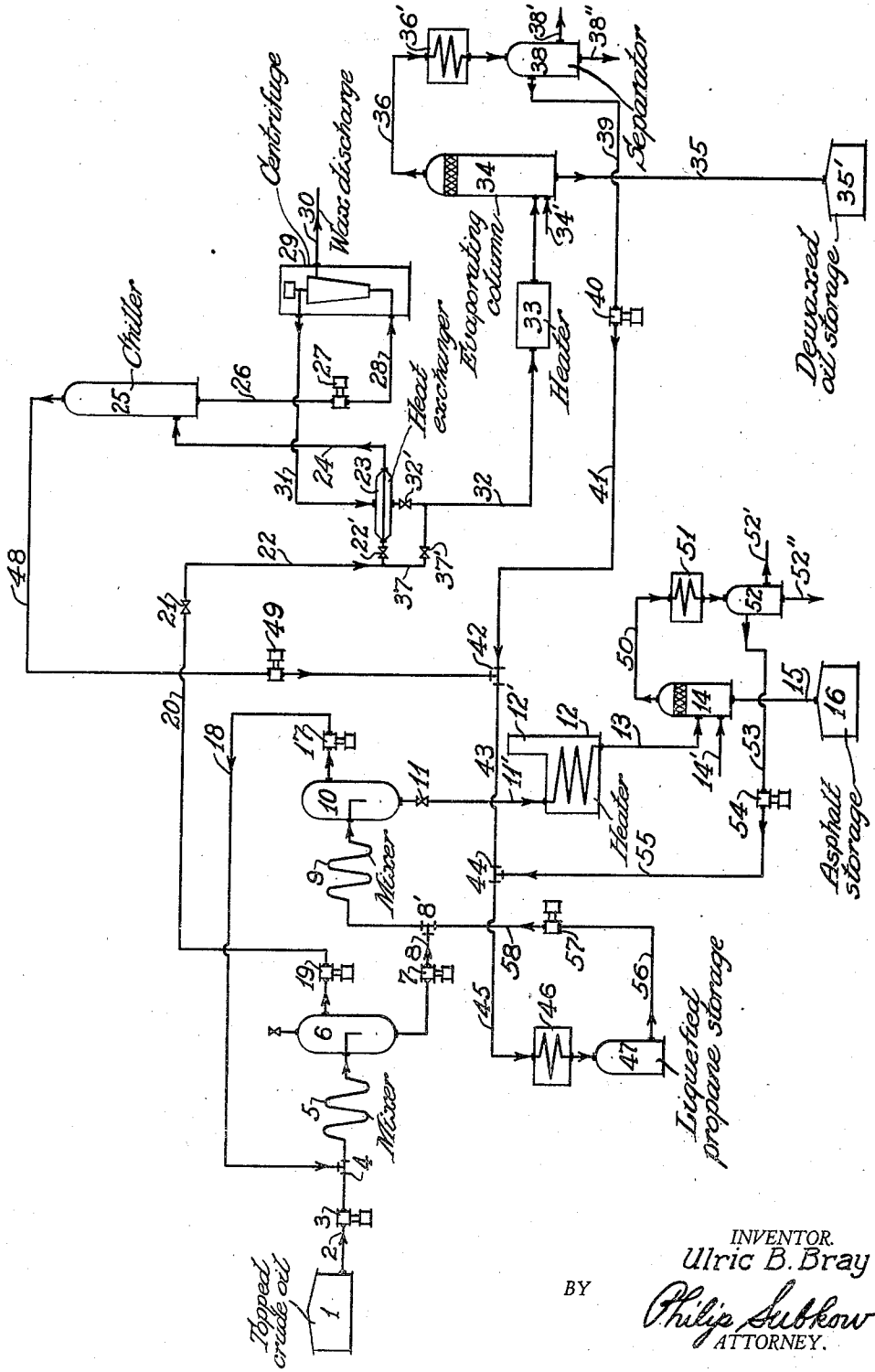
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ASPHALT

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ASPHALT

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12 Claims. (Cl. 196—152)

This invention relates to a process for the production of asphalt and is a division of my patent application Serial No. 466,190, filed July 7, 1930 and is a continuation in part of my patent application, Serial No. 466,189, filed July 7, 1930.

