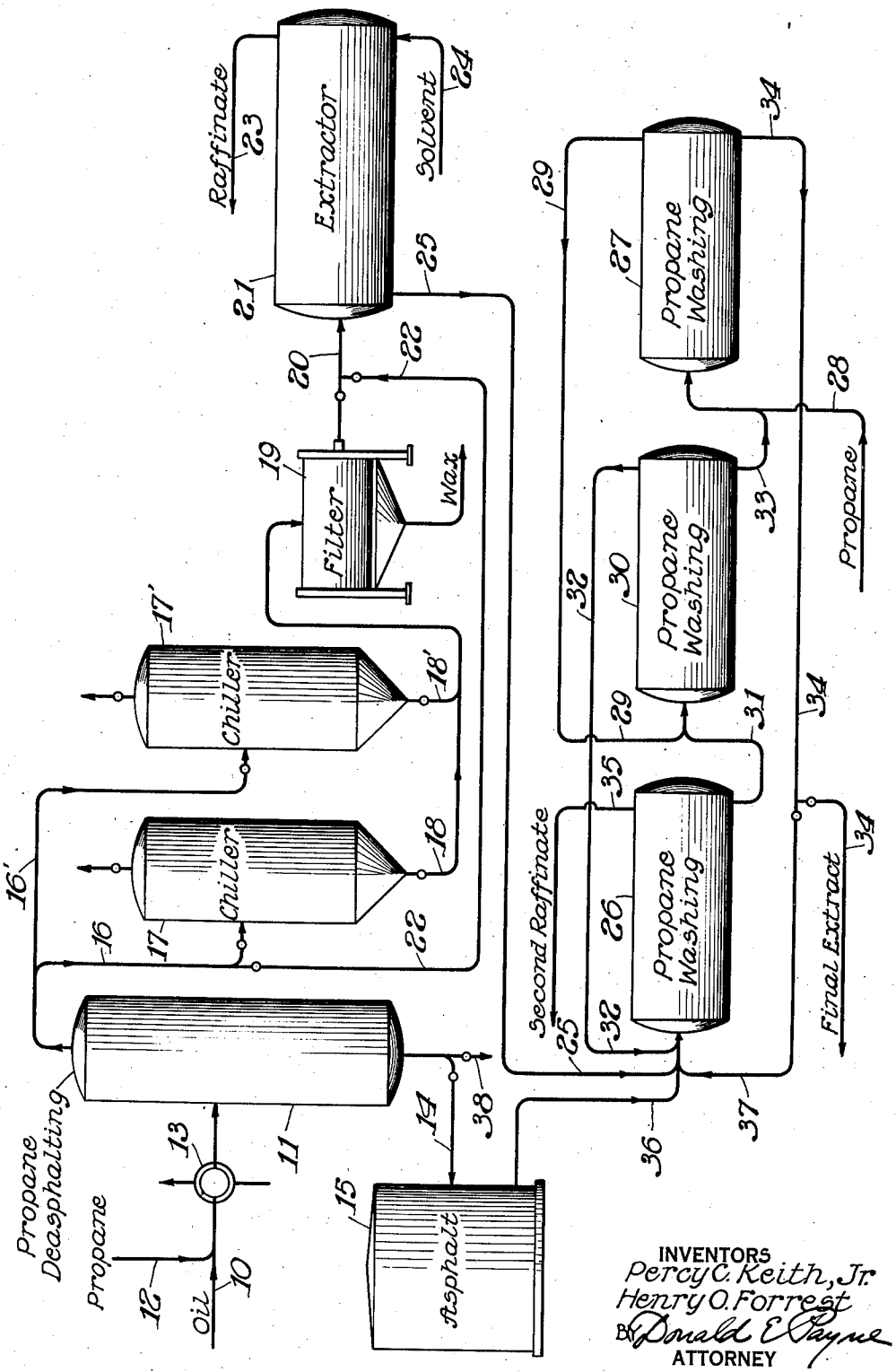
May 11, 1937. P. C. KEITH, JR., ET AL 2,079,911

