March 24, 1959 B. C. BENEDICT ET AL 2,879,219

ASPHALT COMPOSITION, AN ADDITIVE THEREFOR AND METHOD FOR PRODUCING SAME

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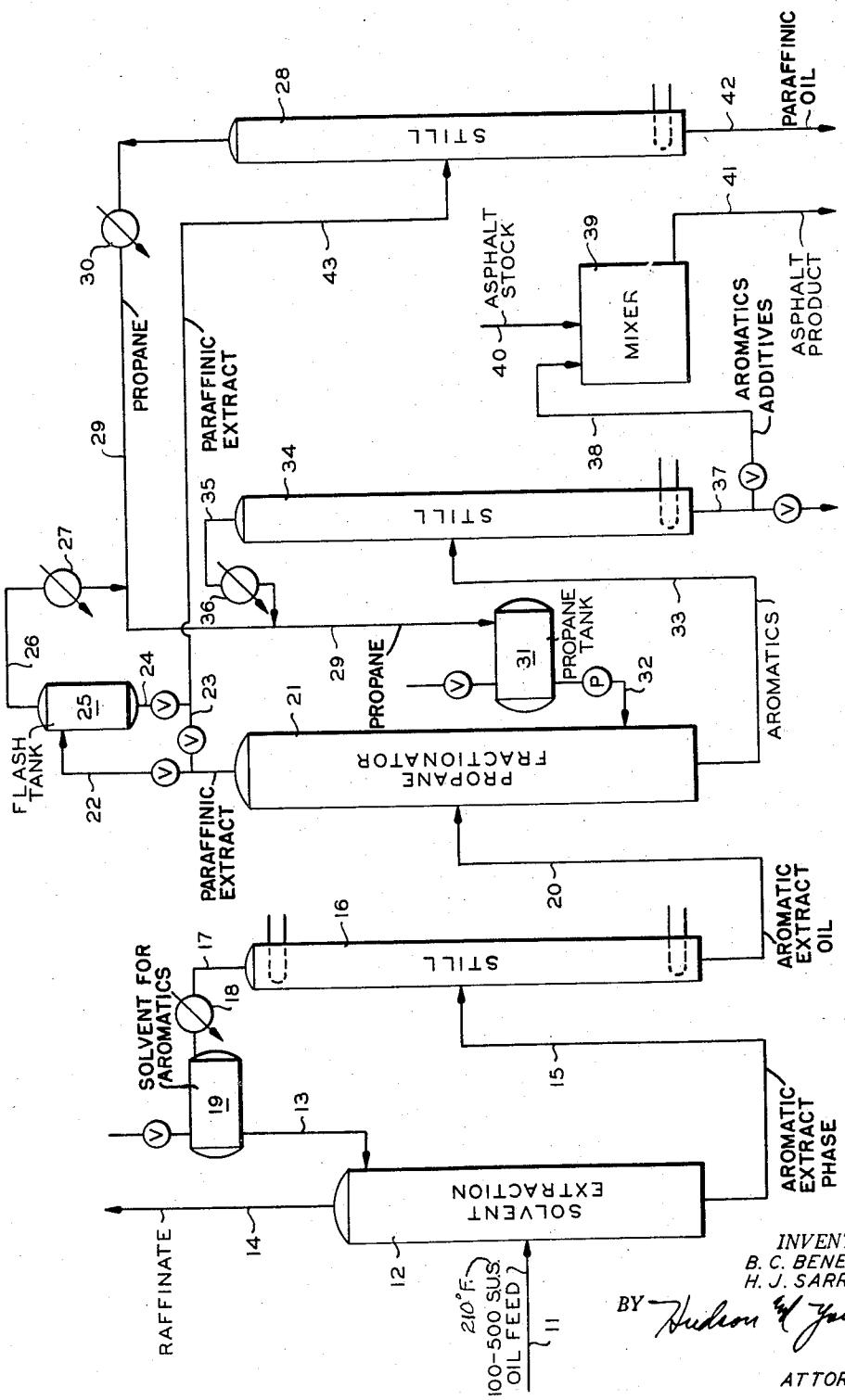


FIG. 1.

