May 11, 1937. V. VOORHEES 2,079,886

OIL REFINING PROCESS

Filed Dec. 29, 1934 2 Sheets-Sheet 1

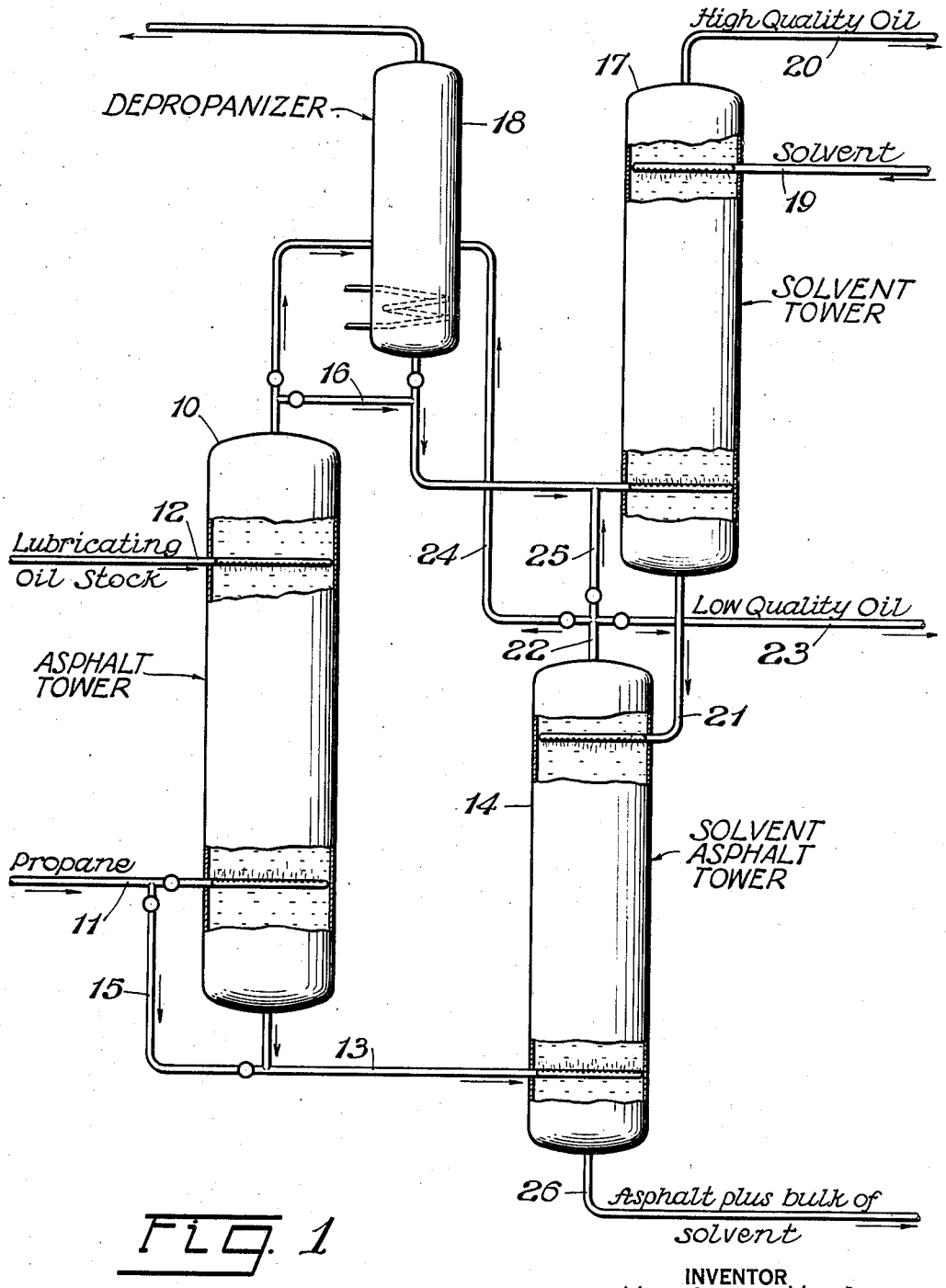


Fig. 1

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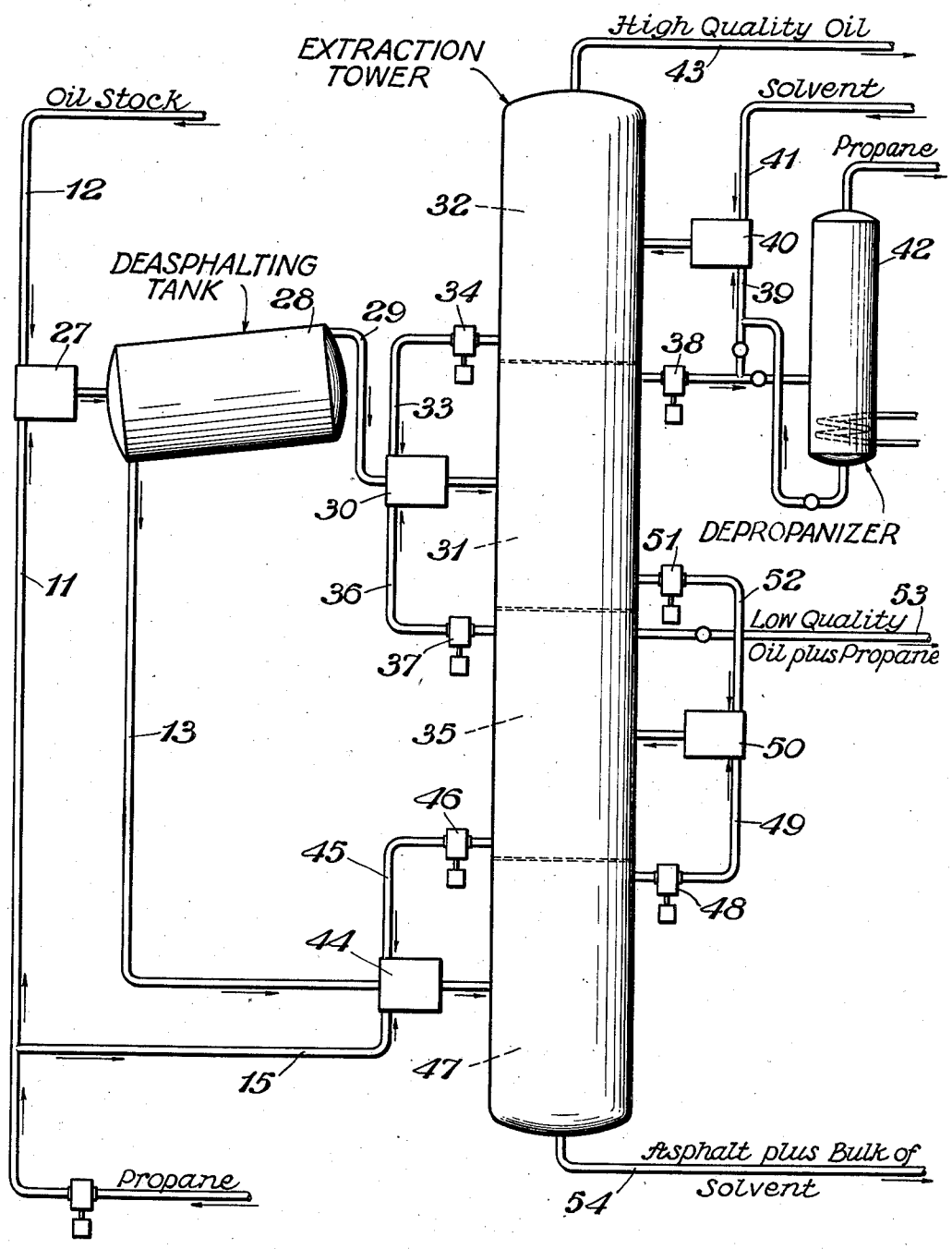


Fig. 2

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OIL REFINING PROCESS

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2 Claims. (Cl. 196—13)

This invention relates to an oil refining process and it pertains more particularly to the sharp fractionation of high quality lubricating oils from low quality materials and resins with which the high quality oils are normally associated.

An object of my invention is to provide a unique combination of propane treating and solvent refining processes wherein the propane-insoluble material from the former is treated with extract material from the latter so that desirable high molecular weight paraffinic oils are recovered from asphalts and resins and a larger yield of high quality and intermediate quality lubricating oils are obtained. A further object is to decrease the amount of solvent required to obtain a given yield and quality of paraffinic oil from a lubricating oil residuum or distillate. A further object is to provide an improved method of rectification in the extract end of a solvent extraction system. Other objects will become apparent as the following detailed description of my invention proceeds.

