United States Patent [19]

Pitchford et al.

[11] **3,919,072**

[45] **Nov. 11, 1975**

[54] **RESINS FROM HIGH BOILING HYDROCARBONS AND ASPHALTS CONTAINING THE SAME**

[75] Inventors: **Armin C. Pitchford; Gene N. Woodruff,** both of Bartlesville, Okla.

[73] Assignee: **Phillips Petroleum Company,** Bartlesville, Okla.

[22] Filed: **Sept. 17, 1973**

[21] Appl. No.: **398,083**

[52] **U.S. Cl.** **208/4;** 208/6; 208/23; 208/39; 208/44; 208/45

[51] **Int. Cl.²** **C07C 3/08**

[58] **Field of Search** 208/4, 6, 23, 39, 44, 45

[56] **References Cited**

UNITED STATES PATENTS

2,179,988	11/1939	Whitacre	208/4
2,627,498	2/1953	Fink et al.	208/4
2,687,989	8/1954	Goodwin	208/6
2,691,621	10/1954	Gagle	208/23
2,773,004	12/1956	Martin	208/45
2,774,724	12/1956	Watson	208/6
2,904,494	9/1959	Griffin	208/23
3,338,813	8/1967	Van Pool	208/6
3,440,074	4/1969	Stern,et al.	208/23
3,462,359	8/1969	Fauber	208/23
3,628,975	12/1971	Van Pool	208/44

Primary Examiner—Veronica O'Keefe

[57] **ABSTRACT**

An aromatic oil say from catalytic cracking of hydrocarbon oil and/or a paraffinic oil as from solvent deasphalting of topped crude is air blown at elevated temperature and then further treated at elevated temperature in the presence of a catalyst, e.g., zinc chloride, to produce a hydrocarbon resin. The oil in which the resin has been produced is combined with a topped crude from which asphalt is to be produced or with an asphalt following which the admixture thus obtained is subjected to vacuum distillation or to a solvent deasphalting to remove unreacted or non-resinous, petroleum-derived fractions. An asphalt suitable for paving, having improved ductility and other properties, is obtained.

10 Claims, No Drawings

RESINS FROM HIGH BOILING HYDROCARBONS AND ASPHALTS CONTAINING THE SAME

This invention relates to the production of an improved asphalt composition. More particularly it relates to the production of an asphaltic resin containing asphalt composition and to the production of such a resin from an oil, e.g., a waxy crude oil, as distinguished from a petroleum residuum or asphalt. In one of its aspects, the invention can produce a final product containing in an asphalt, obtained upon vacuum reduction or a solvent extraction, a desired improved or increased amount or proportion of resinous material as distinguished from asphaltenes. In another of its aspects, the invention relates to the production of resinous materials from a petroleum oil, e.g., an oil derived from a synthetic crude oil obtained by catalytic cracking a virgin gas oil, a solvent gas oil, a heavy residual oil, a whole crude oil, and similar feedstocks.

The terms employed herein, e.g., "oil," "resin," "petroleum residuum," etc., have generally accepted meanings in the petroleum refining art and are employed to convey said meanings.

During the refining of certain crude oils an excess of a particular distillate or residual fraction may be produced while a shortage of another component will occur. Frequently this component can be of value in the preparation of a refined product for some specific application. Therefore, it is advantageous to convert a less desirable fraction of the crude oil to the most useful product without altering the overall crude charged to the refinery. Thus a change in refinery operation is made.

An example of this situation exists when a waxy crude oil is used to produce a distillate fuel and an asphaltic residue containing a deficiency of asphaltic resins. Asphaltic resins are necessary to impart certain characteristics to the asphalt and to overcome the adverse effects of the excess wax, which remains in the asphalt phase after vacuum flash distillation or solvent deasphalting of the oil, as with propane or with a mixed solvent, e.g., propane and butanes.

In one of its concepts, this invention provides a two stage process for preparing a resin-containing additive for improving the quality of asphalts, e.g., as derived from a waxy crude oil, which involves (1) air blowing of an aromatic oil or a heavy vacuum gas oil and (2) subsequently treating the airblown product with a catalyst, say, zinc chloride, at an elevated temperature such that there is formed in the oil a substantial proportion of resin.

In another of its concepts, the invention provides a process in which a resin-containing fraction or resin is added to an asphalt, or to a topped crude from which asphalt is to be prepared, to increase the resin content of the asphalt without substantially increasing the asphaltene content of the resulting blend, which comprises adding a resin or resin-containing fraction or petroleum resin to a topped crude and subjecting the admixture to a vacuum distillation thus to prepare a paving grade asphalt. In a further concept of the invention, the admixture is solvent deasphalted to obtain such a grade of asphalt. In the operation just described the resin remains in the asphalt to improve considerably its properties, e.g., ductility, etc.

