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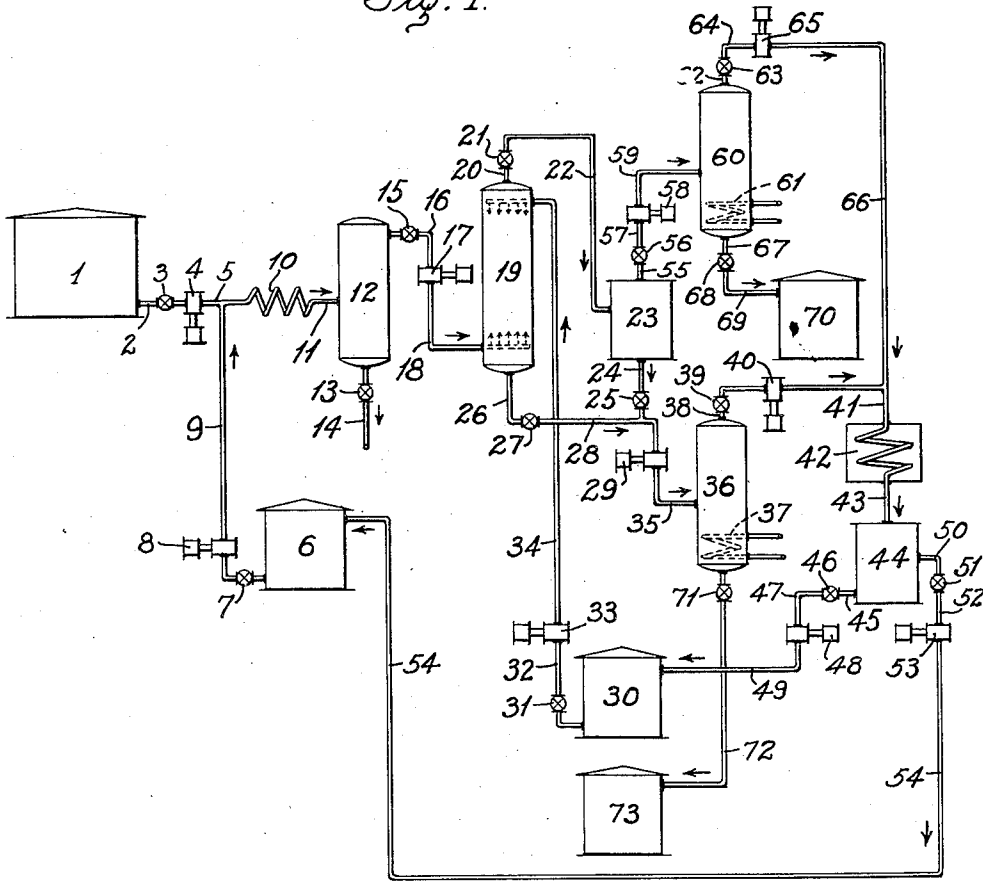
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PROCESS FOR PRODUCING LUBRICATING OILS

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Fig. 1.



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PROCESS FOR PRODUCING LUBRICATING OILS

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12 Claims. (Cl. 196—13)

This invention relates to a process for the production of lubricating oil. More specifically, it relates to a process for the production of lubricating oil from crude oil containing asphalt.

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 asphalt 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 susceptibility of an oil. One of the characteristics of Western lubricating oils, as manufactured by present methods, is 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 phenomena 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 viscosi-

ties 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 the application of Ulric B. Bray, Serial No. 466,189, filed July 7, 1930.

In order to preserve the inherent characteristics of the lubricating oil components of asphaltic crude oil which are impaired by distillation methods, as previously described, we have in accordance with the process of the above application caused the separation of part of the asphalt from the oil under conditions which are not destructive to the inherent viscosity temperature characteristics of the oils present. As a means of attaining this end, a portion of the asphalt is separated from the oil by means of solvents which are capable of partially separating the asphalt from the oil. Such solvents as naphtha or gasoline may be employed advantageously to cause the partial separation of the asphalt from the oil and especially naphtha or gasoline which has been previously subjected to treatment with liquid sulphur dioxide. Furthermore, we may employ light liquid hydrocarbons which are vaporous at ordinary temperature and pressure. Light liquid hydrocarbons recovered during the stabilization of casinghead gasoline, such as ethane, propane, butane and isobutane or mixtures of these components may be employed under pressure to carry out the partial separation of the asphalt from the oil. However, for most purposes a solvent which has a vapor pressure at ordinary temperature lower than atmospheric pressure is very satisfactory, for example, a naphtha or a gasoline. Other solvents, such as alcohol, alcohol and gasoline, alcohol and ether, acetone and acetone and gasoline may be employed.