In practicing my invention, I first treat the oil with propane under conditions which will cause the separation of a propane-insoluble fraction. I extract the propane-soluble fraction with a selective solvent either in the presence or absence of propane and I then contact, preferably in a countercurrent manner, the propane-insoluble fraction from the first step with the extract and solvent from the second step, either separating the raffinate from this last-named treatment as a low quality oil or returning it to the solvent extraction system for increasing the yield of high quality oil.

The invention will be more clearly understood by reference to the accompanying drawings which form a part of the specification and in which,

Figure 1 represents in diagrammatic elevation how my invention may be used with countercurrent towers; and

Figure 2 represents in diagrammatic elevation how my invention may be employed in continuous multiple batch countercurrent extraction systems.

The invention will be described in connection with the prepartion of high quality lubricating oils from a Mid-Continent residuum, but it should be understood that the invention is equally applicable to any lubricating oil stock which contains paraffinic and naphthenic components and material which is insoluble in propane. The invention may even be employed on heavy distillate stocks and on Pennsylvania oils wherein the propane can be employed to throw down "resins" which are not usually called "asphalt." The word "asphalt", as used in this specification and in the appended claims, is also intended to include resins.

Referring to Figure 1, a deasphalting tower 10 which may be a vertical cylindrical pressure vessel which is properly insulated and designed to withstand pressures of about 200 to 1,000 pounds per square inch is filled with propane at about 110° F. from line 11. Lubricating oil stock is then introduced through line 12 at about 150° to 160° F. into the upper part of the tower. The asphaltic material is insoluble in the propane and being of greater specific gravity it falls to the bottom of the tower and is withdrawn through line 13 to solvent-asphalt tower 14, preferably in admixture with propane from line 15. The propane-oil solution is withdrawn from the upper part of the tower through line 16 and introduced at the base of solvent tower 17 as such or it may be passed through depropanizer 18 before being introduced at the base of the solvent tower. The flow of lubricating oil stock and propane into the deasphalting tower should be so regulated that there is a propane-oil ratio of about 4:1 to 8:1, preferably 6:1. The temperature in the deasphalting tower is preferably higher at the upper end than at the lower end so that the material discharged through line 13 may be at about 100° to 110° F. and the propane-oil solution at the top of the tower may be at about 140° to 160° F. The particular propane ratios and temperatures for obtaining the desired phase separation can readily be determined by simple preliminary tests.

In solvent tower 17 the propane-soluble oil is countercurrently extracted with a selective solvent introduced by line 19, preferably of the type exemplified by dichlorethyl ether, phenol, cresol, cresylic acid, wood tar acid, nitrobenzene, furfural, chloraniline, aniline, sulfur dioxide and benzol, etc. or mixtures of these solvents with each other or with other solvents. The characteristic of the solvent is that it is partially miscible with the oil. The solvent-oil ratio and temperature will naturally depend upon the nature of the solvent used and the desired results, but ordinarily I prefer to employ about one to three volumes of solvent per volume of oil and I prefer to operate at about room temperature. High quality oil is withdrawn through line 20 and any remaining propane and solvent is removed therefrom by distillation or chemical means and the oil may be given a finishing treat-

ment such as a contacting to color with clay. These features *per se* form no part of my present invention and they will therefore not be described in detail.

The extract from solvent tower 17 is introduced through line 21 into the top of solvent-asphalt tower 14 and is passed countercurrent to the asphalt which is introduced at the base of this tower through line 13. An outstanding feature of my invention is this use of asphalt from the propane treating process to throw out of solution a large amount of paraffinic oil which would otherwise be lost with this extract. The introduction of asphalt into the base of this solvent-asphalt tower causes the separation of a paraffinic oil phase, which paraffinic oil moves upwardly in the tower countercurrent to the flow of solvent and is removed from the top of the tower through line 22. It may be withdrawn through line 23 as an intermediate or low quality lubricating oil, or it may be passed by line 24 to the depropanizer or by line 25 directly to the solvent tower for increasing the yield of high quality lubricating oil obtainable from the stock undergoing treatment. Any oil which is withdrawn through line 23 will, of course, have to be freed from propane and solvent and will usually require a finishing treatment with acid or fuller's earth in accordance with well known refinery methods.

The material leaving the base of solvent-asphalt tower 14 through line 26 is essentially asphalt and/or resin and solvent, although it may also contain a small amount of propane. By the process hereinabove described I have recovered from the material rejected by the propane-asphalt tower 10 a large amount of high molecular weight paraffinic oil which would otherwise be lost with the asphalt. Also, I have utilized the asphalt to supplement the solvent in this final treatment of the extract material from tower 17 and I have combined the asphaltic or naphthenic constituents extracted by the selective solvent with the high molecular weight asphalt rejected by the propane. If there is no recovery of the intermediate quality lubricating oil the solvent tower and the solvent-asphalt tower may be built as a single unit, the material from the base of tower 10 being introduced at the base of this unit to serve as a rectification medium to effect the separation and recovery of paraffinic oils.

