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ASPHALTIC PRODUCT AND METHOD OF PRODUCING SAME

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This invention relates to the manufacture of asphalts and, in particular, is concerned with the production of oxidized asphalts having a relatively high ductility and a relatively low temperature susceptibility.

In the past blown asphalts have been manufactured from residual oils derived from petroleums by blowing the same with air at elevated temperatures. According to usual practice the residual oil is blown with air at elevated temperatures of from about 400° F. to about 600° F. until the desired consistency of asphalt is obtained, usually requiring several hours to several days. The result of this operation is dehydrogenation, condensation, and polymerization, resulting in an increase in the asphaltic nature of the oil so treated and the production of an asphaltic product. The blowing process is employed to produce asphaltic products of various consistencies or grades as determined by ductility, melting point, penetration, etc., the extent of the alteration being determined by the conditions and length of time of blowing.

When many straight run residua from asphalt-containing crudes, as typified by heavy Eldorado residuum, are blown to asphalts in the conventional manner—and especially those of high melting point and hardness—they have the disadvantage of being "short", or in other words they lack ductility. This tendency sometimes may be minimized to a limited extent by careful preparation, but with very many residual oils capable of being converted into otherwise desirable asphalts by blowing no amount of care will serve to produce products of desirable ductility.

While for certain purposes a ductile product is not absolutely essential, however, in many uses ductility or lack of "shortness" is a very desirable property; and in fact in such uses as paving construction ductility is practically a necessary property, contributing extensively to the capability of pavements and similar structures produced from the asphalt to withstand wear, disintegration under traffic shock, mechanical stress due to temperature changes, weathering, etc. Ductility is a measure of the cementing power of asphalt. The higher the ductility the more filler the asphalt can utilize or bind without impairing the mechanical strength of the mixture. The lack of ductility in the blown residual products heretofore produced has deprived a considerable volume of semi-asphaltic oils from ready access to a desirable market.

In some cases steam reduction of residual oils to asphalts has been employed, as the resulting products are more ductile than the corresponding oxidized products. However, steam-reduced asphalts have the disadvantage of poor (high) temperature susceptibility, i. e., their penetration value changes inordinately with changes in temperature, and, moreover, the yield is usually rather low as compared to oxidized asphalts.

On the other hand, there are certain straight run residual oils which form a relatively ductile asphalt on oxidation. These oils are the residua obtained from Gulf Coastal crudes, which are highly naphthenic in character. However, in general, the asphalts produced by oxidizing the highly naphthenic Gulf Coastal residua also have the disadvantage of being too sensitive to changes in temperature; that is, their temperature susceptibility is rather high. Accordingly, these relatively ductile Coastal asphalts are likewise not desirable for many purposes as their consistency or penetration varies too widely with changes in temperature. For instance, in summer time they may be soft and viscous, while in winter they may be extremely hard and brittle.

Heretofore various processes have been suggested for controlling the physical properties of asphalts, as, for instance, by blending oils of different natures and subjecting the blends to oxidation. While these prior processes have been fairly satisfactory for certain purposes and for treating certain oils, they are entirely inadequate for treating the residual oils with which my invention is concerned in order to produce an asphalt having the combined properties of high ductility and low temperature susceptibility.

It is an object of this invention to provide a process whereby an asphalt having a relatively high ductility combined with a relatively low temperature susceptibility can be produced from a blend of a straight run residuum of a highly naphthenic character and a straight run residuum of a more asphaltic character.

A more specific object of this invention is to provide a process whereby an asphalt possessing relatively high ductility combined with relatively low temperature susceptibility may be produced from a blend of a straight run residuum from a highly naphthenic Gulf Coastal crude, such as a Mirando residuum, and a straight run residuum from an asphaltic base crude.

Still another object of the invention is to provide a process for the production of asphalt whereby the properties of the resultant asphalt may be controlled during the manufacture thereof.

