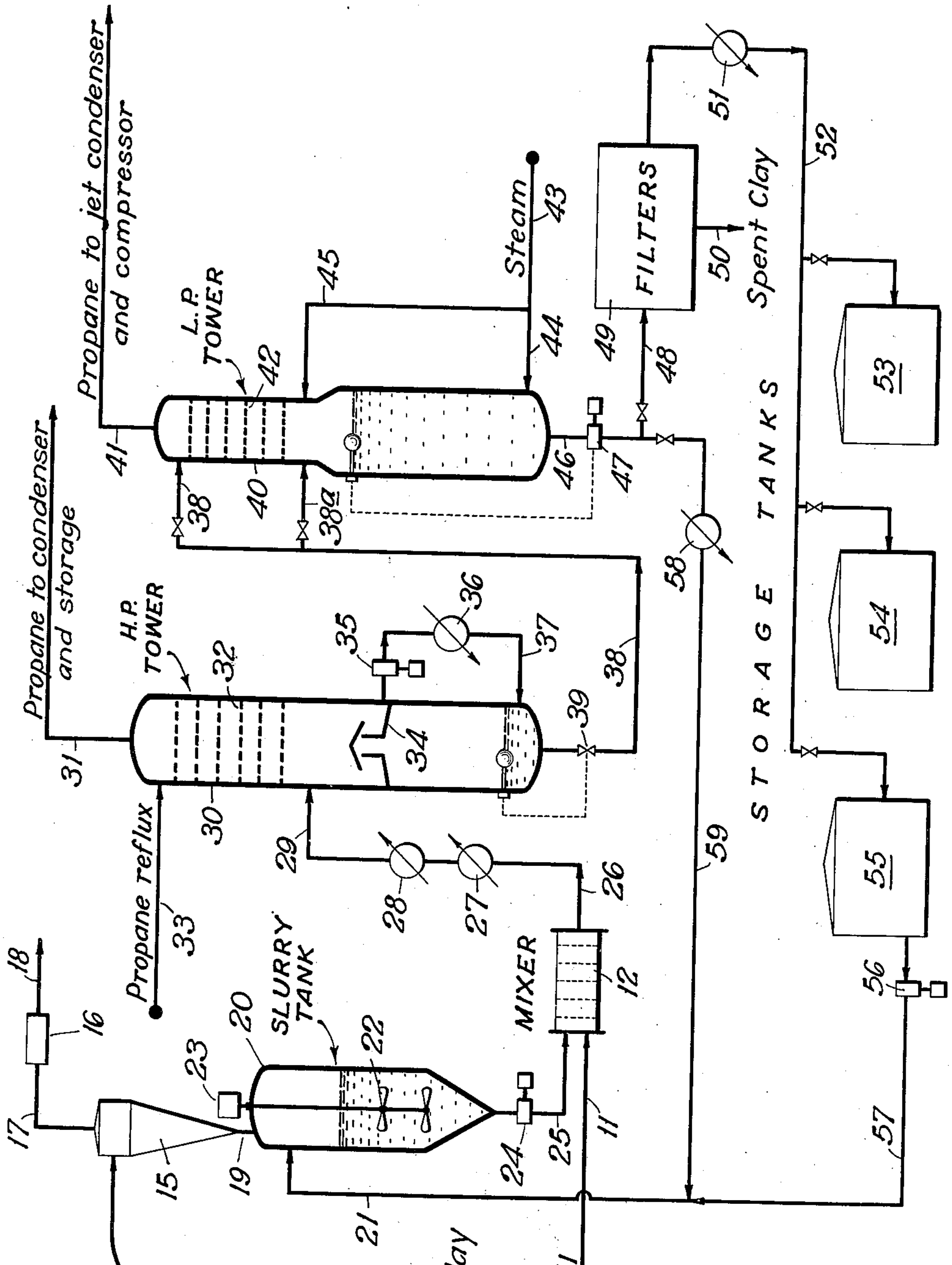
Feb. 26, 1952 L. A. HAYS, JR., ET AL 2,586,947

PROPANE-CLAY TREATING

Filed Nov. 29, 1949



INVENTORS:
Leonard A. Hays, Jr.
Robert B. Selund
BY Donald E. Payne
ATTORNEY

Patented Feb. 26, 1952

2,586,947

UNITED STATES PATENT OFFICE

2,586,947

PROPANE-CLAY TREATING

Leonard A. Hays, Jr., Hammond, and Robert B. Selund, Highland, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application November 29, 1949, Serial No. 129,918

7 Claims. (Cl. 196—147)

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This invention relates to the clay treatment of charging stocks particularly of the lubricating oil boiling range in propane solution, and it pertains more particularly to an improved method and means for treating a propane solution obtained by propane dewaxing of a wax-bearing lubricating oil stock before the propane is removed from the solution.