Referring to Figure 2, I have shown the introduction of propane through line 11 and oil stock through line 12 into mixer 27 which discharges into deasphalting tank 28. The temperature of this tank will suitably be between 100° and 180° F., more or less, and may be controlled by regulating the temperature of the incoming stocks or by suitable heating means. The propane-soluble material passes through line 29 to mixer 30 which discharges into separating chamber 31. In mixer 30, the propane solution is intimately admixed with solvent and extract material which is forced from separator 32 through line 33 by means of pump 34. It may also be mixed with raffinate material from settler 35 introduced through line 36 by means of pump 37. Raffinate material from settling chamber 31 may be forced by pump 38 directly through line 39 to mixer 40 for admixture with solvent from line 41 or it may be by-passed through depropanizer 42 before being admixed with the solvent. In general it is preferred to eliminate propane from the final extraction stage or stages. The final raffinate or high quality oil is withdrawn from the top of settler 32 through pipe 43.

Asphalt from deasphalter 28 may be withdrawn through line 13 to mixer 44 wherein it is mixed with propane from line 15 and solvent and extract material from settler 35 via line 45 and pump 46. This mixture is introduced into settler 47 which is preferably maintained at about 100° to 110° F. Raffinate from settler 47 is forced by pump 48 through line 49 to mixer 50 wherein it is admixed with extract material from settler 31 via pump 51 and line 52. Instead of returning the raffinate from settler 35 to mixer 30, I may withdraw it through line 53 as an intermediate or low quality lubricating oil.

Asphalt and the bulk of the solvent are withdrawn through line 54 to suitable propane and solvent recovery means.

From the above description it will be seen that the lubricating oil stock is deasphalted before it comes in contact with the selective solvent and the asphaltic material does not meet the selective solvent until it has reached the very end of its travel through the system. Not only is asphalt eliminated in the raffinate stages of the solvent extraction, but propane may also be eliminated so that in the final raffinate extraction stages a small amount of solvent will give an excellent yield of a very high quality lubricating oil. The extract from settler 35 may contain a considerable amount of low quality paraffinic lubricating oil and the asphaltic material from line 13 may contain a large amount of high viscosity paraffinic material which has been rejected by the propane. When these two materials are intimately admixed with propane and allowed to separate in settler 47, the asphaltic material tends to throw out the intermediate or low quality paraffinic oil and the solvent tends to throw out the high viscosity paraffinic oil which is associated with the asphalt. This paraffinic material is further refined in settler 35 by admixture with solvent extract material from settler 31 and I may withdraw the raffinate from settler 35 as an intermediate or low quality lubricating oil or I may return it through line 36 to mixer 30 for combination with the propane-soluble fraction.

It will, of course, be understood that the handling of propane and other hydrocarbon gases such as ethane and butane, suitable for my process, requires the use of superatmospheric pressures. In the case of propane these will usually vary between 100 and 600 pounds per square inch, depending on the temperature. Higher pressures will prevail in the case of ethane. With the latter, however, lower temperatures are required. Apparatus must be built to withstand the high pressure with an adequate factor of safety.

While I have described in detail preferred embodiments of my invention, it should be understood that I do not limit myself to any of the details hereinabove set forth except as defined by the following claims.

I claim:

1. The method of refining a mineral oil containing paraffinic components, naphthenic components and asphalt which comprises treating said oil with a liquefied normally gaseous hydrocarbon selected from the group consisting of ethane, propane and butane under conditions adapted to cause separation of asphalt, extracting the liquefied-hydrocarbon-soluble fraction with a selective solvent, and countercurrently treating the asphalt from the first step with extract material from the second step in the presence of a

liquefied normally gaseous hydrocarbon selected from the group consisting of ethane, propane and butane to recover paraffinic components which would otherwise be discarded with asphalt and extract.

2. The method of refining a lubricating oil stock containing paraffinic components, naphthenic components and asphalt which comprises separating asphalt from paraffinic and naphthenic components, separating paraffinic components from naphthenic components by means of a selective solvent to give a raffinate phase and an extract phase, and countercurrently treating said asphalt with said extract phase in the presence of liquid propane to recover intermediate quality paraffinic materials contained in said asphalt and in said extract phase.

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