In the co-pending application Serial No. 466,189 is described a process for the extraction of asphaltic materials from oil containing lubricating fractions under conditions such as to preserve the inherent characteristics of the lubricating oil. Distillation of oil in the presence of asphalt induces in the oil a chemical and perhaps physical transformation which destroys in it bodies or properties which impart to the oil a relatively small change of viscosity with change in temperature. In order to preserve these characteristics without any change it was found necessary never to heat the oil above those temperatures necessary to remove oil having a viscosity of 400–500 seconds Seybolt universal at 100° F. If the oil is heated in the neighborhood of 600 to 620 F. the distillates produced have their viscosity temperature characteristics impaired. Lubricating oils were therefore produced by removing the light fractions from crude oil up to those fractions having a viscosity of 400–500 seconds Saybolt universal at 100° F. The distillation was carried out with sufficient steam to maintain the temperature below that at which the asphalt induces the deleterious transformations in the viscosity temperature characterics of the oil, i. e., below 600–630° F. The oil is then extracted with solvents which are capable of dissolving the lubricating oil but not of dissolving the asphalt. Such solvents are naphtha, casinghead gasoline, liquid hydrocarbon gases such as propane and/or butane, ether and/or alcohol, and acetone.

I prefer to use liquefied propane and butane to extract the oil from asphalt by mixing the solvent and the oil under pressure. This liquid solvent is obtained in the rectification of natural gas gasoline and a typical analysis of such a solvent is 6.72% ethane, 72.20% propane, 19.91% isobutane and 1.17% normal butane. The asphalt precipitates out and is allowed to settle under pressure. The mixture of lubricating oil and solvent is then withdrawn from the pressure separator by flashing it through a heating coil into a separator where the vaporized propane and butane are withdrawn from the lubricating oil. The vaporized solvent is recondensed by the use of pressure and is cooled and returned to the process. The separated asphalt may be rewashed by liquid propane or butane to insure its freedom from oil. As a particular example of the process and apparatus reference may be had to the accompanying drawing.

Referring to the drawing, oil, containing asphalt and wax, which has been distilled until the desired viscosity fraction is obtained to leave a topped residuum of desired character to be used in the process or the residuum which has been produced from the selected crude in any desired manner, is taken from the topped residuum storage tank 1 through line 2 to the suction of pump 3 to be sent through the T into mixing coil 5, and is discharged into decanter 6. The pressure in 6, 10 and 47 is controlled and equalized by connecting lines and is maintained at about 125 pounds, which at ordinary temperatures will maintain the solvent in liquid condition. At T 4 a stream of liquefied propane containing a small amount of dissolved lubricating oil, coming through line 18, is mixed with the topped residuum. The liquid propane and topped residuum are thoroughly mixed in passing through mixing coil 5 discharging into decanter 6. The asphalt in the topped residuum is precipitated by the liquid propane in the form of a slurry, which settles to the bottom of decanter 6. The asphalt slurry from the bottom of decanter 6 is sent by pump 7 through line 8 to T 8' where it is mixed with fresh liquid propane coming from propane storage 47 through line 56 to pump 57 and thence through line 58 to T 8'. The mixture is passed through mixing coil 9 for complete mixing and then into decanter 10. The asphalt slurry from the bottom of decanter 10 is drawn off through the pressure reduction valve 11 and sent through line 11' to coil 12 in furnace 12' where sufficient heat is applied to effect vaporization of the propane and the melting of the asphalt. The heated material from coil 12 passes through line 13 into evaporator 14, into which steam is introduced via 14' to aid in flashing the last of the propane, and reducing the asphalt to satisfactory flash and fire specifications. The reduced asphalt from evaporator 14 is drawn off through line 15 and sent to asphalt storage tank 16. The overhead from evaporator 14 is sent