It is known in the art to air-blow petroleum residuum at about 300°–500°F for, say, about 600 minutes and to then subject the air-blown material, thus obtained, to a polymerization treatment as by heating it in the presence of aluminum chloride at 300°–400°F for 20 to 30 minutes.

We have conceived that an oil, as distinguished from a petroleum residuum, for example a bottoms obtained from a synthetic crude oil obtained by catalytically cracking a virgin gas oil or a solvent gas oil, as obtained from a topped crude by a propane-butane extraction, can be converted to a resin or resin-containing material or additive which then can be incorporated into a topped crude, as herein described, from which asphalt is to be prepared, and the admixture thus obtained processed to produce paving grade asphalt by a vacuum distillation or a solvent deasphalting to remove unreacted oil or gas oil therefrom, the product thus obtained being resin-enriched and possessing due to the presence therein of the added resin, considerably improved ductility and other properties.

An object of this invention is to prepare a petroleum resin. Another object of this invention is to prepare an improved asphalt derived from petroleum. A still further object of this invention is to prepare a resin to be incorporated into an asphalt, thus to obtain a product suitable for paving use, and other uses, without however increasing asphaltenes content. A still further object of the invention is to incorporate a petroleum resin, prepared according to the invention, into a topped crude from which an asphalt is to be prepared or into an asphalt. Another object of the invention is to produce an asphalt of improved properties from an oil low in resin content.

Other aspects, concepts, object and the several advantages of the invention are apparent from a study of this disclosure and the appended claims.

According to the present invention, an oil such as herein described is heated and air blown and still later while at an elevated temperature is further heated in presence of a catalyst which will produce resinous materials in the air-blown material, while avoiding the formation of asphaltenes, say, $ZnCl_2$, $FeCl_3$ and $SnCl_2$, as distinguished from $CuCl_2$ and $SnCl_4$, to produce a resin or resin-containing material suitable for incorporation into a topped crude to be converted to asphalt, say, a paving grade quality. Also according to the present invention, a petroleum derived resin as herein described, as it may be contained in an oil in which produced, is incorporated into an oil to be converted to an asphalt which comprises admixing said material and said oil, e.g., topped crude or a solvent gas oil and then producing an asphalt in known manner, obtaining an asphalt of, say, paving quality, having properties considerably better than otherwise obtained to date in the art from such topped crudes and such solvent gas oils.

Generally, the resin-containing material will improve to an extent the properties of the final asphalt even when added in small proportions of the order of about five percent or even less. However, for now desirable in uses there will be incorporated into the topped crude or asphalt, or the like, from about 1 percent up to equal proportions or even more of the resin-containing material depending upon the natures of the materials to be admixed and further treated. Thus, one skilled in the art in possession of this disclosure having studied the same will understand that for each oil, treated according to the invention, and for each set of conditions of treatment, there will be a certain proportion of beneficial resin contained therein and therefore this will have

to be taken into account in admixing the treated oil containing the resin with the topped crude or asphalt to be benefited.

Thus according to the present invention, in one of its broad concepts, a petroleum fraction or oil is treated to produce a petroleum derived resin containing oil or oily material which is then admixed with a topped crude or asphalt, or equivalent material, from which by vacuum reduction or solvent extraction a final asphalt is obtained, as herein described.

The invention will now be described further with respect to the application of feedstocks, used for the preparation of the synthetic asphalt resins or resin-containing material, as given in Table I.

Table I

PROPERTIES OF FEEDSTOCKS USED IN THE PREPARATION OF SYNTHETIC ASPHALT RESINS

	Syn Tower Bottoms*			Solvent Gas Oil
Identification	A	B	C	D
API Gravity at 60 F	6.8	13.6	3.8	23.2
Specific Gravity, 60/60 F	1.0231	0.9752	1.0458	0.9147
Viscosity, SFS, 122 F	27.0	47.6	52.2	—
Viscosity, SUS, 180 F	—	—	—	177.6
Viscosity, SUS, 210 F	—	—	—	105.8
Pentane Insolubles, Wt %	11.8	5.9	—	—
Carbon Residue, Rams., Wt %	7.86	—	—	0.78
Elemental Analyses, Wt %				
Carbon	89.2	88.47		
Hydrogen	8.7	11.25		
Oxygen	0.14	—		
Nitrogen	0.09	—		0.14
Sulfur	1.42	—	—	0.77
Metals, ppm				
Nickel	—	—	—	0.7
Vanadium	—	—	—	<0.3
Iron	—	—	—	2
Distillation, ASTM D 1160				
IBP, °F	577	564	564	780
2 %	616	571	655	805
5 %	703	680	724	853
10 %	737	730	755	877
20 %	776	768	789	913
30 %	805	802	817	949
40 %	822	819	841	972
50 %	839	847	859	985
Distillation Residue				
Per Cent of Feed	50	50	50	61.8
Viscosity, SFS, 210 F	13.1	7.5	31.4	18.4

*Bottoms of a fractionator from the catalytic cracking unit.