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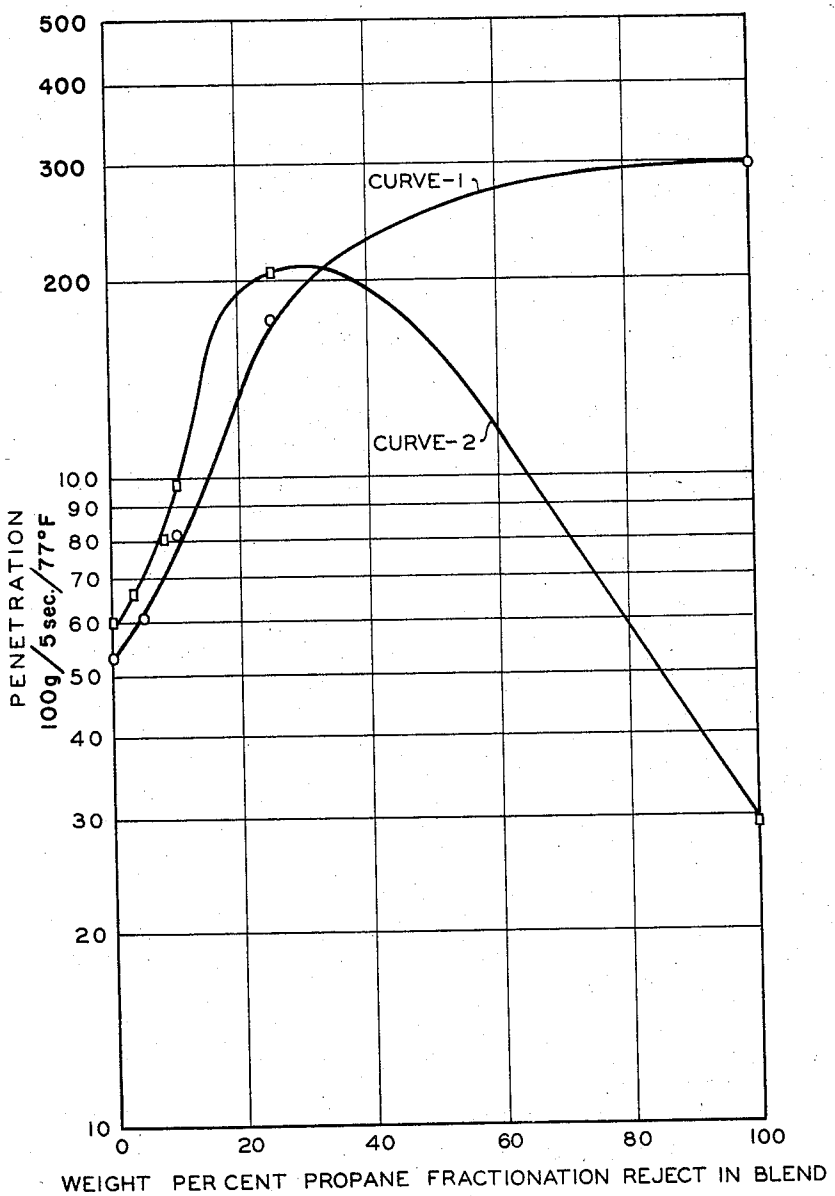


FIG. 2.

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2,879,219

ASPHALT COMPOSITION, AN ADDITIVE THEREFOR AND METHOD FOR PRODUCING SAME

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7 Claims. (Cl. 208—23)

This invention relates to blended asphalts. In one aspect it relates to the production of an additive for adding to asphalt for the production of asphalts having unusual properties. In another aspect it relates to a method for producing said additive.

An object of our invention is to produce asphalts having unusual properties.

Another object of our invention is to provide blended asphalt products having properties which adapt them to special uses.

Another object of our invention is to provide an additive for the production of such blended asphalts.

Yet another object of our invention is to provide a novel additive which when added to asphalt and particularly air-blown asphalt yields useful asphaltic products.