through line 50 to condenser 51 and into separator 52. The uncondensed propane from separator 52 is sent through line 53 to propane compressor 54. Water is removed through line 52'' and condensed light lubricating oil through 52'. The compressed propane is sent through line 55, T 44, and line 45 to cooler 46 where the propane is liquefied, and passes into propane storage 47. The overflow from decanter 10 consisting of a propane solution of lubricating oil passes through pump 17 and line 18 to T 4, where it is mixed with the incoming topped residuum as described above. The overflow from decanter 6 is passed through pump 19 and line 20 to the pressure reduction valve 21. The pressure is now to be released on the propane so that the evaporation of propane will produce a sufficiently low temperature in the remaining solution to permit a satisfactory dewaxing operation. The propane solution passing pressure reduction valve 21 goes through line 22 into heat exchanger 23, where it gives up heat to the oil discharged from the centrifuge 29, valves 22' and 32' being open and valve 37' in by-pass 37 being closed. The pressure reduction valve 21 may be placed before or after interchanger 23. The propane mixture leaving interchanger 23 passes through line 24 into cooling chamber 25, where sufficient propane is evaporated at a suitable pressure to-wit, 0 pounds gauge, to produce the desired temperature, to-wit, —40° F. in the remaining material. The propane carried to this point in the system thus acts as a direct refrigerant, thus eliminating the use of expansion coils or other indirect cooling apparatus. The cooled mixture in the bottom of cooling chamber 25, consisting of a propane solution of lubricating oil and precipitated amorphous wax, is sent through line 26 to pump 27 and then through line 28 to the gas tight centrifuge 29.

The wax is discharged from the centrifuge through line 30. This wax may be worked up in any desired manner to recover propane, oil and wax.

The dewaxed oil solution is discharged from the centrifuge through line 31 and is passed through interchanger 23 in order to pick up heat from the propane solution going into the cooling chamber as described above. Leaving interchanger 23, the dewaxed solution then passes through line 32 into heater 33 which may be any type of heating equipment, such as a pipe still or heat interchanger. The heated solution from heater 33 is passed into evaporating column 34, into which steam via 34' is introduced for the purpose of aiding the flashing of the last of the propane and reducing the remaining oil to satisfactory flash and fire specifications. The bottoms from evaporator 34 are drawn off through line 35 and sent to dewaxed lubricating oil stock storage tank 35'.

The overhead from evaporator 34 is passed through line 36 to cooler 36' and into separator 38. Condensed light lubricating oil is withdrawn through 38' and water from 38''. The uncondensed propane in separator 38 is passed through line 39 to propane compressor 40 and then through line 41, T 42, line 43, T 44, and line 45 to cooler 46 where the compressed propane is liquefied and passes into propane storage 47.

The overhead from cooling chamber 25, consisting of propane vapors is passed through line 48 to propane compressor 49, from which it passes through T 42, line 43, T 44, and line 45, to cooler 46 where it is condensed and passes into propane storage 47.

If the oil to be treated is an asphaltic base oil free of wax, the oil may be sent via by-pass 37, valve 37' being opened and valves 22' and 32' being closed, directly to heater 33 and processed as above.

The above treatment separates substantially all the oil from the bitumens forming the asphalt and also separates substantially all of the wax, if the oil contains wax, from the bitumen.

The asphalts thus produced have peculiar properties quite unlike any asphalts produced from petroleum oil. The appended table gives the properties of the asphalts as produced from a great number of crude oils. The asphalts are unchanged in chemical character, i. e., they have the chemical composition as present in the original crude. The comparison of these asphalts with previous asphalts refers to asphalts of like nature, i. e., unoxidized asphalts conventionally produced by steam or fire distillation without introduction of any chemical reagent such as air, sulfur, etc. While for strict accuracy, comparison should be made with distilled asphalts produced from the same oil, yet since the melting point, ductility, penetration, solubility relationships of all distilled asphalts, independent of their source is the same, the comparison is equally valid when made with distilled asphalts produced from any asphalt containing oils.