To demonstrate the operability of the proposed process the sample of syntower bottoms designated as Sample A in the above tabulation was first air blown at conditions presented in Table II. Included in Table II are properties of the resulting air-blown product and properties after the second stage catalytic treatment.

Table II shows properties of asphaltic resins derived from syn tower bottoms by air blowing and catalytic treatment in a second stage.

The data in the foregoing Table are for purposes of illustration only. Such data will vary from time to time in the normal refining of crude oil at any particular refinery. At such times, as one skilled in the art in possession of this disclosure having studied the same will understand, the conditions of the treatment of the feeds will be adjusted to obtain the results desired. Clearly, properties of oils will vary substantially with crude oil source, operating conditions, and the extent to which a particular oil has been fractionated prior to the reactions which are involved in the production of the resin-containing oil of the present invention.

Table II

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS PREPARED FROM SYN TOWER BOTTOMS

	Feedstock	First Stage Air Blowing	Second Stage Catalytic Treatment		
Run Number	A	F	G	H	J
Material Charged		A	F	F	Blend*
Catalyst Used		none	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
Wt % Catalyst		none	1.0	1.0	—
Gas used in test		Air	Nat.Gas	Nat.Gas	—
Gas Rate, SCFH		2.0	1	1	—
Temperature, F		492	540	565	—
Reaction Time, Hours		3.5	6.0	7.0	—
API Gravity at 60 F	13.6	8.3	6.8	5.9	6.7
Specific Gravity, 60/60 F	0.9752	1.0122	1.0231	1.0298	1.0239
ASTM D 1160 Distillation					
IBP, F	564	705	725	—	730
2%	571	749	755	768	768
5%	680	770	795	796	786
10%	730	786	811	813	807
20%	768	811	834	833	829
30%	802	830	851	853	846
40%	819	852	867	868	859
50%	847	871	880	880	879
Distillation Residue					
Per cent of Feed	50	50.8	56.2	55.2	49.3

Table II-continued

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS PREPARED FROM SYN TOWER BOTTOMS

	Feedstock	First Stage Air Blowing	Second Stage Catalytic Treatment		
Viscosity, SFS, 210 F	7.5	68.7	166.6	123.5*	149.8

*The blend was comprised of about 61 wt % G and 39 wt % of product H.
*Calculated viscosity from G and J assuming a straight line function.

The preceding data indicate that air blowing of the Syntower bottoms produces a material which, upon distillation, yields a high boiling residue which is considerably more viscous than the corresponding fraction obtained from the untreated syntower bottoms. Further treatment of the airblown product with zinc chloride at about 550 F yields an 880 F+ residue having a much higher viscosity than resulting from air treatment alone. Maximum viscosity increase is obtained when $ZnCl_2$ is used to treat the air blown intermediate while $FeCl_3$ and $SnCl_2$ were each effective to a slightly lesser extent. Neither $CuCl_2$ nor $SnCl_4$ were effective in the second stage treatment. These data are reported in Table III.

measuring the viscosity of the distillation residue. Higher viscosities as compared to those of a control containing no catalyst indicate a more reactive catalyst. Based upon viscosity data neither $CuCl_2.2H_2O$ nor $SnCl_4.5H_2O$ were considered effective as second stage catalysts as compared to anhydrous $ZnCl_2$ or to $FeCl_3.6H_2O$. Note also that $ZnCl_2.2H_2O$ was not as effective as the anhydrous zinc chloride.

Similar laboratory tests were made to determine the feasibility of using solvent gas oil, produced on the solvent deasphalting unit, as a feedstock for the preparation of asphaltic resins. This feed was considered since the amount of resins which can be prepared from a syn-

Table III

EFFECT OF VARIOUS SECOND-STAGE CATALYSTS FOR INCREASING THE VISCOSITY OF THE 880 F+ DISTILLATION RESIDUE DERIVED FROM AIR BLOWN SYNTOWER BOTTOMS

	Feed-stock	1st Stage Air Blowing Control	Second Stage, Catalytic Treatment 1	2	3	4	5	6
Catalyst, Wt %	0	0	1.0	1.0	1.0	1.0	1.0	1.0
Catalyst Composition	None	None	$FeCl_3.6H_2O$	$FeCl_3.6H_2O$	$ZnCl_2$	$SnCl_2.2H_2O$	$CuCl_2.2H_2O$	$SnCl_4.5H_2O$
Reaction Temp., F	—	—	550	600	540	550	550	550
Reaction Time Hours	—	—	5.75	6.0	6.0	6.5	6.0	6.0
880 F+ Distillation Residue, Wt %	50	50.8	50.0	51.2	56.2	48.7	53.4	52.8
Viscosity of 880 F+ Residue, SFS at 210 F	7.5	68.7	105.4	108.7	166.6	82.9	48.0	36.2

Note: In these tests, the initial oil was feedstock A of Table II.