Another object of our invention is to provide a method for production of such an additive.

Still other objects and advantages of our invention will be realized upon reading the following description which, taken with the attached drawing, respectively described and illustrates embodiments of our invention.

In the production of asphalts the problem of adapting the asphalts for their intended uses by blending procedures is of major importance. Asphalt compositions vary widely in their physical properties even when procured from the same source. Hence, when making blends of asphalts with other materials to improve the properties of the asphalts, it is not always possible to predict with accuracy the characteristics of a final asphalt product.

We have found that by blending a reject oil resulting from the propane fractionation of an aromatic material-containing extract from a solvent extraction operation with an air-blown asphalt that an asphaltic composition possessing unique and useful properties is obtained. Thus, our invention comprises a blend of asphalt and an aromatic material produced by the propane fractionation of a solvent extract oil produced by the solvent extraction of a lubricating bright stock oil containing aromatic hydrocarbons with a solvent adapted to extract aromatic hydrocarbons.

We have further found that a residual product produced by the propane fractionation of an aromatic hydrocarbon containing extract oil resulting from the solvent extraction of an aromatic hydrocarbon containing lubricating bright stock oil, said solvent being selective

to aromatic hydrocarbons, is useful in the production of the above-mentioned blended asphalt.

Furthermore, we have discovered a process for producing an additive for use with asphalt comprising contacting under propane fractionation conditions a lubricating bright stock oil extract containing aromatic hydrocarbons and nonaromatic hydrocarbons with liquid propane, from this operation removing a bottoms material comprising aromatic hydrocarbon containing oil containing dissolved propane, and recovering the aromatic hydrocarbon containing oil from the dissolved propane as the product of the operation.

In the drawing Figure 1 illustrates, in diagrammatic form, an arrangement of apparatus parts suitable for carrying out the process of our invention.

Figure 2 illustrates the relationship of penetration versus weight percent of additive in the asphalt blend of a blend made according to our invention in comparision to a blend made according to prior art methods.

The term additive as used throughout this specification and claims is intended to be a first material which, when added to a second material, improves the properties of the second material. The asphalts which are adapted to blending with our additive are particularly air-blown asphalts resulting from direct reduction of asphalt containing crude oils, residual asphalts resulting from cracking operations and native asphalts.

While air-blown asphalts are preferred for use according to our invention, residual asphalts, which are not air-blown but have a peentration of 50 or less (100 grams/5 seconds), when blended with our additive, produce results substantially comparable to those with air-blown asphalts. The term "penetration" as used throughout this specification and claims is the penetration value as determined by the accepted A.S.T.M. standard method of determination of penetration, and determined at a temperature of 77° F.

The lubricating oil bright stocks employed for producing our additive are oil stocks having viscosities of from about 90 to 500 or more SUS at 210° F. (Saybolt Universal seconds). Also, bright stock oils having viscosities greater than 500 SUS at 210° F. are, under some conditions, used in making our blending agent. The bright stock oils must contain aromatic constituents because it is these constituents which are extracted by solvents selective to aromatic constituents which yield our additives. Details of the solvent extraction operations which yields suitable solvent extract oils will not be explained in detail because the particular solvent and extraction methods employed do not form a part of our invention. Any suitable solvent extraction process which yields an aromatic-rich extract from an aromatic containing bright stock oil of the above viscosity can be used. There are many known solvent extraction processes employing such extraction solvents as phenol, furfural, nitrobenzene, and chlorex and others, which are suitable for use as herein disclosed.

The propane fractionation step of our process is an operation in which preferably liquid propane is employed

for fractionating the above-mentioned solvent extract into a reject oil (raffinate) and a solution of oil in propane (extract). When propane fractionating such high molecular weight materials as will be included in solvent extracts of bright stock oils of 90 to 500 SUS at 210° F., the aromatic materials will be concentrated in the reject material or raffinate phase from the propane fractionation operation. This propane fractionation operation is carried out, in some respects, in a manner similar to a conventional solvent extraction operation. However, operating conditions are quite different from those employed in solvent extraction operations. Liquid propane possesses the peculiar property of extracting the more paraffinic materials thus leaving the more aromatic materials in the reject or raffinate phase. According to our invention, the liquid propane is intended to reject as a raffinate phase the high molecular weight more aromatic material of the particular solvent extract being treated and this reject or raffinate material, when freed of dissolved propane, is the additive of our invention.