Advantages obtainable by the clay contacting of lubricating oil stock in propane solution have long been known (note U. S. 2,215,362) and in commercial operations dewaxed propane-lubricating oil solutions have been contacted with clay either with or without an intermediate acid treating in propane solution. It has been the practice, for example, to slurry a contacting clay in a small amount of hot oil from the low pressure propane stripper and inject said slurry to the propane oil solution which is then routed to the high pressure propane recovery tower. Operating difficulties have arisen in such practice because of foaming in the slurrying vessel and because of poorer treating resulting and the production at times of off-color products. The object of our invention is to provide a method and means for avoiding such operating difficulties and for improving the efficiency and effectiveness of the propane clay treating.

We have found that the activity of solid adsorbents, such as activated clay, in removing color bodies from hydrocarbons of the lubricating oil boiling range is greatly influenced by temperature. At temperatures in the range of about 60° to 150° F. and in the absence of propane, solid adsorbent is relatively inactive, but at temperatures of the order of 200 to 400° F., it is highly active. If active adsorbent clay is contacted with a small portion of hot oil before being contacted with the bulk of an oil to be treated, the clay becomes deactivated by the treating effect which it exerts on the hot oil and thus becomes too spent for effective decolorization of the larger portion of the oil with which it is subsequently admixed. In practicing our invention, we slurry the solid adsorbent clay in a portion of previously treated charging stock which has been freed from propane and cooled to a temperature substantially below 200° F., usually below 175° F. and preferably in the range of 60° F. to 150° F., then intimately mix this slurry with a large and relatively cooler mass of a solution of charging stock to be treated dissolved in propane so that the resulting mixture will be at a temperature of the order of about 100° F. After obtaining this intimate mixture at a relatively low temperature,

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the temperature of the mixture is increased to the extent required for obtaining the desired decolorization. The propane is then separated from the decolorized charging stock solution and a small fraction of the propane-free decolorized charging stock is cooled to a temperature below about 175° F. and employed for slurrying additional amounts of active solid adsorbent.

The invention is applicable to any charging stocks in the lubricating oil boiling range and particularly to stocks in the SAE 10 to SAE 60 range. The invention is particularly applicable to dewaxed lubricating oil stocks which have previously been treated with a selective solvent such as phenol, furfural, dichlor-ethyl ether, etc., and/or has been acid treated. The wax removed from a hydrocarbon of the lubricating oil boiling range may itself be propane-clay treated in accordance with our invention. The invention is also applicable broadly to materials fractionatable by propane and in addition to hydrocarbon oils and waxes, it is applicable to fatty oils and waxes of animal or vegetable source, fatty acids, etc., which are fractionatable by propane in the manner described for example in U. S. 2,383,535.

The propane-clay treatment is preferably effected by initially contacting the charging stock (which has previously been thoroughly mixed with the adsorbent slurry prepared with the cooled slurrying medium) in the presence of a large amount of propane at a temperature of about 200° F, then removing the bulk of the propane and finally contacting the charging stock in the presence of a small amount of propane at a temperature of the order of about 400° F. Alternatively, however, the treating may be effected at other temperatures in the range of about 200 to 400° F. and in the presence of various amounts of propane, the propane to charging stock ratio usually being in the range of about .1:1 to 4:1.

The solid adsorbent may be of any type known to those skilled in the art, such as fuller's earth, acid treated clay, such as Filtrol (an acid treated montmorillonite), attapulgus clay, etc., or it may be a synthetically prepared adsorbent such as activated alumina or silica alumina compositions, all of which are well known to those skilled in the art and require no further detailed description. The particle size of the clay should be sufficiently large to enable easy removal by filtration, but sufficiently small to provide maximum surface area and ease of handling, particle sizes usually being in the range of about 100 to 400 mesh. The amount of clay will, of course, be dependent upon the nature of the charging stock and the specifications to be met; for most purposes the clay will be employed at the rate of about .02 to 2 pounds per gallon of charging stock to be treated, about .2 pound per gallon giving excellent results for the clay treating of an SAE 40 Mid-Continent lubricating oil charging stock which has previously been phenol extracted but not acid treated. When the invention is applied to fatty materials, the adsorbent may be vegetable or animal charcoal of the type usualy employed for that purpose.

The invention will be more clearly understood from the following detailed description of a specific example which is illustrated in the accompanying drawing which forms a part of this specification and which schematically illustrates a simplified flow diagram of a commercial propane-clay treating plant employing the invention.

