then finally distilled in a manner to segregate an overhead distillate substantially completely free of reaction products and other undesirable constituents which comprise inorganic salts, naphthenates, sulphonates, and heavy oil constituents. These constituents, comprising a relatively small amount of the feed oil to the distillation operation, are removed as a bottoms product from the still. Various suggestions have been made for treating this bottoms product for the purpose of recovering additional oil fractions and also for recovering valuable naphthenic and sulfonic acid constituents which are very suitable as emulsifying agents and the like. For example, one operation employed for removing naphthenic soaps and the like from oily constituents is to extract the mixture with an aqueous alcohol solution. However, due to the solubility of the oil constituents in the soap solutions, it is necessary to treat the separated aqueous alcohol solution with another solvent such as naphtha in order to completely free the soap solution of oily constituents. It has also been the practice to remove the oily constituents from the bottom products by distillation. That latter operation, however, is not particularly satisfactory and only the lower boiling oil constituents can be efficiently removed in this manner.

I have, however, now discovered a method for removing acidic type constituents from petroleum oils containing the same and for the recovery of oil constituents and other valuable products which comprises neutralizing the acid oil with a neutralizing medium such as alkali or earth alkali, oxides, hydroxides, or carbonates, or other suitable neutralizing medium, followed by distilling the neutralized product to secure a relatively high boiling fraction comprising inorganic salts, naphthenates, sulphonates, and heavy oil constituents. This segregated latter fraction is treated, in accordance with the present process, with a liquefied normally gaseous hydrocarbon, as for example propane, butane, and the like, or mixtures of the same. The process of my invention may be readily understood by reference to the accompanying drawings illustrating modifications of the same. Referring specifically to Figure 1, for purposes of illustration it is assumed that the naphthenic acid-containing feed oil is a petroleum oil boiling in the lubricating oil boiling range. The feed oil is introduced into acid contacting plant 1 by means of feed line 2 in which it is treated with a suitable mineral acid which for the purpose of illustration is taken to be sulfuric acid. The fresh acid is introduced by means of line 3 and the spent acid is withdrawn by means of line 4. The acid treated oil is withdrawn by means of line 5 and introduced into neutralization unit 6 wherein it is contacted with a suitable alkali which for the purpose of description is taken to be an aqueous solution of sodium hydroxide. The sodium hydroxide solution is introduced by means of line 7 while spent alkali is withdrawn by means of line 8 and handled in any manner desired. The neutralized oil is withdrawn from neutralization unit 6 by means of line 9 and introduced into distillation unit 10. Temperature and pressure conditions are adjusted in distillation unit 10 to remove overhead by means of line 11 a major portion of the treated oil as lubricating oil distillate and to remove as a bottoms product by means of line 12, a heavy residual product comprising inorganic salts, high boiling oil constituents, waxy constituents, and various soaps such as soaps of naphthenic acids originally present in the oil, as well as sulphonates which may have been produced in the treating process. This bottoms product is mixed with a quantity of a low boiling hydrocarbon solvent which is withdrawn from solvent storage 13 and introduced into line 12 by means of line 14. The mixture is passed through cooling zone 15 and introduced into separation zone 16 in which a phase separation occurs. The solvent layer comprising the petroleum oil constituents is withdrawn from

separation zone 16 by means of line 17 and passed into solvent recovery unit 18. Conditions are adjusted to remove from the solvent recovery unit 18 by means of line 19 the solvent, which is passed through cooling zone 20 and reintroduced into solvent storage 13. The recovered solvent-free oil constituents are withdrawn from separation zone 18 by means of line 20 and handled or further refined in any manner desirable. The naphthenic soap layer comprising soaps, inorganic salts and waxy oil constituents is withdrawn from separation zone 16 by means of line 21, and preferably blended with an additional quantity of solvent which is introduced by means of line 22. This mixture is passed into separation zone 23, in which a solvent phase comprising the waxy oil constituents is formed. This phase is withdrawn by means of line 24 and passed to solvent recovery unit 25. Temperature and pressure conditions are adjusted to remove overhead by means of line 26 the solvent which is passed back into the solvent storage 13 by means of lines 26 and 19. Solvent-free waxy oil constituents are withdrawn from separation zone 25 by means of line 27 and handled or further refined in any manner desirable. The naphthenic acid soap layer is withdrawn from separation zone 23 by means of line 28 and mixed with a solvent having a preferential selectivity for the naphthenic acid soaps as compared to inorganic salts. This solvent, which for the purpose of description is taken to be a blend of benzol and isopropyl alcohol, is withdrawn from secondary solvent storage 29 and introduced into line 28 by means of line 30. The solution is passed through filtering unit 31 and the inorganic salts removed by means of line 32. The secondary solvent, containing dissolved therein the naphthenic acid soaps, is withdrawn from filter unit 31 by means of line 33 and passed through solvent recovery unit 34. Temperature and pressure conditions are adjusted to remove overhead by means of line 35 the secondary solvent which is condensed in condenser 36 and returned to secondary solvent storage 29. A substantially pure naphthenic acid soap fraction is withdrawn from recovery unit 34 by means of line 37 and handled in any manner desirable. This fraction may be treated to regenerate the coresponding naphthenic acids from the soaps by acidification or other equivalent means, or the soaps may be employed directly as emulsify-agents in various cutting oils, spray oils and the like, or be otherwise utilized.

