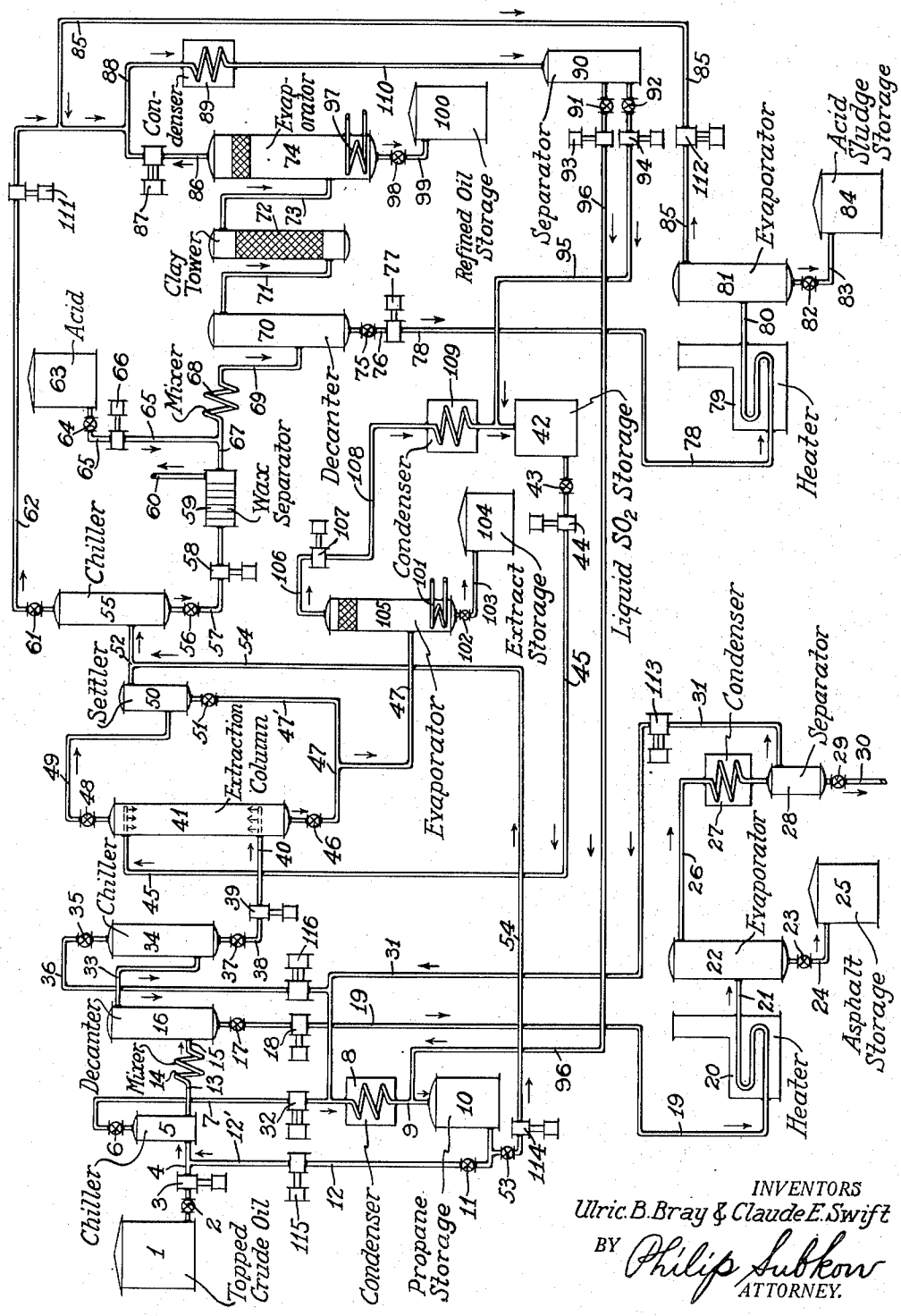
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PROCESS FOR TREATING OIL

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PROCESS FOR TREATING OIL

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5 Claims. (Cl. 196—40)

This invention relates to a method and apparatus for treating petroleum to produce lubricating oil. This invention is a division of our co-pending application, Serial No. 555,018, filed August 4, 1931 and which has issued as Patent 2,006,092, June 25, 1935.