Referring to said drawing, a propane-oil solution enters the system from source **10** and is introduced by line **11** to mixer **12**. In this example the charging stock is a phenol extracted Mid-Continent distillate which has been dewaxed in a commercial dewaxing plant of the type illustrated in U. S. 2,143,872, the propane solution being withdrawn from the filtrate solution tank of the dewaxing plant and passed through heat exchangers to bring it to a temperature of approximately 80° F. The oil in this case is an SAE 40 stock diluted with propane to give a propane to oil ratio of about 2.3:1, the stream consisting of about 1800 barrels per day of oil dissolved in 4200 barrels per day of propane. The term "propane" as used in this specification refers to commercial grades of propane and is intended to include propane which contains minor amounts of other hydrocarbons, such as isobutane, butane, propylene, butylene, etc.

The solid adsorbent in this case is an activated montmorillonite clay, commonly known as Filtrol (specifically, Filtrol X-417) and it is preferably withdrawn from a storage hopper or other source **13** by suction through line **14** to cyclone separator **15**, the suction being applied by eductor **16** which withdraws separated gas from a cyclone through line **17** and discharges it through line **18**. The solid adsorbent particles may be introduced directly through cyclone dip leg **19** into slurry tank **20** or if desired it may be discharged into an upper clay hopper (not shown) and introduced therefrom into slurry tank **20** in controlled amounts by a screw conveyor.

The slurrying medium is introduced by line **21** into tank **20** and the adsorbent is thoroughly dispersed in and mixed with the slurrying medium by stirrer **22** driven by motor **23**. The temperature at which the slurry is prepared should be as low as feasible; since in this case the liquid slurrying medium is very viscous, the temperature is in the range of about 100° to 150° F. It is important that high temperatures (of the order of 212° to 400° F.) be avoided in the slurry tank because such high temperatures cause foaming difficulties and with some adsorbents liberated water vapors condense and plug or otherwise interfere with the solids inlet portion of the system. Also, we have found that when high temperatures are employed in the slurry tank, the activity of the adsorbent is materially diminished before it even contacts the charging stock to be treated and thereby loses its effectiveness in obtaining the required decolorization. In other words, the use of relatively low temperatures in the slurrying tank enables the ultimate attainment of better decolorization with a given amount of adsorbent or the requirement of less adsorbent to meet a given color specification. In this particular example, about 600 pounds per hour of the adsorbent and about 300 gallons per hour of slurrying medium is charged to tank **20**.

The slurry from tank **20** is introduced by pump **24** and line **25** to mixer **12** which may be a baffled chamber such as a knot hole mixer or a stirred mixer or any other type of mixer known to those skilled in the art. The propane-oil solution from line **11** is preferably cooler than the introduced slurry so that the resulting mixture in this case does not exceed a temperature of about 100° F. This mixture, with the adsorbent intimately dispersed throughout the propane-oil solution, is then passed by line **26** through heat exchanger **27** wherein it is heated by indirect contact with at least a portion of the hot finished product, as will be hereinafter described, and next it is heated with low pressure steam in heater **28** to bring its temperature to about 200° F., at which temperature it is introduced through line **29** at an intermediate point into high pressure tower **30** which operates at a pressure of approximately 250 pounds per square inch. Most of the propane flashes from the introduced mixture and is withdrawn through line **31** to the propane condenser and storage tank of the propane dewaxing system. The upper part of tower **30** is provided with a series of baffle plates **32**, and propane reflux is introduced through line **33** above this baffle section of the tower in amounts sufficient to hold the tower top temperature at about 150° F.; this prevents the carry over of any oil with the propane discharged through line **31**.

Below the inlet point of line **29**, the tower is provided with a total trap-out plate **34** for collecting the liquid slurry which is then passed by pump **35** through one or more reboilers **36** heated with high pressure steam to raise the temperature of the oil slurry to at least about 400° F., at which temperature the slurry is returned through line **37** at a low point in the tower. Liquid solid adsorbent slurry is withdrawn from the base of tower **30** by line **38** in amounts regulated by valve **39** which in turn is controlled by the liquid level in the lower part of the tower. The withdrawn slurry at a temperature of approximately 400° F. then passes through line **38** or line **38*a*** to the low pressure tower **40** which operates at about atmospheric pressure, from the top of which propane is withdrawn through line **41** to a jet condenser and thence to a compressor in the propane dewaxing plant. A plurality of trays **42** may be provided in the upper part of tower **40** and stripping steam is introduced into the tower through lines **43** and **44**. Alternately a portion of the steam may be introduced to the tower through line **45**. The stripping steam removes all propane from the oil slurry and the hot oil slurry, which is still in the vicinity of about 400° F., is withdrawn through line **46** by pump **47** which is controlled in accordance with the liquid level to be maintained in tower **40**.

The bulk of the slurry thus withdrawn by pump **47** is introduced by line **48** to precoated filters **49** for removing the spent adsorbent from the oil, the oil being preferably passed through a blotter press for insuring the removal of fine adsorbent particles. Before or after passing through the blotter press (one of the filters), at least a portion of this hot oil may be employed for supplying the heat in heat exchanger **27**.