In these tests, syntower bottoms (air blown at 492 F for 3.5 hours in the first stage of the process) were treated at 550 F with 1.0 weight percent catalyst for 5.75 to 6 hours. After this treatment the liquid product was vacuum distilled to yield an 880 F+ bottoms product. Effectiveness of the catalyst was determined by

tower bottom alone may not meet the demands for asphalt production. Mixtures of resins derived from the several procedures can be used to produce the final asphalts. Processing details and properties of the airblown intermediate and the $ZnCl_2$ treated materials are given in Table IV and Table V.

Table IV

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS PREPARED FROM SOLVENT GAS OILS

	Feedstock, Solvent Gas Oil	First Stage Air Blowing	Second Stage Catalytic Treatment
Identification	D*	—	—
Catalyst Used	—	NONE	$ZnCl_2$
Wt. % Catalyst	—	NONE	1.0
Gas Used in Test	—	O_2 + steam	CH_4
Gas Rate, SCFH	—	2.0	< 1
Reaction Temperature, °F	—	515	560
Reaction Time, Hours	—	5.5	6.75
API Gravity, 60°F	23.2	—	19.7
Specific Gravity, 60/60° F	0.9147	—0.9358	
Distillation, ASTM D 1160			
IBP° F	780	—	886
2 %	805	—	923
5 %	853	—	945
10 %	877	—	949
20 %	913	—	
30 %	949	—	
40 %	972	—	
50 %	985	—	
Distillation Residue			
Per cent of Product	61.8	86.8(1)	88.6

Table IV-continued

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS PREPARED FROM SOLVENT GAS OILS

	Feedstock, Solvent Gas Oil	First Stage Air Blowing	Second Stage Catalytic Treatment
Viscosity, SFS 210° F	18.4	27[1]	35.9

[1]Estimated
*See Table I

Table V

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS FROM SOLVENT GAS OIL

	Feedstock Solvent Gas Oil	First Stage, Air Blowing	Second Stage Catalytic Treatment
Identification	D*	—	—
Catalyst Used		NONE	$ZnCl_2$
Wt. % Catalyst		NONE	1.0
Gas Used in Test		Air	CH_4
Gas Rate, SCFH		2.0	<1
Reaction Temperature, °F		550–575	560
Reaction Time, Hours		7.0	6.0
API Gravity, 60° F	23.2	19.4	17.1
Specific Gravity, 60/60 °F	0.9147	0.9377	0.9522
Distillation, ASTM D 1160			
IBP °F	780	874	901
2 %	805	901	945
5 %	853	937	972
10 %	877	960	—
20 %	913		
30 %	949		
40 %	972		
50 %	985		
Distillation Residue			
Per cent of Product	61.8	87.6	94.4
Viscosity, SFS at 210° F	18.4	50.5	81.0

*Table I

Attention is directed to Table V, showing a substantial increase in viscosity of the distillation residue after the second stage catalytic treatment (81 SFS) as compared to the original feedstock (18.4 SFS) and the air blown intermediate (50.5 SFS). Higher viscosity (81.0 SFS) of the distillation residue is obtained upon $ZnCl_2$ catalytic treatment when the gas oil is subjected to more severe air blowing (Table V) prior to the second stage catalytic treatment as compared to the less severe air blowing of Table IV (viscosity of 35.9 SFS).

The material obtained as the distillation residue after the two-stage treatment in Table V having a viscosity of 81 SFS was very tacky and resembled the resins separated from paving asphalts by other methods.

Additional tests have been made to determine whether a combination of syntower bottoms and solvent gas oil could be used as a feedstock for the production of synthetic resins. While the reaction mechanism is not known, it is believed that the more aromatic components of the feedstocks are possibly alkylated in the presence of $ZnCl_2$ with the more paraffinic materials. Therefore, a mixture of air blown syntower bottoms, which are more aromatic, and air blown solvent gas oil which is paraffinic, should result in a highly resinous material with properties substantially different from those of corresponding products obtained from each of the separate feedstocks. Preparation and some properties of the resins from the mixed air blown feedstocks are shown in Table VI.