In carrying out our propane fractionation step we prefer to employ a propane-to-oil ratio of from about 5:1 to 15:1. The fractionation operation must be carried out in liquid phase and accordingly sufficient pressure is maintained in the fractionation column to make certain that the column contents are always liquid. Pressures ordinarily required vary from about 300 to about 625 p.s.i. (pounds per square inch) depending upon the temperature. Temperatures employed in the head of the column for effecting our propane fractionation operation vary from about 120° to 210° F. depending upon the viscosity of the extract oil fed to the column and upon the particular raffinate product desired to be produced. Lower temperatures maintained in the propane fractionation operation yield reject or raffinate oil possessing a wider range of molecular weight components while higher fractionation temperatures yield reject oil of higher molecular weight aromatic materials to the exclusion of lower molecular weight aromatic materials. Thus, by a proper selection of propane to oil ratio, and temperature, with a corresponding pressure sufficient to maintain liquid phase conditions, unique additives for asphalt are produced which, when blended with asphalts, produce compositions of our invention.

We prefer to use propane in making this fractionation operation which we herein term propane fractionation, but it is to be understood that other low boiling normally gaseous paraffinic hydrocarbons are sometimes used. Such other hydrocarbons which are used in some cases are ethane, butane, and isobutane in addition to propane. It will be obvious, however, that when employing any one or more of the above-enumerated paraffins in the fractionation operation, alteration of the hydrocarbon-to-oil ratio, alteration in temperature and alteration in pressure will need to be made, dependent, of course, upon the physical properties, for example, the critical temperature and pressure of the particular paraffinic hydrocarbon used. All fractionation operations employing any of these paraffins are, of course, made in liquid phase.

When making our blended asphalt from the additive and asphalt, we merely introduce the two ingredients into a blending vessel and mix them by any suitable means. Mechanical mixers which stir the ingredients in a tank or mixing vessel can be used. Also, mixing valves or proportioning valves can be employed for proportioning the ingredients in the mixture. Such mixing or proportioning valves may not necessarily produce a perfectly uniform mixture and it is preferable that a stream of proportioned ingredients be further mixed for the production of a material of uniform composition.

In making our blend of asphalt with additive, we employ from about 5 percent to about 50 percent by weight, or more, of the additive based on the final weight of the blend. While the above-mentioned limits are preferred, we use, under certain conditions, blends outside the above-mentioned limits when asphaltic compositions possessing particular properties are required.

In refineries or asphalt production plants where the number of crude oils available is limited, as regards source and type of asphalt which can be produced directly therefrom, common practice is to prepare the asphalt from the crude oil (or oils) available and then modify the asphalt with additives to make the various asphalt products desired.

The extract oil from a lubricating oil solvent extraction plant possesses little value because it is a very high boiling point material and is largely aromatic. Such materials are not suitable for use as lubricating oils and they possess little to no value as cracking stocks for the production of gasoline. These stocks are frequently employed as fuel for boilers or stills. By use of such relatively valueless material we produce an additive which when blended with asphalt yields a final asphalt product which commands a fair market price. In this manner the value of the extract oil from a lubricating oil extraction operation is markedly upgraded. Furthermore, the propane soluble material formed in our process having been increased in paraffinicity is useful as a catalytic cracking stock and also a medium viscosity index lubricating oil of satisfactory properties has been prepared from such material.

The propane fractionation operation is carried out under the aforementioned operating conditions until approximately 25 to 75 volume percent of the extract oil fed to the operation is removed as overhead product in solution in the propane thereby producing a bottoms or reject raffinate product containing about 75 to 25 percent of the extract oil feed depending upon the aromatic content of the extract oil feed and also upon the particular properties desired of the additive.

