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PROPANE REFINING PROCESS

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This invention relates to refining processes employing propane and it pertains more particularly to the refining of hydrocarbon lubricating oils with liquid propane and to methods for removing propane from the resulting products.

Propane is being used more and more for the refining of lubricating oils, particularly in processes of deasphalting, deresinating, dewaxing, solvent extraction, acid treating, claying, etc. One of the major problems in all of these processes is the efficient recovery of propane from the resulting products and by-products. Particularly in deasphalting or in the treating of heavy residual stocks, there is a problem of heating the propane mixtures and maintaining efficient heat transfer rates in preheaters and heat exchangers. It appears that there is a tendency for the propane to cause a fouling of the tubes by throwing out resins or other sticky, gummy materials which form an insulating skin on the tube walls. Also, there appears to be a tendency for hot propane mixtures to foam in tubes and flash chambers and to carry entrained oil or asphalt into transfer lines, pumps, storage tanks, etc. An object of my invention is to overcome these difficulties and provide an improved system for heating propane solutions and recovering propane therefrom.

I have discovered that the capacity of a commercial deasphalting plant can be markedly increased by my improved heat exchange system, the throughput of the plant being increased in some cases nearly 50%. This is accomplished chiefly by the use of a very simple expedient, the splitting of the propane solution enroute to the flash chamber into two streams, sending one stream directly to the top of the flash chamber to act as a reflux and entrainment arrester and passing the other stream through first an exhaust steam heater and then a live steam heater, and introducing this stream into the flash chamber at a higher temperature than such streams have heretofore been introduced. This system eliminates much of the foaming difficulty, increases the capacity of the recovery system and in one plant where the recovery system was the "bottle neck" it enabled the throughput to be raised from 75% of the rated capacity to 110% thereof.

The invention will be more clearly understood from the following detailed description and from the accompanying drawing which forms a part of the specification and in which I have diagrammatically illustrated an elevational view of my improved system.

The invention will be described as applied to the treatment of a residual Mid-Continent petroleum stock reduced by noncracking distillation to a viscosity of about 400 seconds Saybolt at 210° F. It should be understood, however, that the invention is equally applicable to the treatment of any residual or distillate stocks as well as the treatment of synthetic oils and oil products, particularly products produced by the polymerization of hydrocarbons, the condensation of hydrocarbon radicals with aromatics, products produced by oxidizing, sulfonating, chlorinating or otherwise chemically treating hydrocarbon oils or products, etc. While the invention is described as employing propane, it should be understood that other normally gaseous hydrocarbons may be employed in place thereof, and the term "propane" is intended to include such hydrocarbons or admixtures thereof with pure propane. In the preferred example I will state conditions for a gas consisting essentially of propane and those skilled in the art will appreciate the necessity and manner of modifying the conditions when other gases than propane are used.

About 3 to 5 volumes of propane from storage tank 10 are introduced by pump 11 through heater 12 and line 13 into mixer 14 wherein the propane is intimately mixed with the residual stock from storage tank 15, steam discharge heater 16, pump 17 and line 19. The propane is preferably added to the mixer in stages 19 to avoid entrainment of oil in asphalt particles, i. e., I desire to avoid the agglomeration of insoluble particles prior to the thorough mixture of propane with the stock.

The propane-residuum mixture is then transferred through line 20 to asphalt settler 21, preferably of a temperature of from 110 to 150° F. and a pressure of 390 to 400 pounds gauge. Under these conditions the propane soluble materials separate in an upper layer which is continuously withdrawn through line 22. This solution may either be passed through line 23 directly to the propane recovery means, or it may be passed through reducing valve 24, acid mixer 25, sludge settler 26, caustic mixer 27 and caustic settler 28, and line 29. Alternatively, the propane solution may be passed through a propane dewaxing system, a propane-solvent extraction system or other propane refining process.

In the acid treating process I prefer to use about .2 to .3 pound of 93% sulfuric acid per gallon of residual stock charged and I prefer to effect the acid treating and settling at a tem-

perature of about 105° F. and a pressure of about 210 to 220 pounds gauge. The sour oil is neutralized in caustic mixer 27 wherein about 0.2 gallon of 2% sodium hydroxide are introduced per gallon of sour oil to be neutralized. Acid sludge is withdrawn from the base of settler 26 and caustic wash liquid from the base of settler 28, the propane being recovered from these by-products in a separate recovery system.

The propane-oil solution from line 23 is split into two streams. About $\frac{1}{3}$ is passed through line 30 to the upper part of flash tower 31 above bubble plates 32. The other stream, about $\frac{2}{3}$ of the original solution, is passed through line 33, exhaust steam heater 34, line 35, live steam heater 36 (steam at about 95 to 100 pounds gauge) and line 37 into the flash tower underneath the bubble plates. Line 37 may lead into the flash tower at a point above baffle plates 39 or all or a part of this hot stream may be introduced through line 38 at the base of the flash tower. The flash tower is preferably maintained at a pressure of 195 to 205 pounds gauge with a vapor exit temperature of about 120° F. and an oil exit temperature of about 275° to 290° F. The oil leaving the exhaust steam heater is preferably at a temperature of about 260 to 275° F. and the oil leaving the live steam heater and entering the flash tower is preferably about 300° F.