Table VI

	Feedstock		First Stage Air Blowing		
Charge	Syntower Bottoms	Solvent Gas Oil	Syntower Bottoms	Solvent Gas Oil	Second Stage Catalytic
Identification	B[1]	D[1]	—	—	Blend*
Catalyst Used	NONE	NONE	NONE	NONE	$ZnCl_2$
Wt. % Catalyst	NONE	NONE	NONE	NONE	1
Gas Used	—	—	Air	Air	CH_4
Gas Rate, SCFH	—	—	2.0	2.0	1.0
Reaction Temperature, °F	—	—	375	530	560
Reaction Time, Hours	—	—	2.5	6.0	5.5
API Gravity, 60° F	13.6	23.2	—	—	13.7
Specific Gravity, 60/60° F	0.9752	0.9147	—	—	0.9745
Distillation, ASTM D 1160					
IBP °F	564	780	—	—	693
2 %	571	805	—	—	743
5 %	680	853	—	—	780
10 %	730	877	—	—	817
20 %	768	913	—	—	853
30 %	802	949	—	—	889
40 %	819	972	—	—	935
50 %	847	985	—	—	—
Distillation Residue					
Per cent of Product	50	61.8	—	—	56.0

Table VI-continued

Charge	Feedstock		First Stage Air Blowing		Second Stage
	Syntower Bottoms	Solvent Gas Oil	Syntower Bottoms	Solvent Gas Oil	Catalytic
Viscosity, SFS at 210° F	7.5	18.4	—	—	72.2

*Blend consisted of 47.4 wt. % air blown syntower bottoms and 52.3 wt. % blown solvent gas oil.
[11]Table I

While the actual viscosity of the distillation residue of the blend of air blown syntower bottoms and air blown solvent gas oil followed by second stage catalytic treatment was 72.2 SFS at 210°F., the material was tacky and resembled resins separated from paving asphalts by various methods.

These results confirm that resinous materials are formed by the preceding sequence of reactions. However, the viscosity increase in this example is believed to be minimum and is expected to increase with an increase in the severity of the air blowing at higher temperatures of the syntower bottoms. Feedstocks that can be used in this invention are those containing a substantial amount of aromatics, i.e., at least about 15 percent aromatics to obtain ordinarily economically feasible results. That is, sufficient aromatics must be available to form reasonable quantities of resin in the oil subjected to the two-stage treatment of the invention; syntower bottoms, light and heavy cycle oils, phenol extract oils, SO_2 extract oil, vacuum and solvent extract oils.

Properties of feedstocks which are suitable for the preparation of synthetic resins for use as asphalt additives are given in Table VII.

Table VII

PROPERTIES OF FEEDSTOCKS SUITABLE FOR THE PREPARATION OF SYNTHETIC RESINS FOR USE AS ASPHALT ADDITIVES

	Range of Properties	
	Broad	Preferred
API Gravity, 60° F	2.0–30.	5.0–25.0
Aniline Point, °F	75–230	85–185
Viscosity, SFS, 122° F	5–500	25–250
H/C Mol Ratio	1.2–2.0	1.3–1.8
IBP, °F	500–1000	575–800
50%, Point, °F	700–1100	800–1000
Carbon Residue, Rams.,%	0.2–18.	0.5–15.
No. Avg. Mol. Wt.	200–1000	300–600
Paraffin Hydrocarbon Content, Wt.%	0.1–80	10–50

The temperature for air blowing may range from about 350° to about 600° F., preferably 400° to 550° F.

The temperature of the catalytic treatment may range from about 500° F to about 600° F, preferably 530° to 570° F.

The selected temperature, in any case, whether within or outside the Gwen ranges can be determined by test.

When compared with corresponding asphaltic materials obtained from the same feedstock containing none of the added synthetic resins, asphalts prepared in the manner disclosed in this invention have improved quality as determined by viscosity, ductility and other temperature dependent characteristics.

While the asphalt prepared in accordance with this invention can be prepared in a number of different ways, the following method illustrates the process and shows the improvement in the properties of the final asphaltic product containing the synthetic resins.

Ordinarily, the amount of resin-containing oil from the second stage or catalytic treatment added to a topped crude or to an asphalt will be in the range of from about 1/10 to about 10 weight percent, or more, depending upon the properties of the resin, and, of course, of the final asphalt desired to be obtained.

It is possible within the scope of the appended claims to first treat the second stage catalytically treated, resin-containing oil to remove the oil therefrom, as by solvent deoiling, and to recover resin and to then add the thus concentrated resin to an asphalt cement to improve its properties. In such instance, the proportion of resin added can be smaller understandably because with oil has been largely, if not completely, removed from the resin.

The a priori treatment to concentrate the resin is not now preferred because this involves additional steps and equipment. Obviously, the addition of the resin containing oil to a topped crude, which is to be a vacuum distilled and/or solvent deasphalted, is more attractive from an economic viewpoint.

In the following Table VIII product J of Table II, obtained by the successive dual stage treatment of "syntower" bottoms with air and then with $ZnCl_2$ at temperatures ranging from 250 to about 600 F, was added to a 430 F+ topped crude representing the current total charge to the refinery. The mixture thus obtained contained 4 wt. percent of the synthetic resin fraction. It was further distilled to yield a 650 F+ bottoms which was subsequently charged to a semi-continuous isothermal vacuum flash distillation unit to yield various grades of asphalt cements for use in highway paving applications. These asphalts containing the synthetic resins are compared to similar materials, in the following tabulations, derived from the same 430 F+ topped crude but which contained no additive. Solvent extraction can be employed with even greater success, to yield asphalts of improved quality from the 650 F+ topped crude.