A further modification of the process is illustrated in Figure 2, in which the soap and salt containing oil is passed from storage 50 through line 51 into mixer 53 together with propane from storage 54. The mixture is then passed through line 55 into a filter 56 where the inorganic salts are separated from the solution and removed through line 57. The propane solution of oil, wax and soap is then passed through line 58 into a cooler 59 which may be an auto-refrigerator as shown and from there through line 60 into settler 61 where the soaps settle out as a lower layer together with some waxy oil. The top layer which is a solution of oil in propane, is passed through line 62 into still 63 where the propane is distilled off and passed through line 64, compressor 66 and cooler 65 back to the propane storage 54. The oil is removed from still 63 by means of line 67 and handled or further refined as desired. The bottom layer in settler 61 comprising soaps and waxy oil, is passed through line 68 into mixer 69 together with propane from storage added through line 70. The mixture is then passed into settler 71 where the oil and salt-free purified soaps settle to the bottom and are removed through line 72 while the propane solution of waxy oil is passed through line 73 into still 74 where the propane is distilled off and passed back into line 64 and propane storage 54. The waxy oil is removed through line 75 and further refined or treated as desired.

The process of the present invention may be widely varied. The invention essentially comprises employing a low boiling hydrocarbon or liquefied normally gaseous hydrocarbon such as propane or butane in a manner to recover valuable petroleum oil constituents and valuable naphthenic acid soaps from mixtures containing the same. In accordance with the preferred modification of the invention, the process comprises an initial stage in which the inorganic salts are separated from the solution of oil, wax and soaps in the propane before the solution is chilled and settled to remove a top layer containing the greater proportion of the oil constituents, and a secondary solvent treating stage in which the waxy oil constituents are removed from the soap bottoms.

The present operation may be adapted for the segregation and recovery of oil and naphthenic soap constituents from any mineral oil containing the same. It is, however, particularly desirable in the segregation and recovery of these constituents from a fraction resulting as a bottoms product when distilling an acid treated and neutralized petroleum oil fraction boiling in the lubricating oil boiling range. In general the feed stocks preferably comprise mixtures of oil and soaps derived from heavy mineral oil distillates or paraffin waxes. The operation is particularly adapted for the recovery of naphthenic acid soaps and heavy oil constituents from heavy residues as for example from residues which have gravities in the range below about 20° A. P. I., especially below about 15° A. P. I.

Any suitable low boiling hydrocarbon solvent may be used, as for example, propane, ethane, butane and the like, or mixtures of the same. However, in general it is preferred to employ liquefied propane. The quantity of solvent utilized may vary widely depending upon the character of the soap-containing feed oil fraction and the particular solvent or solvent mixture used. In general it is preferred to employ from two to six volumes of liquefied hydrocarbon solvent per volume of soap-containing oil.

Temperatures and pressures are similarly adjusted depending upon the type of feed oil and the solvent used. In general it is preferred to blend the solvent and the oil at substantially atmospheric temperatures and to remove the inorganic salts by filtration. The mixture is then cooled to a temperature in the range below about 50° F., preferably to a temperature in the range from about 0° F. to 30° F. in order to separate a soap phase and a solvent-oil phase. The soap phase is removed from the solvent phase containing the oil constituents and is mixed with an additional smaller quantity of solvent the exact amount of which may vary considerably. In general it is preferred that from about one to three volumes of solvent per volume of soap phase be added.

In order to further illustrate the invention the following example is given which should not be

construed as limiting the same in any manner whatsoever.