One of the distinctive characteristics of a lubricating oil is its viscosity. For many purposes lubricants are preferred which exhibit a minimum variation in viscosity with variations in temperature, i. e., have low viscosity temperature susceptibility. It is generally known that the viscosity of lubricating oil produced from Western crude, such as California naphthene base crudes, that is, crude containing asphalt varies more with change in temperature than do lubricating oils produced from paraffin base crudes.

That is, if two such oils have the same viscosity at 100° F., the Western oil will have a much lower viscosity at 210° F. than will the paraffin base oil. This change in viscosity with temperature is sometimes called the temperature viscosity susceptibility of an oil. It is one of the characteristics of Western lubricating oils that they are distillates, that is, are vaporized from crude oil and condensed. Lubricating oils produced from paraffin base oils, containing substantially no asphalt, are generally produced by first distilling light oils overhead, including the kerosene and gas-oil and also taking overhead light lubricating oils called "neutrals" having a viscosity in the neighborhood of 100–200 seconds, Saybolt Universal at 100° F., leaving an undistilled residue termed "bright stock." The oils of various viscosity are made by blending these "neutrals" and "bright stock" in any desired proportion to obtain the desired viscosity.

It has been observed by one of us that many oils containing asphalt and wax are mixtures of hydrocarbons analogous both to the hydrocarbons present in paraffin base oils and those present in asphalt base oils. It has further been observed by one of us that during the heating of an oil containing asphalt, the asphalt apparently induces certain chemical and perhaps certain physical reactions at relatively low temperatures which tend to destroy the inherent low viscosity temperature susceptibility of the lubricating oil fractions. This apparent catalytic phenomenon seems to explain the observed changes although we do not wish to be understood as being bound by this theory. It has been observed that these temperatures at which the changes appear are below the vaporizing temperatures in batch distillation (vacuum or steam) of the lubricating oil fractions which have Saybolt Universal viscosities above 400–500 seconds at 100° F. It is safe to say that no oil containing asphalt can be topped to the point where fractions above 400–500 seconds, Saybolt Universal viscosity at 100° F. are vaporized without a degeneration of those characteristics of the paraffin hydrocarbons which impart to the oil a low temperature viscosity susceptibility. During the distillation of the heavy oils in the presence of asphalt some change in molecular structure or configuration takes place which is attended by a change of viscosity temperature characteristics. This behavior is thought to be due to pyrolytic reactions which are catalyzed by the presence of asphalt. The above discovery is made the subject matter of application Serial No. 466,189, filed July 7, 1930, by Ulric B. Bray.

In order to preserve the inherent characteristics of the lubricating oil components of crude oil containing asphalt which are impaired by distillation methods as previously described, we have, in accordance with the process of the above application, caused the separation of the oil and wax from the asphalt by a method wherein the lubricating oil constituents present in the crude oil are separated from the asphalt present in such a manner that the oil retains those characteristics which it possessed in the original crude oil. As a means of attaining this end it has been found advisable to cause the separation of the asphalt from the oil by means of solvents which are capable of dissolving the oil and which do not dissolve the asphalt. Such solvents are light petroleum fractions, such as naphtha, casinghead gasoline and petroleum fractions normally vaporous at ordinary temperature and pressure. Other solvents which may be used are alcohol, ether, mixtures of alcohol and ether, acetone, etc. We prefer to use as our solvent a petroleum fraction obtained by the rectification of natural gasoline. For most purposes a fraction composed of 6.72% ethane, 72.2% propane, 19.91% isobutane and 1.17% normal butane is satisfactory and is an example of commercially obtainable propane. This fraction is characterized by an average molecular weight and an average vapor pressure substantially the molecular weight and vapor pressure of pure propane. It will be understood, however, that these merely illustrate the type of fractions which may be used and that the composition may vary. This fraction will hereinafter be referred to as propane for purposes of simplicity. It is obvious that pure propane or commercial propane, i. e., propane contaminated

with methane, ethane, propylene, butane and the like, are equally applicable for use in our process.

In carrying out the extraction of the oil with this light liquid fraction the solution is maintained at a pressure sufficient to maintain the propane liquid at ordinary temperatures. The fraction described above is liquid at ordinary temperatures at a pressure of about 125 pounds per square inch. The extraction of the oil from the petroleum at such pressures results in an asphalt substantially free of oil consisting chiefly of pure bitumen and a solution of oil and wax in the liquid petroleum fractions. The oil dissolved in the liquid propane contains substantially all of the lubricating oil components which are present in the crude oil and in substantially the same form as they exist in the original crude oil and also the major portion of the wax present in the crude oil.