According to the invention, the synthetic resins can be concentrated by either vacuum reduction or by solvent extraction and then added to asphalt previously produced by some other means. It is within the scope of the invention to at least partly effect a concentration of the resins containing product, to then admix it with a topped crude or asphalt and to then produce the final asphaltic product as herein described. In either instance more resinous portion of the reaction product would remain in the final asphaltic residue.

Table VIII

EFFECT OF SYNTHETIC RESINS DERIVED FROM SYNTOWER BOTTOMS ON THE PROPERTIES OF TOPPED CRUDES AND ASPHALTS FROM SIMULATED CRUDES CHARGED TO THE REFINERY

Composition of Feed	Control	Additive Blend
Topped Crude, 430 F+, wt %	100.0	96.0
Product J*,wt %	0.0	4.0
API Gravity, 60 F	26.1	25.3
Distn. to Yield 650 F+ Btms.		
Yield, vol % of 450 F+ Feed	59.0	59.4
API Gravity at 60 F	20.3	19.0
Specific Gravity, 60/60 F	0.9321	0.9402
Viscosity, SUS at 210 F	112.0	114.1
Viscosity, SFS at 122 F	93.2	134.7
Pour Point, F	+95	+100
Sulfur, Wt %	1.60	1.46
Carbon Residue, Rams., %	0.02	0.02
Ash, Wt. %	0.02	0.02
Ni, ppm		14.7
Fe, ppm		
V, ppm		22.2

Vacuum Asphalt Properties	Control		Additive Blend		
Test No.	1	2	3	4	5
Cor. Flash Temp., F	960	975	955	960	975
Yield, vol % of 430 F+	36.4	33.6	36.6	35.6	36.4
API Gravity at 60 F	9.9	9.1	9.0	9.1	8.4
Penetration, mm/10					
200 g/60 sec/39.2 F	35	25	33	29	24
100 g/ 5 sec/77 F	135	73	129	113	66
Penetration Ratio	25.9	34.2	25.6	25.7	36.4
Viscosity					
SFS, 210 F	442	849	524	580	981
SFS, 275 F	70.7	112.4	79.4	85.3	125.0
Poises, 140 F	265.3	862.4	332.1	478.0	1,067.1
Ductility, cm					
1 cm/min., 39.2 F	4.5	6.5	5.5	4.5	4.0
5 cm/min., 77 F	86	108	115	113	150+
Softening Point, R & B, F	118	124	115	118	123
Spot Test (1)	Pos	Pos	Pos	Pos	Pos
Solubility, CCl_4, wt %	99.94	99.83	99.53	99.85	99.97

(1) Positive spot denotes the presence of wax, not cracking.
*Table II

Table IX

PREPARATION AND PROPERTIES OF ASPHALTIC RESINS PREPARED FROM SOLVENT GAS OIL FEEDSTOCK D (TABLE I)

	First Stage Air Blowing		Second Stage Catalytic Treatment		
Run Number	K	L	M	N	P
Material Charged	D	K	L	K	Blend*
Catalyst used	NONE	NONE	$ZnCl_2$	$ZnCl_2$	
Wt. % Catalyst	NONE	NONE	1.0	1.0	
Gas used in test	air	air	CH_4	CH_4	
Gas rate, SCFH	2.0	2.0	<1	<1	
Reaction Temperature, °F.	515	550	560	560	
Reaction Time, Hours	5.5	7.0	6.0	6.75	
API Gravity at 60° F.	—	19.4	17.1	19.7	18.1
Specific Gravity, 60/60°F.	—	0.9377	0.9522	0.9358	0.9459
ASTM D 1160 Distillation					
IBP °F.	—	874	901	886	
2%	—901	945	923		
5%	—	937	972	945	
10%	—	960	—	949	
Distillation Residue					
Percent of Product	88.8[2]	87.6	94.4	88.6	
Viscosity, SFS, 210° F.	27[2]	50.5	81.0	35.9	63 [1]

*Blend of 40 wt. % of Run N and 60 wt. % of Run M.
[1]Calculated viscosity from Run N & M assuming a straight line function.
[2]Estimate.