In carrying out the step of partially separating the asphalt from the oil, the oil is brought into intimate contact with one of the foregoing solvents. The solvent dissolves all of the oil present but causes a portion of the asphalt present to precipitate. The precipitated asphalt is then

removed from the solvent solution of oil and remaining asphalt by settling, filtration, centrifuging or other means, obvious to the art, for the separation of solids from liquids.

5 Many lubricating oils obtained from crude oil or crude oil residuums by extraction with solvents are composed of oils which have a relatively high viscosity temperature susceptibility and oils which have a relatively low viscosity temperature
10 susceptibility. For convenience we will hereinafter refer to the oils which exhibit a low viscosity temperature susceptibility as "paraffinoid" oils and to those which exhibit a high viscosity temperature susceptibility as "non-paraffinoid"
15 oils.

This mixture of paraffinoid and non-paraffinoid oils obtained by extracting asphaltic crude oil with naphtha, gasoline, or the other foregoing mentioned solvents may be separated by the use
20 of solvent agents which will selectively dissolve out the non-paraffinoid components. Solvents which are useful for this purpose are liquid sulphur dioxide, furfural, nitrobenzene, selenium oxychloride, aniline or methyl formate.
25 The use of liquid sulphur dioxide has been found to be especially valuable as a solvent to separate this hydrocarbon mixture into its paraffinoid and non-paraffinoid constituents. The sulphur dioxide not only dissolves the non-paraffinoid hydrocarbons present but also removes as an extract
30 the remaining asphalt present in the oil mixture.

Thus the products which result from the foregoing extraction consist of an extract having a
35 higher temperature viscosity susceptibility than the oil undergoing extraction and a fraction insoluble in the solvent which possesses a lower temperature viscosity susceptibility than the oil undergoing extraction.

40 We have found it advantageous to carry out the separation of the paraffinoid oil from the non-paraffinoid oil and remaining asphalt in the presence of the solvent used to partially separate the asphalt from the crude oil. The oil dissolved in the solvent has a low viscosity and
45 when treated with liquid sulphur dioxide separates into layers readily without emulsification difficulties which usually attend the sulphur dioxide extraction of undiluted oils. As stated
50 above, we prefer to use a liquid sulphur dioxide extracted naphtha or gasoline as a solvent to cause partial separation of the asphalt present in the crude oil. Such a fraction aids materially in the extraction of the oil with liquid sulphur
55 dioxide to cause the remaining asphalt present to dissolve in the liquid sulphur dioxide layer.

In a prior application, Serial No. 555,018, dated August 4th, 1931, we have described a process for
60 the production of lubricating oil from asphaltic residues by treating the residues with a light liquid hydrocarbon, such as propane, to separate the asphalt from the oil and then treating the propane solution of oil with liquid sulphur dioxide to separate the paraffinoid from the non-paraffinoid oils. We have discovered that it is unnecessary to obtain a substantially complete removal
65 of the asphalt from the oil prior to extraction with liquid sulphur dioxide for the separation of the paraffinoid from the non-paraffinoid oils. By removing a major portion of the asphalt present in the oil by the use of naphtha or gasoline and then subjecting the partially de-asphaltized oil dissolved in one of the foregoing solvents to the solvent action of liquid sulphur dioxide the re-

maining asphalt present is removed along with the non-paraffinoid oil in the extract phase without any difficulty.

By using such solvents as naphtha or gasoline for removing asphalt from the oil instead of liquid propane we are able to eliminate the use of
5 high pressure equipment which adds materially to the cost of operating the process.

While our process works satisfactorily with crude oil we sometimes find it desirable to remove
10 the light oil fractions present by distillation prior to the treatment with the first solvent for the partial separation of the asphalt present. The distillation step may be employed to remove from the crude oil the naphtha, gasoline, kerosene and
15 gas oil fractions prior to the extraction with suitable solvents for the partial separation of the asphalt present.