LUBRICATING OIL REFINING

Filed June 28, 1934



INVENTORS
Percy C. Keith, Jr.
Henry O. Forrest
By Donald E. Payne
ATTORNEY

Patented May 11, 1937

2,079,911

UNITED STATES PATENT OFFICE

2,079,911

LUBRICATING OIL REFINING

Percy C. Keith, Jr., Peapack, and Henry O. Forrest, Teaneck, N. J., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application June 28, 1934, Serial No. 732,918

9 Claims. (Cl. 196—13)

This invention relates to lubricating oil refining and it pertains more particularly to an improved process for separating asphalt, naphthenic components and wax from paraffinic components. Our invention is an improved process for employing propane and selective naphthenic solvents for obtaining both high and intermediate grade lubricating oils from asphaltic and mixed base lubricating oil stocks, either residues or distillates.

The object of our invention is to obtain maximum effectiveness of naphthenic solvent and to obtain maximum yields of premium and high grade oils from any given stock with minimum installation and operating costs. A further object is to provide an improved process wherein the asphaltic and/or naphthenic products produced in the system may supplement the action of the naphthenic solvent without contaminating the high quality paraffinic oil. A further object is to provide a system for recovering an intermediate grade of paraffinic oil from asphaltic and/or naphthenic oil fractions. A further object is to increase the efficiency and effectiveness of a batch countercurrent propane-naphthenic solvent system. Other objects will be apparent as the detailed description of our invention proceeds.

In practicing our invention we first effect a separation of asphaltic components from paraffinic and naphthenic components in the absence of naphthenic solvents. This step is preferably effected by precipitation from a propane solution either at high or low temperatures. The propane solution is then extracted with a naphthenic solvent and it may be dewaxed either before or after this solvent extraction. The raffinate, when freed from solvent and propane, constitutes the premium high quality paraffinic lubricating oil. The extract from the solvent extraction system is washed in a countercurrent batch system with propane and the naphthenicity in this propane washing system is increased either by adding the asphalt precipitated from the first step of the process or by recycling a part of the final extract leaving the countercurrent washing system or both.

We have discovered that by adding asphalt to the solvent extraction extract before washing it with propane we can increase the yield and quality of second grade oil obtainable from any given stock and that similar results can be obtained by recycling a portion of the final extract through the countercurrent propane system. We believe that the oil or extract itself acts in the nature of a selective solvent and that the presence of this asphaltic precipitate or this recycled extract causes further phase separation in the countercurrent propane washing system. However, we do not limit ourselves to any particular theory since it is the process itself and the new, unexpected and important results accomplished thereby which characterize our invention.

The invention will be more clearly understood from the accompanying drawing which forms a part of this specification and which illustrates a diagrammatic plan of our improved system.

In the following description we will disclose the refining of an S. A. E. 40 Mid-Continent steam refined stock. It should be understood, however, that the invention is equally applicable to distillate as well as residual stocks of grades from S. A. E. 10 to S. A. E. 70 whether or not they have been subjected to acid treatments or other refinery operations. We will describe the use of cresylic acid as our selective naphthenic solvent, but it should be understood that this is only an example of a naphthenic solvent and we contemplate the use of any equivalent solvent or solvent mixture, particularly a solvent such as phenol, cresol, ortho, meta and para cresylic acids, nitrobenzene, furfural, dichlorethyl ether, chloraniline, chlorphenol, sulfur dioxide, benzol, etc. and mixtures of two or more of said solvents. We will describe propane as the deasphalting and washing agent, but it should be understood that we contemplate the use of other normally gaseous hydrocarbons such as ethane, butane, isobutane, cyclopropane, propylene, ethylene, etc. and mixtures of the same. The present invention relates primarily to process steps and it should be understood that suitable solvents may be used which will serve the same purpose as the solvents herein described.

The S. A. E. 40 steam refined Mid-Continent lubricating oil stock is introduced directly from a pipe still or from a suitable storage tank through line 10 to deasphalting vessel 11. This vessel should preferably be designed to withstand pressures of from 600 to 1000 pounds per square inch and it should be provided with suitable drawoff means for separating the liquid layers which are formed in the deasphalting step. Propane may be introduced through line 12 into line 10, preferably through suitable mixing apparatus and the mixture may be passed through a suitable heat exchanger 13 before being introduced into the deasphalting vessel. Heating and cooling coils may, of course, be employed in the deasphalting vessel itself.