The melting point in the appended table is given by the ball and ring method known as the A. S. T. M. method D 36—26 described on page 496 of the A. S. T. M. Book of Standards, (1927).

The penetration is given at two temperatures, that is, at 77 and 32° F. The penetration method is A. S. T. M. method D 5—25 described on page 493 of the A. S. T. M. Book of Standards, (1927). Ductility is given at 77° F. and is determined by the A. S. T. M. method D 113—26T described on page 481 of the A. S. T. M. Tentative Standards, (1929). Solubility in carbon bisulfide, carbon tetrachloride or 86° naphtha is determined by the A. S. T. M. method D 4—27 described on page 484 of the A. S. T. M. Book of Standards, (1927). These are the conventional and universally known methods of determining asphalt characteristics. The difference in solubility between carbon bisulfide and carbon tetrachloride, that is, the difference obtained by subtracting from the total solubility in carbon bisulfide, the solubility in carbon tetrachloride, is known as the carbene content of the oil.

The solubility in 86° naphtha determines the ease with which the oil will blend with petroleum fractions.

The carbene content is related to their quality. The lower the carbene content, the higher the quality and, in fact, if the carbene content exceeds 0.5% the trade refuses to accept the asphalt. These carbenes are insoluble in petroleum fluxes. A high carbene content is considered an indication of poor refining and is prohibited in most commercial specifications for paving and similar grades of asphalt. The penetration and ductility and the relationships between penetration and ductility determine its usefulness and its workability. Observation of these properties will indicate the peculiar usefulness of the new asphalt.

Our new asphalts having a penetration ranging from 1 to 16 at 77° F. have solubilities in 86° naphtha ranging from 71.06 to 91.02. It will be observed that for the same penetration, the new

asphalts will be much more soluble in 86° naphtha than previously known petroleum asphalts, particularly those produced by steam distillation. These asphalts are, therefore, more readily fluxable.

substantially zero. This is much less than in steam distilled asphalts of less than 10 penetration commonly obtained.

The new asphalts have a lower penetration test for the same melting point than previously

Asphalt

Source of crude	Specific gravity 60/60	Melting point ball and ring, °F.	Pen. at 77° F. (100 grams 5 sec.)	Pen. at 32° F. (200 grams 60 sec.)	Ductility at 77° F. cm.	Solubility in CS_2 %	Solubility in CCl_4 %	Solubility in 86° API naphtha %	Sulfur (bomb) %
Montebello	1.083	185	2		0.0	99.08	99.04	77	1.3
McKittrick	1.058	153	8	3	0.0	99.76	99.84	87.2	
Do	1.044	138	16	3	100+	99.88	99.78	91.2	
Santa Maria	1.027	117	100	24	100+	99.8	99.75	81.9	4.32
Santa Fe Springs	1.009	110	Soft.	32	38	99.87	99.91	88.2	0.95
Montebello	1.066	177	3		0.0	99.76	99.69	84	1.52
Santa Fe Springs	1.066	165	2		0.0	99.95	99.93	82.4	1.1
Elwood	1.032	138	47	10	100+	99.67	99.72	83.6	0.61
Torrance	1.066	179	9	3	0.0	99.85	99.64	76.9	3.29
Poso Creek	1.066	147	7	2	100+	99.84		86.9	0.72
Coalinga	1.060	151	8	0	0.0	99.90	99.83	83.1	1.06
Summerland	1.080	186	1	1	0.0	99.84	99.85	84.7	0.66
Santa Barbara	1.076	199	1	1	0.0	99.87	99.84	84.3	0.80
Santa Maria	1.073	178	2	2	0.0	99.88	99.87	74.1	4.86
Sunset	1.061	175	3	0	0.0	99.78	99.81	83.6	1.48

It will be observed that the crudes treated are both the asphaltic and mixed base types (i. e., containing both wax and asphalt). Thus McKittrick, Poso Creek, Coalinga, Summerland, Sunset are typical asphalt base oils. While Montebello, Santa Maria, Santa Fe Springs, Elwood, Torrance and Santa Barbara contain both asphalt and wax and may be classed as mixed base oils.