Propane from the flash tower is withdrawn through line 40 to cooling water condenser 41 wherein it is liquefied and then returned to propane storage tank 10. Hot oil from the base of the flash tower is withdrawn through line 42 and pressure reducing valve 43 to the upper part of oil stripper 44 over baffle plates 45, so that the hot oil passes in countercurrent contact with steam introduced through line 46. The oil leaves the stripper at a temperature of about 265 to 270° F. through line 47 which introduces it over plates 48 in dehydrating tower 49. The oil is blown in this tower with air from line 50, the gases being vented through line 51 and the finished oil being withdrawn through line 52 to storage tank 53.

Propane from oil stripper tower 44 is withdrawn through line 54 to a steam condenser 55 for separating water therefrom. Propane gas leaves the condenser through line 56, compressor 57, line 58 to high pressure line 40, thence to condenser 41 where it is liquefied and returned to storage tank 10.

Asphalt is removed from settler 21 through liquid level control valve 59, line 60 and heater 61 to asphalt flash drum 62. Material entering the asphalt flash drum is preferably about 315 to 320° F. and since this material has a tendency to foam when flashed at this temperature, I introduce a hot fluxing oil through line 63 at the top of the flash tower for breaking this foam. The hot flux oil may be gas oil from line 64 or it may be residual stock from line 65. Under the conditions stated I have found it necessary to employ about equal volumes of flux and separated asphalt.

Propane from the top of the asphalt flash tower is withdrawn through line 66 to high pressure line 40 and propane condenser 41, thence to storage tank 10. Asphalt from the base of the flash tower is withdrawn at a temperature of about 300 to 310° F. through line 67 and reducing valve 68 to asphalt stripper 69, wherein it is stripped with steam from line 70 on baffle plates 71. The stripper operates at a tempera-

ture of about 240° F., the stripped asphalt being withdrawn through line 72 to asphalt storage 73 and the propane and steam being withdrawn through line 74, thence through line 54 to steam condenser 55 from which the propane gas is returned to storage as described above.

The previous method for heating the propane-oil solution entering the oil flash tower was to heat the solution in the exhaust steam heater, introduce the solution at an upper point in the tower and then to use live steam heater 36 as a reboiler, bypassing all of the material there-through and returning the heated oil therefrom to the base of the oil flash tower. Exhaust steam heater 34 is commonly referred to as the "pre-heater" and the live steam heater 36 is called the "reboiler". In accordance with my invention I connect the preheater and the reboiler in series and route about $\frac{2}{3}$ of the stream through these heaters, passing the other third of the solution directly to the top of the flash tower. This process lowers the vapor outlet temperature in the flash tower from about 225-250° F. to about 120-140° F., thus effecting a considerable saving in the amount of condensing water necessary for liquefying the propane returned to storage for reuse. Since less propane solution is put through the preheater and the reboiler (heaters 34 and 36), much less steam is required than has heretofore been necessary, and even with the increased throughput I have effected a saving of from 13 to 18% in steam consumption. The solution introduced through line 30 not only acts as a reflux and cooling means, but it arrests entrainment of oil from the flashing step in the lower part of the flash tower.

Even with my present arrangement of preheater and reboiler in series, I find that with certain stocks the heater tubes are fouled. Cleaning these tubes mechanically is a rather costly job, but I have discovered that these tubes may be cleaned by washing them with hot water. This simple expedient makes it possible to clean the tubes in a very short time so that the plant only has to be off stream about three or four hours. This water method of cleaning simply consists in closing the steam heaters off from the rest of the system and passing hot water through the coils through lines 75.

While I have described my invention in detail, it should be understood that I do not limit myself to any of the particular conditions hereinabove set forth except as defined by the following claims which should be construed as broadly as the prior art will permit.

I claim:

1. The method of removing propane from a solution of propane and deasphalted oil which comprises heating a major part of the deasphalted oil solution to a temperature of about 300° F. and introducing it into a flash zone at a pressure of about 200 pounds per square inch, introducing a minor part of said solution at a temperature of about 100° F. into the upper part of said flash zone, whereby it serves as a reflux liquid and entrainment arrester, and regulating the size of the major and minor parts of the solution so introduced to obtain a vapor exit temperature of about 120° F. and an oil exit temperature of about 290° F. from said flash zone.

2. The method of removing propane from a propane solution of a viscous lubricating oil stock which comprises dividing said solution into minor and major streams, heating the major stream to a temperature of about 300° F. and introducing it

5 into a flash zone at a pressure of about 200 pounds per square inch, introducing the minor stream at a temperature of about 100° F. into the upper part of said flash zone whereby it serves as a reflux liquid and entrainment arrester, maintaining a flash drum vapor exit tem-

perature of about 120° F. and a flash drum oil exit temperature of about 290° F. and steam stripping the oil from the flash zone at a temperature of at least 265° F., and at a lower pressure than the pressure in the flash zone.

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