Similar tests were made in which synthetic resins prepared from solvent gas oil, Table IX, was used as an additive for the 430 F+ topped which was then topped to 650 F and vacuum flashed to yield asphalts. Results follow in Table X:

Table X

EFFECT OF SYNTHETIC RESINS DERIVED FROM SOLVENT GAS OIL ON THE PROPERTIES OF TOPPED CRUDES AND ASPHALTS FROM SIMULATED CRUDES CHARGED TO THE REFINERY

Composition of Feed	Control	Additive Blend
Topped Crude, 430 F+, wt %	100.0	96.0
Product P*, wt %	0.0	4.0
API Gravity, 60 F	26.1	25.8
Distn. to Yield 650 F+Btms.		
Yield, vol % of 450 F+ Feed	59.0	59.9
API Gravity at 60 F	20.3	20.1
Specific Gravity, 60/60 F	0.9321	0.9334
Viscosity, SUS at 210 F	112.0	124.1
Viscosity, SFS at 122 F	93.2	128.4
Pour Point, F	+95	+100
Sulfur, wt %	1.60	1.40
Carbon Residue, Rams., %	6.73	7.59
Ash, wt %	0.02	0.04
Ni, ppm		
Fe, ppm		
V, ppm		12.0

Vacuum Asphalt Properties	Control		Additive Blend		
Test No.	1	2	6	7	8
Cor. Flash Temp., F	960	975	960	970	975
Yield, vol % of 430 F+	36.4	33.6	39.7	38.8	36.4
API Gravity at 60 F	9.9	9.1	10.4	10.3	9.8
Penetration, mm/10					
200 g/60 sec/39.2 F	35	25	46	37	31
100 g/ 5 sec/77 F	135	73	185	146	103
Penetration Ratio	25.9	34.2	24.9	25.3	3.1
Viscosity					
SFS, 210 F	442	849	319	441	653
SFS, 275 F	70.7	112.4	58.2	71.1	96.8
Poises, 140 F	265.3	862.4	171	291.6	491.1
Ductility, cm					
1 cm/min., 39.2 F	4.5	6.5	11.5	6.5	5.5
5 cm/min., 77 F	86	108	54	59	83
Softening Point, R&B, F	118	124	115	118	120
Spot Test (1)	Pos	Pos	Pos	Pos	Pos
Solubility, CCl_4, wt % 99.94	99.83	99.90	99.95	99.90	

(1) Positive spot denotes the presence of wax, not cracking.
*See Table IX

The preceding test data show that synthetic asphaltic resins prepared by the two-stage treatment of syntower and solvent gas oil were effective as additives for improving the quality of paving asphalts derived from crudes being processed at a refinery.

The second tabulation shows that similar resins prepared from the solvent gas oil derived from the same crudes in the plant were not as effective. Since solvent extraction would have been used to prepare the asphalts in the plant instead of vacuum reduction, which was used in the laboratory, more of the unreacted paraffinic portions of the solvent gas oil additive would have been extracted from the asphalt, thereby leaving more aromatic resins in the asphalt phase. Therefore it is contended, reasonably and as one skilled in the art will understand, that further improvement in the ductility of asphalts prepared by solvent extraction to the 650 F+ feed would have been apparent than observed for the vacuum asphalts prepared in the laboratory.

A similar series of tests were made in which a mixture of air blown and $ZnCl_2$ treated syntower bottoms and solvent gas oil was added to the 430 F+ topped crude which was then further distilled and vacuum flashed to yield asphalts. Results are presented in Tables XI and XII.

Table XI

PREPARATION AND PROPERTIES OF RESINS PREPARED FROM A MIXTURE OF SYNTOWER BOTTOMS AND SOLVENT GAS OIL

	First Stage Air Blowing		Second Stage Catalytic Treatment
Product No.			R
Charge to Run	Syntower Bottoms	Solvent Gas Oil	Blend*
Identification**	A	D	—
Catalyst Used	NONE	NONE	$ZnCl_2$
Wt. % Catalyst	NONE	NONE	1%
Gas Used	air	air	CH_4
Gas Rate, SCFH	2.0	2.0	1.0
Reaction Temperature, °F	375	530	560
Reaction Time, Hours	2.5	6.0	5.5
API Gravity, 60°F	—	—	13.7
Specific Gravity, 60/60°F	—	—	0.9745
ASTM D 1160 Distn.			
IBP °F	—	—	693
2%			743
5%			780
10%			817
20%			853
30%			889
40%			935
Distillation Residue			
Percent of Product			56.0

Table XI-continued

PREPARATION AND PROPERTIES OF RESINS PREPARED FROM A MIXTURE OF SYNTOWER BOTTOMS AND SOLVENT GAS OIL

	First Stage Air Blowing	Second Stage Catalytic Treatment
Viscosity, SFS, 210°F		72.2

*Blend consisted of 47.7 wt. % A and 52.3 wt. % D.
**See Table I

Table XII

EFFECT OF SYNTHETIC RESINS DERIVED FROM SYNTOWER BTMS. AND SGO ON THE PROPERTIES OF TOPPED CRUDES AND ASPHALTS FROM SIMULATED CRUDES CHARGED TO THE REFINERY