We have discovered that many lubricating oils obtained by extraction with solvents, for instance, propane, from crude oil containing asphalt and wax are composed of oils which have a relatively high temperature viscosity susceptibility and oils which have a relatively low temperature viscosity susceptibility and that these oils may be separated into oils which exhibit a low temperature viscosity susceptibility resembling oils produced from non-asphalt containing crude and oils which exhibit a high temperature viscosity susceptibility corresponding to oils produced by distillation. For convenience we will call the oils which exhibit a low temperature viscosity susceptibility "paraffinoid" and those which exhibit a high temperature viscosity susceptibility and resemble the Western lubricating oil distillates "non-paraffinoid." The propane extract which consists of such a mixture of paraffinoid and non-paraffinoid oils may be separated into these respective oils by the use of solvent agents which will selectively dissolve out the non-paraffinoid components. We have found that certain solvents have a selective solvent action for the non-paraffinoid oils. As solvent agents which will effect this separation we have found liquid sulphur dioxide, mixtures of acetone and benzol, aniline or methyl formate useful. Acetone alone, in addition to being an asphalt precipitant, also has in some measure the ability to split the oil in the above manner. The use of liquid sulphur dioxide has been found especially valuable as a solvent to separate the propane extract into oils which exhibit low temperature viscosity susceptibility and into oils which exhibit high temperature viscosity susceptibility.

As the propane extract from the crude oil consists of a mixture of wax and oil normally solid at ordinary temperatures, it cannot be separated into its paraffinoid and non-paraffinoid components by the use of sulphur dioxide, without considerable difficulty, unless dissolved in a carrying medium. We have found it advantageous to carry out the extraction of the wax oil mixture with sulphur dioxide in the presence of the liquid propane used in separating the asphalt. The wax oil mixture is dissolved in liquid propane after which it is extracted with liquid sulphur dioxide to remove therefrom the non-paraffinoid components. The propane solution of paraffinoid oil is then chilled to precipitate the wax present after which the chilled mass is cold settled, centrifuged, or filtered to separate the wax from the propane solution of oil. By removing the sulphur dioxide soluble bodies from the propane solution of waxy oil prior to the c waxing operation we are able to obtain a fi product with a lower pour point, i. e., wax co tent than could be obtained if the sulphur dio ide extraction operation were performed subs quent to wax removal. The sulphur dioxide moves from oil certain bodies present which s good wax solvents and which have a tendency prevent precipitation of the wax during the c waxing operation.

The propane solution of oil recovered from t dewaxing operation substantially free of s phalt and wax may be further purified by trea ment with sulphuric acid. Such treatment r moves from the paraffin oil further impuriti which were not removed from the oil by the trea ment with liquid sulphur dioxide.

Generally stated, it is the object of our inve tion to isolate from crude oil those oils havi characteristics which impart to it the low tem perature viscosity susceptibility typical of para fin base oil.

More particularly, it is an object of our inve tion to isolate from asphalt containing oils tho components which impart to the oil the reduc susceptibility to change in viscosity with tem perature which is characteristic of oils obtain from non-asphalt containing oils; that is, to se arate the paraffinoid from the non-paraffino components of the asphalt containing crude oil

It is a further object of our invention to se arate asphalt from an oil containing aspha oil and wax by means of a solvent, to separa the wax and paraffinoid oil from the non-para finoid oil by means of a second solvent used the presence of the first solvent, to separate t wax from the paraffinoid oil and thereafter treat the paraffinoid oil dissolved in said fir solvent with sulphuric acid.

It is a further object of our invention to se arate oil and wax from an oil containing asphal oil and wax by the use of liquid propane; to se arate the wax and paraffinoid oil from the no paraffinoid oil by the use of liquid sulphur d oxide in the presence of liquid propane; to se arate the wax from the paraffinoid oil an thereafter to treat the paraffinoid oil with su phuric acid.

The drawing represents one form of apparatu which we may employ to carry out our proces

Referring more particularly to the drawing, th crude oil which has been distilled to remove ligh oils such as gasoline and kerosene and is itsel a residual oil containing lubricating fraction asphalt and wax in tank 1 is withdrawn throug valve 2 and sent by means of pump 3 throug line 4 where it meets a stream of liquid propan coming from tank 10 through valve 11, line 1 pump 115 and line 12'. The mixture of toppe crude and liquid propane passes from line 4 t chiller 5 where a portion of the propane is al lowed to vaporize through valve 6 and passes b means of line 7 to pump 32 where it is compresse and sent to condenser 8 where it is liquefied an sent by means of line 9 to storage tank 10. Th vaporization of the propane in chiller 5 cause the temperature of the mass therein to be low ered. The cool mass from chiller 5 passes b means of line 13 to agitator 14 where it is thor oughly mixed and sent by means of line 15 t decanter 16 where the asphalt is allowed to set tle out.