Spent clay is removed from the filters by line 50. The filtered oil is cooled in cooler 51 and then introduced by line 52 into the proper storage tank 53, 54, or 55. One of these storage tanks 55 is preferably set aside for receiving any filtered oil which does not meet color specifications and this filtered oil, which has previously been cooled in cooler 51, may be passed by pump 56 and lines 57 and 21 to slurry tank 20 to supply the required slurrying medium and simultaneously to receive the additional treatment which it may require.

Normally, the slurry medium is obtained by diverting a small fraction of the propane-free, adsorbent-containing oil discharged by pump 47 through cooler 58 and lines 59 and 21 to slurry tank 20. The amount of oil so diverted may be of the order of about 10 per cent but the amounts used may vary with the amount of adsorbent being charged. The cooling step in this case is of vital importance since this diverted oil stream must be reduced in temperature from about 400° F. to a temperature less than 200° F. and preferably to a temperature in the range of about 60 to 150° F., the lower temperature being used with relatively non-viscous oils and the higher temperatures being employed for oils of relatively high viscosity.

In the above example, we have described the propane adsorbent clay treating of a dewaxed oil solution, the clay contacting being effected prior to propane removal (the high pressure propane removal tower 30 and low pressure stripper 40 being in fact a part of the propane dewaxing system). In other words, the clay contacting step is interposed between the filtering step and the propane removal step in the propane dewaxing system. The filtered wax stream may likewise be propane-clay treated in the propane dewaxing system between the filtration step and the steps of removing propane from the wax. The invention is not limited, however, to these particular streams or to operation in conjunction with propane dewaxing. It is applicable to other systems of propane fractionation wherein at least one of the fractions may be contacted with solid adsorbent prior to the removal of propane therefrom. Examples of such other systems include the so-called "destearining" of animal or vegetable fats or fatty acids by low temperature propane fractionation, and the so-called "Solexol" process of fractionating animal or vegetable fats or fatty acids by high temperature propane fractionation. The term "oleaginous" may be employed to describe the broad class of charging stocks to which the invention may be employed, i. e., viscous hydrocarbon oils, hydrocarbon waxes, fatty oils and waxes of vegetable or animal origin, and fatty acids derived therefrom.

We claim:

1. The method of treating with an active solid adsorbent an oleaginous charging stock in propane solution for improving the color of said charging stock, which method comprises slurrying said adsorbent in a fraction of previously treated charging stock which has been freed from propane and cooled to a temperature substantially below 200° F., intimately admixing said slurry with a large mass of a solution of charging stock to be treated dissolved in propane, heating the resulting mixture to a higher temperature in the range of about 200° F. to about 400° F. effective for obtaining decolorization, separating propane from decolorized charging stock, cooling at least a small fraction of the decolorized charging stock to a temperature substantially below 200° F. and employing said cooled fraction for the slurrying of active adsorbent.

2. The method of claim 1 wherein the charging stock is a hydrocarbon of the lubricating oil boiling range.

3. The method of claim 1 wherein the charging stock is a wax separated from a hydrocarbon of the lubricating oil boiling range.

4. The method of claim 1 wherein the charging stock is a fatty material selected from the class consisting of animal and vegetable waxes, fatty oils and fatty acids.

5. The method of claim 1 wherein the small fraction of decolorized charging stock employed for slurrying said adsorbent is cooled to a temperature in the range of 60° to 150° F. prior to the slurrying step.

6. The method of claim 1 wherein the heating is effected by first heating the mixture in the presence of a large amount of propane to a temperature of about 200° F., then removing most of the propane and heating the mixture in the presence of a small amount of residual propane to a temperature of the order of 400° F.

7. The method of adsorbent clay treating a partially refined hydrocarbon charging stock of the lubricating oil boiling range in propane solution, which method comprises slurrying said adsorbent clay in amounts in the range of .02 to 2 pounds per gallon of charging stock in an aliquot fraction of previously treated charging stock which has been freed from propane and cooled to a temperature not substantially higher than 150° F. to obtain a slurry, intimately admixing said slurry with a large and cooler mass of a solution of charging stock to be treated dissolved in at least about two volumes of propane, heating the resulting mixture to a temperature of about 200° F. under a pressure sufficient to maintain the propane in liquid phase, then separating most of the propane from the heated mixture and heating the residual mixture containing only a small amount of propane to a temperature of approximately 400° F. while at a pressure of the order of about 250 pounds per square inch, then reducing the pressure on the heated solution and stripping it with steam at about 400° F. to remove residual propane, filtering spent adsorbent clay from at least the bulk of the hot stripped oil, cooling at least a small fraction of the hot stripped oil to a temperature in the range of about 60° to 150° F. and employing said cooled fraction for the slurrying of active adsorbent clay.

LEONARD A. HAYS, Jr.
ROBERT B. SELUND.

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