The appended table shows the variation of solubility for different penetrations.

Penetration at 77°	Source of crude	Solubility in 86° naphtha
		Percent
1	Santa Barbara	84.3
1	Summerland	84.7
2	Santa Fe Springs	82.4
3	Sunset	83.6
3	Montebello	84.0
7	Poso Creek	86.9
8	McKittrick	87.2

In like manner, for the same melting point the new asphalts are much more soluble in 86° naphtha than previously known petroleum asphalt. The asphalts exceeding 170° melting point have solubility exceeding 76% in 86° naphtha. This is much greater solubility than ordinary petroleum asphalt.

It will be observed that these high solubilities result in a high melting point asphalt which is much more readily fluxible than previously known high melting petroleum asphalts.

M. P. (ball and ring) °F.	Source	Solubility in 86° naphtha (by weight)
		Percent
110	Santa Fe Springs	88.2
117	Santa Maria	81.9
138	McKittrick	91.2
147	Poso Creek	86.9
151	Coalinga	83.1
153	McKittrick	87.2
165	Santa Fe Springs	82.4
175	Sunset	83.6
177	Montebello	84.0
179	Torrance	76.9
185	Montebello	77.0
186	Summerland	84.7
199	Santa Barbara	84.3

The new asphalts, including those having penetrations of less than 10, have carbene contents

known asphalts, facilitating their application as high melting temperatures are unnecessary.

Melting point (ball and ring)	Penetration—	
	At 77° F.	At 32° F.
138	16	3
141	7	2
151	8	0
153	8	3
165	2	
175	3	0
177	3	0
178	2	2
179	9	3
185	2	
186	1	1
199	1	1

Since the asphalts produced by this process are harder than previous process asphalts of the same melting point, thus high melting point asphalts having relative low penetration may be produced. It is one of the characteristics of these asphalts that they have not been exposed to high temperature in their preparation and are substantially oil-free. They are pure bitumens.

Thoroughly extracted bitumens have lower melting points for a given penetration than asphalts produced by distillation, particularly steam distillation. They have approximately the same solubility in carbon disulfide, but the extracted bitumens are lower in carbenes as determined by the solubility in carbon tetrachloride, and are more soluble in 86° F. naphtha. Unlike ordinary distilled asphalts and particularly steam distilled, they have no general melting point-penetration relationship, since this relationship for extracted bitumens varies greatly with, first, different crudes, and, second, the thoroughness with which the bitumen is freed of oil. The melting point-penetration relationship of extracted bitumens can be governed to a certain extent by the quantity of and character of oil used in fluxing it, as illustrated in the succeeding paragraph. Extracted bitumens have very nearly the same specific gravity as distilled asphalt and particularly steam distilled of equal melting point.

A valuable peculiarity of extracted bitumens is that the melting point-penetration relationship of asphalts made by incompletely removing the

oil during extraction, can be controlled to a certain extent. For example, note the following:

Source	M. P. ° F.	Pen. at 77° F. 100 gr. 5 sec.	Normal M. P. for steam distilled asphalt of equal penetration, ° F.	M. P. difference ° F.	Remarks
Santa Maria	117	100	110	+7	Incompletely extracted.
Do	178	2	219	−41	Well extracted.
Santa Fe Springs	110	Soft.	About 96	+14	Incompletely extracted.
Do	165	2	219	−54	Well extracted.

The probable reason for this peculiarity of extracted bitumens as compared to steam distilled asphalts is that the original state of colloidal dispersion has been destroyed by propane extraction of the lubricating oil and when the bitumen is redispersed in oil a different state is obtained from that existing in steam distilled asphalts.