The following is a specific example of the production of a suitable additive for use in blending with an air-blown asphalt to yield our specialty asphalt products. We produced by conventional solvent extraction, using phenol as the solvent, an extract oil from a bright stock oil having viscosity between 90 and 500 SUS at 210° F. This solvent extract, free of solvent, is mixed with liquid propane at about 100° F. in a ratio of about 9 volumes of propane per volume of extract oil. This mixture is then heated to a temperature between about 120° and 210° F. under a pressure within the range of 300 and 625 p.s.i.a. until from 25 to 75 volume percent of the extract oil is dissolved in the propane and removed as extract phase. The bottoms or reject material from this propane fractionation operation is freed of propane and is the additive of our invention.

In Table I are given specific operating conditions within the above mentioned limits by which propane fractionation reject products were obtained. Also included in the table are the inspection data of the overhead oil freed of propane which was removed as the propane-oil (extract phase) solution. This material is a waxy overhead oil in case the original bright stock had not previously been dewaxed. Also in the table are the inspection data of the propane fractionation bottoms or reject material. It is noted that these materials in runs 1, 2 and 3 possess very low API gravities with pour points above 80° F. Viscosities (SUS of 210° F.) are also high, indicating that these materials are very thick and viscous even at 210° F.

TABLE I

Run Number	Feed	Run 1	Run 2	Run 3
Charge Stock	250 Ext. Oil [1]	250 Extract Oil		
Operating Conditions:				
Top Column Temperature, °F		130	170	195
Oil Feed Temperature, °F		106	147	174
Propane Feed Temperature, °F		106	146	175
Bottom Column Temperature, °F		110	143	174
Duration of Run, Hours		0.50	1.00	1.50
Column Pressure, p.s.i.g		303	440	590
Oil Charge Rate, g.p.h. at 60° F		1.44	1.36	1.44
Propane Charge Rate, g.p.h. at 60° F		14.0	13.65	13.65
Propane to Oil Ratio, Volume		9.7	10.1	9.5
Yield of Overhead (Vol. percent), from Specific Gravity		70.5	38.1	19.4
Inspection Data:				
Overhead Oil				
Gravity, API	10.8	14.3	16.6	17.7
Specific Gravity, 60/60° F	0.9942	0.9705	0.9556	0.9484
Viscosity, SUS at 210° F	712	335.9	209.4	156.6
Viscosity, SUS at 130° F		4,990	2,226	1,398
Viscosity, SUS at 100° F		[2] 22,176	[2] 8,316	[2] 4,805
Viscosity Index		[2] 28	[2] 41	[2] 42
Refractive Index, 70° C	1.5469	1.5288	1.5176	1.5129
Viscosity Gravity Constant, at 210° F	0.918	0.893	0.882	0.876
Pour Point, °F	70	70	70+	55
Carbon Residue, Ramsbottom	[3] 6.4	2.35	2.07	0.92
Color, ASTM		6+	4½	4½
Bottoms:				
Gravity, API		3.2	7.5	9.3
Specific Gravity, 60/60° F		1.0508	1.0179	1.0052
Viscosity, SUS at 210° F		7,081	1,906	1,014
Pour Point, °F		80+	80+	80+
Refractive Index, 70° C		1.5682	1.5618	1.5485

[1] An extract oil having a viscosity of approximately 712 SUS at 210° F. produced by solvent extracting a raw lubricating oil stock to produce a lubricating oil having a viscosity index of approximately 100 and a viscosity of 210 SUS at approximately 210° F.
[2] Calculated from viscosities determined at 130° and 210° F.
[3] Conradson carbon residue.

In Table II are data obtained from blends of the propane reject product of Table I with an air-blown asphalt from a Montana Crude oil which blends are products of our invention.

TABLE II

Blends of bottoms from run 1 with air-blown asphalt from a Montana Crude oil

Wt. Percent Run 1 Bottoms	Softening Point, R. & B., °F.	Penetration, 100/5/77° F.	Ductility, 5/77° F.
0	196.0	60	2.5
3	176.0	66	2.7
8	152.5	81	4.0
10	143.0	97	5.7
25	106.0	206	30.9
100	122.0	29	

In Table III are given data obtained from blends of the additive of run 1 of Table I with air-blown asphalt from a Mid-Continent crude oil.