The asphalt is withdrawn from decanter 1 through valve 17 and sent by means of pump 1 through line 19 to heater 20 where the propan

and moisture are vaporized. The heated mass passes from heater 20 through line 21 to separator 22 where the asphalt separates from the vapors and is withdrawn through valve 23 and line 24 in the storage tank 25. The vapors in separator 22 are withdrawn through line 26 into condenser 27 where the water vapor present is condensed. The condensed water and propane vapor pass into separator 28 where the water separates and is withdrawn through valve 29 and line 30. Propane vapor passes from separator 28 through line 31 to compressor 113 thence to condenser 8 where it is liquefied and passes by means of line 9 to storage tank 10.

The solution of oil in liquid propane in decanter 16 is withdrawn through line 33 and sent to chiller 34. A portion of the propane present is allowed to vaporize by opening valve 35 and allowing the vapors to pass through line 36 to compressor 116 where it is compressed and sent to condenser 8 and is liquefied, thereafter being sent to storage tank 10. The vaporization of the propane in chiller 34 cools the mass which is thereafter withdrawn through valve 37, line 38 and sent by means of pump 39 through line 40 to the lower zone of extracton column 41. Liquid sulphur dioxide from tank 42 is withdrawn through valve 43 and sent by means of pump 44 through line 45 to the upper zone of extraction column 41. Due to the difference in specific gravity of the oil introduced through the lower zone of the extraction column and the liquid sulphur dioxide introduced into the upper zone of the extraction column, these two liquids tend to separate. As the liquid sulphur dioxide descends through the extraction column it dissolves certain components present in the oil.

The solution of liquid sulphur dioxide and oil is removed from the extraction column 41 through the valve 46 and sent by means of line 47 to vaporizer 105 where the sulphur dioxide is vaporized by aid of steam introduced through closed coil 101 and passes through line 106 to compressor 107 where it is compressed and sent through line 108 to condenser 109 where it is liquefied and sent to storage tank 42. Sulphur dioxide free oil in vaporizer 105 is withdrawn through valve 102 and sent through line 103 to tank 104.

The ascending column of oil in extraction column 41, from which the liquid sulphur dioxide soluble components have been removed, passes through valve 48 to line 49 to auxiliary separator 50 where any remaining liquid sulphur dioxide is settled out. A clear solution of oil is withdrawn from auxiliary separator 50 through line 52 where it may be mixed with a further quantity of liquid propane coming from storage tank 10 through valve 53, pump 114 and line 54. The solution of oil and propane carrying a small quantity of sulphur dioxide passes into chiller 55 where a portion of propane is allowed to vaporize by opening valve 61. The vaporized propane contaminated with sulphur dioxide, passes through line 62 to compressor 111 where it is compressed and sent through line 88 to condenser 89 where both the sulphur dioxide and the propane are condensed and pass by means of line 110 to separator 90 where these two materials separate due to their great difference in specific gravity. The liquid propane in separator 90 is withdrawn through valve 91 and sent by means of pump 93 through line 96 to storage tank 10. The liquid sulphur dioxide in separator 90 is withdrawn through valve 92 and sent by means of pump 94 through line 95 to storage tank 42. The vaporization of the propane in chiller 55 cools the remaining solution of oil present which passes out through valve 56 and line 57 to pump 58 which forces it through filter press 59 where the precipitated wax is removed through line 60.

The wax-free oil from filter press 59 passes through line 67 where it meets a stream of sulphuric acid coming from tank 63 through valve 64, line 65 and pump 66. The mixture of acid and oil passes from line 67 through agitator 68 where the mass is thoroughly agitated, after which it passes through line 69 to separator 70 where the sludge is allowed to settle out. The sludge in separator 70 is withdrawn through valve 75, line 76, to pump 77 which forces it through line 78 to heater 79 where the mass is heated sufficiently to vaporize the propane present. The heated mass passes from heater 79 through line 80 to separator 81 where the sludge separates from the propane and is withdrawn through valve 82 and sent through line 83 to storage 84. The propane vapor is withdrawn from separator 81 through line 85 to compressor 112 where it is compressed and sent by means of line 86 to condenser 89 where it is liquefied and sent by means of line 110 to separator 90 where it is separated from any liquid sulphur dioxide and sent by means of valve 91, pump 93, line 96 to storage tank 10. The liquid sulphur dioxide in separator 90 is withdrawn through valve 92 and sent by pump 94 to sulphur dioxide storage tank 42.