Composition of Feed	Control	Additive Blend
Topped Crude, 430 F+wt %	100.0	96.0
Product R*, wt.%	0.0	4.0
API Gravity, 60 F	26.1	25.8
Distn. to Yield 650 F+ Btms.		
Yield, vol % of 450 F+ Feed	59.0	59.1
API Gravity at 60 F	20.3	19.6
Specific Gravity, 60/60 F	0.9321	0.9365
Viscosity, SUS at 210 F	112.0	118.6
Viscosity, SFS at 122 F	93.2	95.7
Pour Point, F	+95	+100
Sulfur, wt. %	1.60	1.45
Carbon Residue, Rams., %	6.73	7.03
Ash, wt. %	0.02	0.03

Vacuum Asphalt Properties	Control		Additive Blend		
Test No.	1	2	9	10	11
Cor. Flash Temp., F	960	975	960	965	970
Yield, vol % of 430 F+	36.4	33.6	37.8	34.9	
API Gravity at 60 F	9.9	9.1	10.0	9.5	9.0
Penetration, mm/10					
200 g/60 sec/39.2 F	35	25	38	34	27
100 g/ 5 sec/77 F	135	73	160	133	88
Penetration Ratio	25.9	34.2	23.8	25.6	30.7
Viscosity					
SFS, 210 F	442	849	373	470	692
SFS, 275 F	70.7	112.4	62.2	72.4	97.6
Poises, 140 F	265.3	862.4	187.9	261.0	521.2
Ductility, cm					
1 cm/min., 39.2 F	4.5	6.5	10.5	7.0	5.5
5 cm/min., 77 F	86	108	76	76	119
Softening Point, R&B, F	118	124	113	116	120
Spot Test (1)	Pos	Pos	Pos	Pos	Pos
Solubility, CCl_4, wt. %	99.94	99.83	99.96	99.93	99.98

(1) Positive spot denotes the presence of wax, not cracking.
*Table XI

Reasonable modification are possible within the scope of the foregoing disclosure and the appended claims to the invention the essence of which is that there are produced by a combination of steps, i.e., air blowing at elevated temperature and then while still at elevated temperature treating with a catalyst an oil as herein described to produce a petroleum resin containing material which then, according to the invention, as such or in at least partly concentrated form is added to a topped crude or asphalt or similar material from which a final asphalt of, say, paving grade can be produced as by vacuum distillation, solvent extraction or otherwise as may be desired.

We claim:

1. A process for producing an additive, suitable for use in the production of high quality asphalt usable for paving said additive containing petroleum resin, which process comprises (1) air blowing a hydrocarbon oil fraction having the following properties:

API Gravity, 60° F, 2.0–30
Aniline Point, °F, 75–230
Viscosity, SFS, 122°F, 5–500
H/C Mol Ratio, 1.2–2.0
IBP, °F, 500–1000
50 percent Point, °F, 700–1000
Carbon Residue, Rams., percent, 0.2–18
No. Avg. Mol. Wt., 200–1,000
Paraffin Hydrocarbon Content, Wt. percent, 0.1–80

at an elevated temperature in the range of from about 350° to about 600°F for a period of time sufficient at said temperature to produce a treated fraction containing resin-forming materials and (2) subsequently, heating to a temperature in the range of about 500° to about 600°F said treated fraction in the presence of a catalyst chosen from among $ZnCl_2$, $FeCl_3$, and $SnCl_2$ to produce a treated hydrocarbon oil fraction which contains petroleum resin.

2. A process for the preparation of an asphalt suitable for producing paving grade asphaltic material which comprises incorporating a petroleum resin-containing material of claim 1 into a base material selected from among an asphalt and topped crude to produce a mixture and removing hydrocarbon oil from said mixture to recover an asphalt containing said petroleum resin.

3. A process according to claim 1 wherein the petroleum resin-containing materials are derived from a first bottoms fraction derived in fractionating a synthetic

hydrocarbon mixture produced in a catalytic cracking of virgin gas oil.

4. An operation according to claim 2 wherein the petroleum resin-containing material is first treated to remove hydrocarbon oil at least partly thereby concentrating said petroleum resin-containing material and then said petroleum resin-containing material is added to said base material.

5. A method of improving an asphalt which comprises recovering the resin from the product of claim 1 and adding the recovered resin to an asphalt.

6. A method according to claim 5 wherein the product of claim 1 is solvent deoiled to obtain concentrated resin and said concentrated resin is added to the asphalt.

7. Operation of claim 2 wherein said removing of hydrocarbon oil is by vacuum distillation.

8. The method of claim 2 wherein said removing of hydrocarbon oil is by solvent extraction.

9. The method of claim 4 wherein said removing of hydrocarbon oil is by vacuum distillation.

10. The method of claim 4 wherein said removing of hydrocarbon oil is by solvent extraction.

* * * * *