The temperature of the deasphalting stage will depend upon the nature of the oil stock and the nature of the desired products. If wax is present we prefer to deasphalt at temperatures above 100° F., so that the wax will be carried in the propane solution with the oil. As the temperature is increased from 100° F. to the critical temperature of propane, more and more asphaltic material is thrown out of the solution, together with color bodies and resinous materials. It seems that this fractionation is on the basis of molecular weight, the extremely high molecular weight substances being thrown out of the solution.

We may effect the deasphalting at low temperatures and, in fact, we may precipitate the asphaltic material with the wax and remove the two substances together. This process is advantageous for distillate stocks and stocks containing only small amounts of asphalt and we have found that the asphalt itself assists in dragging the solidified wax out of the solution. The asphalt is discharged through pipe 14 to storage tank 15 and the propane solution is discharged through pipe 16 or pipe 16' to propane dewaxing chiller 17 or 17'. The propane solution may be chilled to −40° F. by vaporizing propane therefrom and this cold slurry may be passed from chiller 17 through pipe 18 or 18' to filter 19 or to any other well known means for separating wax from diluted oil.

The dewaxed filtrate (wax free diluted oil) may be introduced through pipe 20 to solvent extraction system 21 or the propane solution directly from the deasphalting system may be bypassed through line 22 to the solvent extraction system. It should be understood that the amount of propane in the oil as it enters the solvent extraction system may be varied in order to obtain a maximum miscibility temperature with the solvent or, in other words, to obtain maximum phase separation.

The solvent extraction system may be a continuous horizontal extractor wherein solvent is flowed continuously in one direction and the oil is flowed in the opposite direction with mixing and settling means interposed along the length of the extractor to provide intimate contact and to prevent short circuiting during the extraction step. The final raffinate, together with propane and some solvent, is withdrawn through line 23 and reduced in a suitable steam or vacuum still to free the paraffinic oil from propane and solvent, both of which are recovered for reuse. This raffinate is the premium or first grade high quality lubricating oil.

The solvent is introduced into the system through line 24 and it is removed with extract through line 25. This extract contains naphthenic oil components, but it also contains paraffinic components which are miscible with the naphthenic components under the conditions prevailing in the solvent extraction system. In order to recover additional paraffinic components from the extractor, we employ a batch countercurrent propane washing system, the extract being introduced into the first stage 26 thereof and the propane being introduced into the last stage 27 thereof through line 28. Raffinate from stage 27 is introduced through pipe 29 to stage 30 in admixture with extract withdrawn from stage 26 through pipe 31. Raffinate from stage 30 is introduced through pipe 32 to stage 26, together with extract from line 25 and with asphaltic or naphthenic material as will be hereinafter described. Extract from stage 30 is introduced through line 33 to stage 27 in admixture with propane from line 28. Extract from stage 27 is withdrawn through line 34 for final reduction and recovery of solvent and propane or for recycling as will be hereinafter described. The final raffinate from stage 26 is withdrawn through line 35 for vacuum or steam reduction to yield a second grade paraffinic lubricating oil.

We have discovered that both the amount and quality of this second raffinate may be markedly increased by the introduction of naphthenic or asphaltic components with the extract into stage 26. Asphalt may be introduced from storage tank 15 by means of line 36 or naphthenic material may be recycled through line 37. Thus we may operate our process either with asphalt from line 36, naphthenic material from line 37, or both, and by this reintroduction or recycling of asphaltic or naphthenic material we find that the quality and yield of the second grade paraffinic lubricating oil is substantially increased.