The above description is merely illustrative of the invention and is not to be understood as limiting. Many variations will appear to those skilled in the art within the scope of my invention which I claim to be:

1. Asphalt precipitated from an asphalt bearing oil by means of solvents, said asphalt being washed substantially free of oily fractions by means of solvents and having a melting point by the ball and ring method between 138° F. and 199° F., a carbene content of substantially 0, and a penetration at 77° F. between 16 and 0.

2. Asphalt precipitated from an asphalt bearing oil by means of solvents, said asphalt being washed substantially free of oily fractions by means of solvents and having a penetration at 77° F. of 3 or less, a carbene content of substantially 0, and a solubility in 86° naphtha exceeding 74%.

3. Asphalt precipitated from an asphalt bearing oil by means of solvents, said asphalt being washed substantially free of oily fractions by means of solvents and having a melting point by the ball and ring method of over 170° F., a carbene content of substantially 0, and a solubility in 76° naphtha exceeding 86%.

4. An asphalt precipitated from an oil containing asphalt by means of a normally gaseous liquid hydrocarbon solvent, the major portion of which solvent consists of hydrocarbons of less than 4 carbon atoms, said asphalt having a melting point by the ball and ring method between 138° F. and 199° F., a carbene content of substantially 0, and being highly soluble in 86° naphtha.

5. An asphalt precipitated from an oil containing asphalt by means of a normally gaseous liquid hydrocarbon solvent, the major portion of which solvent consists of propane and ethane said asphalt having a penetration at 77° F. of 10 or less, a carbene content of substantially 0 and being highly soluble in 86° naphtha.

6. An asphalt precipitated from an oil containing asphalt by means of a normally gaseous liquid hydrocarbon solvent, the major portion of which solvent consists of propane said asphalt having a lower penetration, a higher solubility in 86° naphtha, and a lower carbene content than an asphalt of the same melting point produced by distillation.

7. An asphalt precipitated from an oil containing asphalt by means of a normally gaseous liquid hydrocarbon solvent, the major portion of which solvent consists of hydrocarbons of less than 3 atoms said asphalt having a lower carbene content and a higher solubility in 86° naphtha than an asphalt of the same melting point produced by distillation.

8. An asphalt precipitated from an oil containing asphalt by means of a hydrocarbon solvent having an average molecular weight less than butane, said asphalt having a melting point by the ball and ring method between 138° F. and 199° F., a penetration at 77° F. between 16 and 0, a carbene content of less than approximately .1, and a solubility in 86° naphtha between approximately 71% and 91%.

9. An asphalt precipitated from an asphalt containing oil by means of liquid propane, said asphalt being substantially free of oily fractions and having a lower penetration than an asphalt of the same melting point produced by distillation, a higher solubility in 86° naphtha and a lower carbene content than said asphalt produced by distillation.

10. An asphalt precipitated from an asphalt containing oil by means of liquid propane, said asphalt being substantially free from oily fractions and having a penetration at 77° F. of less than 10, a carbene content of substantially zero, and being highly soluble in 86° naphtha.

11. An asphalt precipitated from an asphalt containing oil by means of liquid propane under pressure, said asphalt being substantially free of oily fractions and having a penetration at 77° F. of less than 10, a carbene content of substantially zero and being highly soluble in 86° naphtha.

12. An asphalt precipitated from an asphalt containing oil by means of liquid propane, said asphalt being substantially free of oily fractions and having a melting point by the ball and ring method between 138° F. and 199° F., a penetration at 77° F. between 16 and zero, a carbene content of less than approximately .1 and a solubility in 86° naphtha between approximately 71% and 91%.

ULRIC B. BRAY.

CERTIFICATE OF CORRECTION.

Patent No. 1,988,714. January 22, 1935.

ULRIC B. BRAY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 48, claim 3, for "76°" read 86°; and line 49, of said claim, for "86%" read 76%; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of March, A. D. 1935.

Leslie Frazer

Acting Commissioner of Patents.

(Seal)