In some cases we have found it more advantageous to use acid instead of solvents to obtain
20 a partial separation of the asphalt from the crude oil prior to the separation of the paraffinoid from the non-paraffinoid fractions. The asphaltic oil is first contacted with a small quantity of sulphuric acid which coagulates a portion of
25 the asphalt present. The coagulated asphalt is separated from the partially refined oil and then the latter is separated by the aid of a solvent, such as liquid sulphur dioxide, into one fraction containing the paraffinoid oils and another
30 fraction containing the non-paraffinoid oils and the remaining asphalt. Where the crude oil is too viscous to obtain a good separation of the acid reaction products from the remaining oil and asphalt, we sometimes find it advisable to
35 add a light diluent, such as liquid sulphur dioxide treated naphtha or gasoline. Thus the crude oil or crude oil residue may first be diluted with liquid sulphur dioxide treated naphtha or gasoline,
40 treated with sulphuric acid to remove a portion of the asphalt present and then extracted with liquid sulphur dioxide for the separation of the paraffinoid oil from the non-paraffinoid oil and remaining asphalt.

It is, therefore, an object of our invention to
45 isolate from crude oil those oils having characteristics which impart to it a low viscosity temperature susceptibility typical of a paraffin base oil.

It is another object of our invention to partially
50 separate the asphalt from asphalt containing oil and then separate the paraffinoid oil from the non-paraffinoid oil and remaining asphalt; employing a method of separating the oils and asphalt which will not change or impair the inherent
55 characteristics of the oils from the form in which they exist in the original crude oil.

It is another object of our invention to extract oil containing asphalt with a first solvent to obtain
60 a partial separation of the asphalt present and extract the oil dissolved in the first solvent containing the remaining asphalt with a second solvent capable of separating the paraffinoid oils from the non-paraffinoid oils and remaining asphalt.
65

It is another object of our invention to extract oils containing asphalt with gasoline to obtain a partial separation of the asphalt present and extract the gasoline solution of oil and remaining
70 asphalt with liquid sulphur dioxide to separate the paraffinoid oils from the non-paraffinoid oils and remaining asphalt, and then separate the gasoline and sulphur dioxide from the oil fractions.

Figure 1 is illustrative of one form of apparatus in which we may carry out our process.

Referring more particularly to Figure 1, asphaltic oil in tank 1 passes by means of line 2 and valve 3 to pump 4 which forces it through line 5 into agitator 10 where it meets a stream of naphtha or gasoline coming from tank 6, through valve 7, pump 8 and line 9. The mixture of asphaltic oil and gasoline or naphtha is thoroughly mixed in agitator 10 and then passes by means of line 11 into separator 12 where the asphalt precipitated by diluting the asphaltic oil with the solvent settles out and is removed through valve 13 and line 14. The amount of asphalt which is precipitated by the gasoline or naphtha will depend largely upon the degree of dilution of the asphaltic oil with the light solvent. In general, we find that the use of three parts of solvent to one part of asphaltic oil will precipitate sufficient asphalt to enable us to operate the subsequent steps of our process without encountering emulsion difficulties due to the presence of excessive quantities of asphalt.

The partially de-asphaltized oil dissolved in solvent is withdrawn from separator 12 through valve 15 and line 16 into pump 17 which forces it through line 18 into the bottom of treating column 19. The solvent solution of oil introduced into the bottom of column 19 passes upward countercurrently to a stream of liquid sulphur dioxide introduced into the top of column 19 and coming from tank 30 through valve 31, line 32, pump 33 and line 34. The liquid sulphur dioxide during its passage downward in column 19 through the ascending stream of oil dissolved in solvent removes from the latter oil constituents present which exhibit a high temperature viscosity susceptibility along with the remaining asphalt which was not removed in separator 12. The sulphur dioxide carrying the high temperature viscosity susceptibility oil and asphalt is removed from treating column 19 through line 26, valve 27 into line 28 where it is combined with liquid sulphur dioxide containing high temperature viscosity susceptibility oil and asphalt removed from the treated oil in supplementary settling chamber 23 through line 24 and valve 25. The solution of oil and asphalt in liquid sulphur dioxide passes from line 28 into pump 29 which forces it through line 35 into evaporator 36 where by aid of steam introduced through closed coil 37 the sulphur dioxide is vaporized from the oil and asphalt. The vaporized sulphur dioxide is removed from evaporator 36 through line 38 and valve 39 into compressor 40 which forces it through line 41 into condenser 42 where it is liquefied and passes by means of line 43 into liquid separator 44. The sulphur dioxide free oil and asphalt in evaporator 36 are removed through valve 71 and line 72 to storage tank 73.