Although we have shown the propane dewaxing system placed between the deasphalting and the solvent extraction steps, it should be understood that the dewaxing may be effected after the solvent extraction step or with the deasphalting step. A particularly simple method of procedure is to precipitate both asphalt and wax from the propane solution in vessel 11 at temperatures of −40° F. or lower, to remove the cold propane solution for solvent extraction through lines 16 and 22, and then to heat the remaining mixture in vessel 11 with additional propane to high temperatures at which the wax is in solution and the asphalt is thrown out of solution. This makes possible a liquid phase dewaxing which is much simpler and much less expensive than the ordinary dewaxing. The asphalt may be withdrawn through line 14 to storage and the hot wax solution through line 38 to a propane still and then to storage. It should be understood that if this batch method is used for deasphalting and dewaxing it may be necessary to employ a collector or feed tank so that the extraction process may be continuous. The drawing is diagrammatic and does not purport to show the necessary pumps, storage tanks, piping, valves, stills, etc., the proper use of which is well known to those skilled in the art.

While we have described in detail a preferred embodiment of our invention, it should be understood that we do not limit ourselves to said details 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 lubricating oil containing naphthenic, paraffinic and asphaltic components which comprises treating said oil with liquid propane under pressure to separate asphaltic components from a propane solution of paraffinic and naphthenic components, countercurrently extracting said solution with a naphthenic solvent to separate paraffinic components from naphthenic components, and separately washing the extract from the countercurrent extraction step with propane in the presence of asphaltic material precipitated in the first step of the process whereby a second grade paraffinic lubricating oil is produced.

2. The method of refining a lubricating oil containing paraffinic, naphthenic and asphaltic components which comprises separating asphaltic components from a propane solution of naph-

thenic and paraffinic components, countercurrently extracting said solution with a naphthenic solvent, washing paraffinic oil out of the extract from said countercurrent extraction process in a countercurrent batch propane system to form a second grade paraffinic oil and a final extract, and recycling a portion of the final extract to the first stage of the countercurrent batch propane washing system whereby the yield and quality of the second grade raffinate is improved.

3. The method of claim 1 wherein wax is separated from the paraffinic oil while it is in propane solution.

4. The combination of claim 2 wherein wax is removed from the paraffinic oil while it is in propane solution.

5. The method of increasing the yield and quality of a second grade paraffinic oil obtained by washing a solvent extraction extract (from which the selective naphthenic solvent has not been removed) with propane which comprises adding an asphaltic material to the extract undergoing washing.

6. The method of increasing the yield of paraffinic mineral lubricating oils from a lubricating oil stock consisting chiefly of naphthenic and asphaltic components, which method comprises countercurrently washing said stock with propane in the presence of a naphthenic solvent, whereby the propane dissolves the paraffinic oil out of said stock, and adding asphaltic material to said stock undergoing the propane washing to increase the amount of paraffinic oil dissolved in said propane.

7. The method of refining a lubricating oil containing naphthenic components, paraffinic components and asphalt which comprises treating said oil with liquid propane to separate asphalt from the mixture of naphthenic and paraffinic components, extracting said mixture of paraffinic and naphthenic components with a selective solvent for removing naphthenic components from paraffinic components, removing said solvent which contains naphthenic components together with a small amount of paraffinic components from the separated paraffinic components, adding asphalt to said solvent mixture to cause a further separation of paraffinic components from naphthenic components, removing said separated paraffinic components from the solvent-asphalt-naphthenic component mixture and recovering solvent from each of said paraffinic components and from the asphalt-naphthenic component mixture.

8. The method of refining a mineral oil containing paraffinic components, naphthenic components and asphalt which comprises treating said oil with liquid propane under conditions adapted to cause separation of asphalt, extracting the propane-soluble fraction with a selective solvent, and treating the asphalt from the first step simultaneously with additional propane and with extract material from the second step to recover paraffinic components which would otherwise be discarded with asphalt and extract.

9. The method of recovering relatively paraffinic hydrocarbons contained in an asphalt and in an extract phase from a lubricating oil solvent extraction process which comprises deasphalting a lubricating oil stock containing paraffinic components, naphthenic components and asphalt, solvent extracting a lubricating oil stock containing paraffinic components and naphthenic components, simultaneously commingling the asphalt from said deasphalting step and the extract phase from said solvent extraction step with each other and with a liquefied normally gaseous hydrocarbon selected from the group consisting of ethane, propane and butane, and separating said liquefied normally gaseous hydrocarbon containing said relatively paraffinic hydrocarbons in solution from the remaining materials.

PERCY C. KEITH, JR.
HENRY O. FORREST.