TABLE III

Blends of bottoms from run 1 with air-blown Mid-Continent asphalt

Wt. Percent Run 1 Bottoms	Softening Point, R. & B., °F.	Penetration, 100/5/77° F.	Ductility, 5/77° F.
0	215.0	18	2.5
2	203.0	19	2.6
5	193.0	20	3.2
8	178.0	22	4.2
25	138.0	36	58.5
100.0	122.0	29	

In Table II it is noted that the penetration of the air-blown asphalt which contains 0 percent additive was 60 at 77° F. and upon addition of 3 percent, 8 percent and 10 percent of additive the penetration of the blends increased more or less uniformly. However, a blend containing 25 percent propane bottoms possessed a penetration of 206 at 77° F. while the penetration of the additive in the absence of air-blown asphalt was only 29 at 77°; thus, the penetration of the 25 percent blend was markedly greater than the penetration of either of the constituents of the blended asphalt (the run 1 bottoms was a very heavy resinous material). Furthermore, the ductility of the 25 percent blend was considerably greater than the ductility of blends containing less additive. The ductility of the pure additive was not determined. Also, it is noted that the R & B (ring and ball) softening point in degrees F. of the 25 percent blend is markedly lower than the softening point of either ingredient or of the blends of other composition.

It is also noted in Table III that the penetration of the 25 percent blend is greater than the penetration of either component of the blend similar to that illustrated in Table II but to a lesser extent. The ductility of the 25 percent blend of Table III is considerably greater than the ductility of any of the remaining blends and also is greater than the ductility of the unblended air-blown Mid-Continent asphalt. The ring and ball softening point of the 25 percent blend illustrated in Table III is intermediate those of the blending ingredients.

In the drawing Figure 2 illustrates the blending value of our additive in contrast to the blending value of an additive of the prior art with an air-blown asphalt. Curve 2 is the curve drawn from the penetration data versus weight percent run No. 1 bottoms of Table II. The maximum in this penetration curve is obvious. Curve No. 1 represents the penetration of a blended asphalt with an additive of the prior art and it should be noted that this curve does not possess a maximum as does curve No. 2.

Table IV gives data of a reject bottoms oil produced by the propane fractionation of a phenol extract of a Mid-Continent 20 stock, and of the extract oil.

TABLE IV

	Extract Oil [1]	Propane Bottoms Oil [2]
Viscosity at 210° F. SUS	104.6	522
Gravity, A.P.I.	10.1	0.6
Viscosity Index	−104	
Refractive Index, 70° F.	1.5516	1.5913
Viscosity-Gravity Constant	0.950	

[1] This extract oil was produced by phenol extraction of a Mid-Continent SAE 20 lube oil stock.
[2] This extract oil was then propane fractionated to yield 35.5% bottoms based on the extract oil charged to the propane fractionation.

In Table V are the softening point and penetration data of this propane bottoms from the 20 extract oil of Table IV when blended with the Montana air-blown asphalt. This Montana air-blown asphalt is exactly the same as that used in obtaining the data of Table II.

TABLE V

Wt. Percent Bottoms	Softening Point, R. & B., ° F.	Penetration, 100 g./5 sec./77° F.
0	198	53
5	127	61
10	118	82
25	105	173
100	92	297

Please note in Table V and in curve 1 of Figure 2 the absence of a maximum in the penetration data and curve. The value of the penetration, that is 173, is intermediate that of the air-blown asphalt and the propane reject bottoms which were used in making the 25 percent blend.

The high penetration blends of our asphalt with 25 percent propane reject bottoms are particularly useful as specialty products, for example, such blends are used for automobile undercoatings, sound deadeners, sewer joint compounds, battery sealing compounds and the like. Our blends are particularly useful for such purposes because they are not brittle and will not crack or loosen from the materials to which they are applied.