Example 1

A Colombian petroleum oil boiling in the lubricating oil boiling range was acid treated with sulfuric acid and neutralized with a sodium hydroxide solution. This acid treated neutralized oil was distilled in a pipe still and the greater part of the oil removed as an overhead distillate. The maximum temperature employed was about 775° F. at an absolute pressure of about 100 mms. of mercury. The residuum, having a gravity of about 13° A. P. I., comprised heavy oil constituents, naphthenates, and inorganic salts. This residuum was removed and mixed with about 2500 cc. of propane per 623 grams of residuum at room temperature under equilibrium conditions. The mixture was cooled to 35° F. at which temperature a phase comprising soaps, inorganic salts, and waxy components settled out. The propane-oil phase was removed and the solvent separated. Approximately 500 grams of propane-free oil per 623 grams of residuum comprising about 80.2% by weight of the pipe-still bottoms were recovered from this phase.

The high molecular weight soap phase was mixed with an additional 800 cc. of propane per 623 grams of residuum at 75° F. A propane waxy oil solution was removed and the solvent recovered therefrom. Approximately 53 grams of clear waxy oil per 623 grams of residuum were recovered from this phase which was equal to 8.5% of the original pipe-still bottoms.

The residue left in the bomb, consisting of soaps and inorganic salts, was mixed with a total of 600 cc. of a 50/50 mixture of benzol and 98% isopropyl alcohol per 623 grams of residuum. The soap solution was filtered and the solvents were removed by distillation. Approximately 48 grams of salt-free soap were obtained which was equal to 7.7% of the original pipe still bottoms.

A 25% solution of this soap was made in a highly refined petroleum oil. When this solution was mixed with water a creamy emulsion was formed, showing that these soap constituents will function as emulsifiers, suitable for use in cutting oils, spray oils, and the like.

Inspection of the original pipe still bottoms and of the products obtained was as follows:

	Yield	Gravity, °A. P. I.	Viscosity Saybolt at 210° F.	Ppt. No.	Ash
Original pipe still bottoms	*Percent* 100	13.0	404	0.50	*Percent* 6.94
Oil extracted with propane at 35° F.	80.2	17.1	296.1	Trace	0.23
Oil from propane wash at 75° F.	8.5		202.1	Trace	0.10
Salt free soap (emulsifiers)	7.7				
Inorganic salt and loss	3.6				

From this data it is apparent that while the original pipe still bottoms had an ash content and precipitation number of such a magnitude that it had to be acid treated before it could be used even as a fuel oil, the propane extracted oil had a low precipitation value and ash content and could be used directly or in blends with other oils as lubricant for steam cylinder engines, as lubricant for heavy machinery or as a component of greases.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the segregation and recovery of valuable oil and naphthenic acid soap constituents from residuums secured in the distillation of acid treated and neutralized oils comprising adding to a residuum a primary low boiling hydrocarbon solvent under conditions to form a primary solvent phase and a soap phase, removing the solvent phase containing dissolved therein oil constituents and separating the solvent therefrom, separating the soap phase and adding thereto additional primary solvent under conditions to form a second primary solvent phase and a soap phase, removing said second primary solvent phase containing dissolved therein waxy oil constituents and separating the primary solvent therefrom, then treating said soap phase with a secondary solvent having the ability to dissolve the soap constituents, removing the secondary solvent from undissolved impurities and separating the secondary solvent from the dissolved naphthenic acid soap constituents.

2. Process in accordance with claim 1, in which said primary solvent is a liquefied normally gaseous hydrocarbon and in which said secondary solvent comprises a mixture of benzol and isopropyl alcohol.

3. Process in accordance with claim 1, in which said residuum has a gravity below about 20° A. P. I.

4. Process for the segregation and recovery of valuable oil and naphthenic acid soap constituents from heavy residuum secured in the distillation of acid treated and neutralized oils comprising adding to a feed residuum a low boiling hydrocarbon solvent under conditions whereby inorganic salts are precipitated, separating the inorganic salts, cooling the solvent mixture to a temperature at which a solvent phase containing dissolved therein oil constituents forms, separating said solvent phase and removing the solvent from the oil constituents, separating a naphthenic acid soap phase and adding thereto additional solvent under conditions to secure the formation of a solvent phase containing dissolved therein waxy oil constituents, separating said solvent phase containing the waxy oil constituents and removing the solvent therefrom, separating the naphthenic acid soap phase and removing the solvent therefrom.

5. Process in accordance with claim 4, in which said low boiling hydrocarbon solvent comprises a liquefied normally gaseous hydrocarbon.

6. Process in accordance with claim 4, in which said residuum has a gravity in the range below about 20° A. P. I.

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