The sulphur dioxide extracted oil dissolved in gasoline or naphtha is removed from treating column 19 through line 20, valve 21 and line 22 into supplementary settling chamber 23 where any entrained liquid sulphur dioxide is allowed to settle out as has been previously described. The treated oil dissolved in gasoline and carrying a small quantity of sulphur dioxide passes from supplementary settling chamber 23 through line 55, valve 56, line 57 to pump 58 which forces it through line 59 into evaporator 60 where by aid of steam introduced through closed coil 61 the light solvent consisting of gasoline or naphtha and the sulphur dioxide present are vaporized. These vapors are removed through line 62, valve

63 and line 64 to compressor 65 which forces them through line 66 and line 41 to condenser 42 where they are liquefied and pass by means of line 43 into liquid separator 44. Due to the difference in specific gravity of the liquid sulphur dioxide and the liquid gasoline or naphtha in separator 44 these liquids stratify. The gasoline or naphtha present is removed through line 50, valve 51, line 52 to pump 53 which passes it back through line 54 to storage tank 6. The liquid sulphur dioxide in separator 44 is removed through line 45, valve 46 and line 47 to pump 48 which forces it through line 49 to liquid sulphur dioxide storage tank 30.

The treated oil having a low temperature viscosity susceptibility in evaporator 60 is removed through line 67, valve 68 and line 69 to storage tank 70.

The above is not to be taken as limiting, but merely illustrative of a mode of carrying out our invention, which we claim to be:

1. A process for producing lubricating oil from residual oil which comprises dissolving said oil in liquid propane, separating said oil dissolved in liquid propane into a plurality of fractions with a solvent and subsequently separating the propane and solvent from said fractions.

2. A process of producing lubricating oil from residual oil which comprises dissolving said oil in liquid propane, separating said oil dissolved in propane with sulphur dioxide into a plurality of fractions and subsequently separating the propane and sulphur dioxide from said fractions.

3. A process for the production of lubricating oil from an oil containing asphalt, paraffinic and non-paraffinic fractions which comprises extracting said oil with liquid propane and a solvent capable of dissolving the asphalt and non-paraffinic fractions, separating the paraffinic fractions dissolved in said liquid propane and separating the asphalt and non-paraffinic fractions dissolved in said solvent.

4. A process for the production of lubricating oil from an oil containing asphalt, paraffinic and non-paraffinic fractions which comprises extracting said oil with liquid propane and liquid sulphur dioxide, separating an oil fraction dissolved in said liquid propane and separating the asphalt and an oil fraction dissolved in said liquid sulphur dioxide.

5. A process of selectively extracting an oil containing asphalt which comprises commingling said oil with a liquefied normally gaseous hydrocarbon and a solvent having a selective solvent power for certain fractions of the oil and the asphalt, separating said oil into a plurality of fractions one of which contains asphalt, and separating said fractions.

6. In a process for separating mineral oil containing paraffinic and naphthenic constituents into fractions respectively more paraffinic and more naphthenic than the original oil, the step comprising extracting the oil, in the presence of a liquid having greater solvent power for paraffinic constituents than for naphthenic constituents, with furfural, the said paraffinic solvent and furfural being adapted to form a two-layer liquid system in contact with each other.

7. A process for separating paraffinic hydrocarbons from non-paraffinic hydrocarbons in a hydrocarbon mixture which comprises commingling said mixture in liquid propane, extracting said commingled mixture in liquid propane with furfural and subsequently separating the

furfural and dissolved fractions from the remaining oil.

8. In a process for separating mineral oil containing paraffinic and naphthenic constituents
5 into fractions respectively more paraffinic and more naphthenic than the original oil, the steps comprising contacting the oil with liquid propane and furfural, and separating the resultant solutions by difference of specific gravity, the said
10 propane and furfural being adapted to form a layer solvent system when contacted with each other.

9. The method of refining mineral oil containing naphthenic and paraffinic constituents which
15 comprises extracting the oil in the presence of a light petroleum fraction comprising mainly hydrocarbons having properties of volatility and viscosity characteristic of propane and butane,
20 with a selective solvent liquid comprising mainly furfural, the resulting mixture forming a two-layer system whereby the oil is separated into fractions respectively rich in naphthenic and paraffinic constituents.

10. A process for the separation of oil containing non-paraffinic constituents into fractions which comprises commingling said oil with liquid propane and a solvent having selective solvent
5 power for non-paraffinic fractions of the oil, separating the oil into a plurality of fractions and separating said fractions.

11. A process for separating oil containing paraffinic and non-paraffinic constituents into fractions respectively more paraffinic and more non-
10 paraffinic than the original oil which comprises commingling said oil with liquid propane and a selective solvent, forming a raffinate phase comprising paraffinic oil fractions dissolved in liquid propane and an extract phase comprising non-
15 paraffinic oil fractions dissolved in the selective solvent and separating said phases.

12. A process according to claim 11 in which the selective solvent is sulphur dioxide.

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