Figure 1 of the drawing illustrates diagrammatically an arrangement of equipment for producing the additive of our invention. In this figure the bright stock oil of 100–500 SUS viscosity at 210° F. from a source, not shown, is introduced by way of a pipe **11** into a solvent extraction vessel **12** in which extraction of the more aromatic components of the oil is made. Solvent is introduced into extractor **12** from a pipe **13**, the extract phase being removed by way of a pipe **15**. The raffinate phase is withdrawn through a pipe **14** for such disposal as desired. The extract phase from pipe **15** is distilled in a still **16** for removal of solvent which passes overhead through a pipe **17**, a condenser **18** and is passed to a run tank **19** prior to reuse in the extractor. Extract oil free of solvent is removed from the still through a pipe **20** and is propane fractionated in a fractionator **21**, the propane reject or bottoms being removed through a pipe **33** to a still **34** for removal of dissolved propane. Propane passes from still **34** through a pipe **35** and is condensed in a condenser **36** and condensed propane is then passed to a tank **31** prior to introduction into the propane fractionator through a pipe **32**. Propane reject oil, free of propane, is removed from still **34** through a pipe **37** and is the additive of our invention. This oil is passed from pipe **37** through a pipe **38** into a mixer vessel **39** into which asphalt stock is introduced from a source, not shown, by way of a pipe **40**. Mixing in vessel **39** is performed by a mechanical mixer or by such other mixing means as desired. The blended asphalt as a final product is removed through a pipe **41** to storage or use as desired.

Liquid propane containing the more paraffinic portion and the lower molecular weight aromatic constituents of the extract oil in solution is removed from propane fractionator **21** by a pipe **22** and a large portion of the propane is removed in a flash tank **25**, the propane being passed through a pipe **26**, is condensed in a condenser **27** and the condensed propane is passed on through a pipe **29** into a propane run tank **31**. The overhead oil partially freed of the propane is passed from the flash tank through pipes **24** and **43** into a still **28** in which the remainder of the propane is removed. The propane removed in still **28** passes therefrom through pipe **29**, is condensed in condenser **30** and is combined with the remainder of the propane in the run tank **31**. The still bottoms which represent the overhead oil from the propane fractionator **21** is removed from the still through a pipe **42** for such disposal as desired. This oil is more paraffinic in nature than is the oil which is blended with the asphalt but is still more aromatic in nature than the raffinate produced in the solvent extraction vessel **12** because it was included in the solvent extract phase produced in extractor **12**. Under some conditions it may not be desired to flash a portion of the propane from the overhead product of fractionator **21** and in this case valves in pipes **22** and **24** are closed and a valve in pipe **23** is opened so that the propane-oil solution passes directly to still **28**.

The above described flow diagram is given merely as an example of apparatus which is used in the production of our additive product when operated under the herein disclosed conditions and in the production of a final blended asphalt. It is realized by those skilled in the art that other apparatus can also be used providing the other apparatus is operated under the herein disclosed operating conditions.

While certain embodiments of the invention have been described for illustrative purposes, the invention obviously is not limited thereto.

We claim:

1. An asphalt composition comprising a blend of asphalt and an aromatic material produced by the propane fractionation of a solvent extract oil produced by the solvent extraction of a lubricating bright stock oil containing aromatic hydrocarbons and nonaromatic hydrocarbon with a solvent adapted to extract aromatic hydrocarbons.

2. The asphalt composition of claim 1 further characterized in that the penetration of said blend comprising 75 weight percent of asphalt and 25 weight percent of said aromatic material is greater than the penetration of the aromatic material of which the blend is produced.

3. The composion of claim 1 wherein the asphalt is produced by the direct reduction of an asphalt containing crude oil.

4. The composition of claim 1 wherein the asphalt is an asphalt produced in a cracking operation.

5. The composition of claim 3 wherein the asphalt is an air-blown asphalt.

6. The composition of claim 4 wherein the asphalt is an air-blown asphalt.

7. The composition of claim 1 wherein said blend comprises from about 5% to about 50% by weight of said aromatic material based on the weight of the blend.

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