The acid treated oil in separator 70, dissolved in propane carrying varying amounts of sulphur dioxide, is withdrawn through line 71 and passed through clay tower 72 where any remaining sludge is separated out. The fraction of oil leaving clay tower 72 passes by means of line 73 to evaporator 74 where the propane and sulphur dioxide present are vaporized by aid of steam introduced through closed coil 97 and are sent by means of line 86 to compressor 87 where they are compressed and sent by means of line 88 to condenser 89 where they are liquefied and sent by means of line 110 to separator 90. Liquid propane in separator 90 is returned to storage tank 10 through valve 91, pump 93, and line 96. The sulphur dioxide in separator 90 is returned to storage tank 42 through valve 92, pump 94 and line 95. The oil in evaporator 74 which is free from propane and sulphur dioxide is removed through valve 98 and sent by means of line 99 to refined oil tank 100.

As illustrative of the operation of our process for one type of oil and without intending to limit our invention, water free residual oil in tank 1 of Fig. 1 at a temperature of about 200° F. is mixed with liquid propane and cooled by allowing a portion of the propane to vaporize under reduced pressure until the temperature of the topped oil and propane is about 120° F. after which it is thoroughly mixed in agitator 14. The thoroughly agitated mass is then passed into decanter 16 where the propane solution of lubricating oil and wax is separated from the undissolved asphalt. This oil dissolved in liquid propane contains a mixture of paraffinoid and non-paraffinoid components. By subjecting this mixture to the selective solvent action of liquid sulphur dioxide in the presence of liquid propane it is possible to resolve the mixture into a portion of a non-paraffinoid nature soluble in liquid sulphur dioxide and a portion of a paraffinoid nature soluble in liquid propane. The wax present in the mixture being more soluble in the liquid pro-

pane than in the liquid sulphur dioxide remains in solution in the former. This mixture of paraffinoid oil and wax dissolved in liquid propane is then chilled to a point sufficient to cause precipitation of the wax, after which the chilled mass is filtered, centrifuged or cold settled to remove the wax. The wax-free solution of paraffinoid oil dissolved in the liquid propane is then treated with sulphuric acid to remove further undesirable bodies present, after which the solution formed is settled out and the propane removed by distillation from the refined oil.

The foregoing exemplary description is merely illustrative of a preferred mode of carrying out our invention and is not to be taken as limiting, as many variations may be made within the scope of the following claims by a person skilled in the art without departing from the spirit thereof.

We claim:

1. A process for treating oil which comprises diluting said oil with a liquefied normally gaseous hydrocarbon diluent maintaining the diluted oil under sufficient pressure to keep the liquefied normally gaseous hydrocarbon in a liquid state, clay treating said oil and diluent and separating said clay treated oil from said diluent.

2. A process for treating lubricating oil which includes diluting the lubricating oil with a normally gaseous liquefied hydrocarbon diluent maintained at superatmospheric pressure sufficient to maintain the diluent liquid, contacting said diluted oil with clay at such pressure and separating the treated oil dissolved in said liqu fied diluent at superatmospheric pressure fr the clay, and separating said oil from said dilue

3. A process for treating oil which compris diluting said oil with a liquefied normally gaseo hydrocarbon diluent maintaining the diluted under sufficient pressure to keep the liquefi normally gaseous hydrocarbon in a liquid sta treating said oil and diluent with sulphuric ac treating said acid treated oil and diluent wi clay and separating said oil from said diluent.

4. A process for treating oil which compris diluting said oil with a liquefied normally gaseo hydrocarbon diluent maintained at superatmo pheric pressure to maintain the diluent liqui treating said oil dissolved in said diluent wi sulphuric acid at said pressure, contacting sa acid treated diluted oil with clay at said pre sure, separating the treated oil dissolved in sa diluent at superatmospheric pressure from t clay and separating said oil from said diluent.

5. A process for treating mineral oil whi includes diluting the oil with a diluent compos chiefly of propane, maintaining the oil dilut with the propane under sufficient pressure to ke the propane in a liquid state, contacting the diluted with propane with clay, separating t treated oil dissolved in the propane from t clay and separating the propane from the cl treated oil.

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