My invention is based upon the surprising discovery that a straight run residuum of a highly naphthenic character and a straight run residuum of a more asphaltic character may be oxidized under properly regulated conditions to produce an oxidized asphalt having the combined properties of high ductility and low temperature susceptibility, i. e. a low ratio of penetrations expressed as the quotient of the penetration value at 77° F. divided by the penetration value at

32° F. I have found that this highly desirable oxidized asphalt of high ductility and low temperature susceptibility may be produced by first oxidizing the straight run residuum of a highly naphthenic character, i. e., the residuum which produces the more ductile asphalt on conversion, to approximately the penetration or the melting point desired for the finished asphalt, and then introducing into this oxidized product, either continuously or intermittently, the straight run residuum of a more asphaltic character, i. e., the residuum which it is known will produce on conversion an asphalt of lower ductility but better temperature susceptibility, while continuing the oxidation until the resultant product possesses the desired properties. It will be seen that by my process each successive increment of the straight run residuum of the more asphaltic character (whether added continuously or intermittently) will receive less oxidation than that previously added, and all will receive less oxidation than the original charge of straight run residuum of the more naphthenic character.

The present invention is to be clearly distinguished from the ordinary asphalt blending process because of the specific character of the materials being blended. I have found that when using the materials with which my invention is concerned, I am totally unable to produce an oxidized asphalt of the desired high ductility and low temperature susceptibility by any other method of blending of the materials than the one described above.

For instance, I have tried to blend the materials in the reverse order; that is, by first oxidizing the straight run residuum of the more asphaltic character to the desired penetration or melting point and then adding in increments the straght run residuum of the more naphthenic character while continuing the oxidation and have found it impossible to produce the desired final product of high ductility.

Furthermore, I have prepared mixtures of the straight run residuum of the more asphaltic character and the straight run residuum of the more naphthenic character, which mixtures were of the same proportions as those of satisfactory products produced according to my invention and then oxidized these mixtures to the desired penetration, and I have found that I am entirely unable to produce asphalts of high ductility by oxidizing these mixtures.

Furthermore, I have carried out experiments in which the Mirando residuum was oxidized to the desired penetration or melting point and then an equal part of Heavy Eldorado residuum was all added in one batch while continuing the oxidation. I was unable to obtain the desired blended asphaltic product of high ductility and low temperature susceptibility by this method of blending.

It is apparent, therefore, that by first converting a straight run residuum of a highly naphthenic character, which alone will produce an asphalt of good ductility and relatively poor temperature susceptibility, to the approximately desired melting point for the finished asphalt and then adding intermittently or continuously a straight run residuum of a more asphaltic character, which residuum alone will produce an asphalt of poorer ductility and better temperature susceptibility, a superior asphalt may be made which it would be difficult, if not impossible, to make from these stocks in any other manner.

For the purposes of this invention it is preferred to use a Mirando straight run residuum for the stock which produces an asphalt of good ductility. However, it is to be understood that other similar straight run residuums which are highly naphthenic, such as the highly naphthenic Gulf Coastal straight run residuums, may be used. These Coastal oils from the Gulf Coast territory of Texas and Louisiana are predominantly naphthenic but may also contain small amounts of asphalt.

It appears that my novel process may be employed for preparing blended asphalts of improved properties whenever they are produced by blending straight run residuum of a highly naphthenic character with any straight run residuum of a more asphaltic character. However, the process is particularly applicable for blending straight run residua of asphaltic crudes with the highly naphthenic straight run residua. For instance, residua from Talco and asphaltic California crudes may be used. The preferred asphaltic stock, however, is a Heavy Eldorado straight run residuum.

For many types of work where a product is desired possessing both high ductility and low temperature susceptibility, it is not unusual for a product to have to meet substantially the following specifications taken from a State of Texas specification, or even more rigid specifications, with regard to these two properties:

SPECIFICATION I

	Furol Viscosity at 210° F.
Penetration at 77° F. (100 gms.—5 sec.)	50 to 60
Penetration at 32° F. (200 gms.—60 sec.)	22 minimum
Ductility at 77° F.	50 minimum
Melting point (ball and ring)	113° to 140° F.

However, when using a straight run residuum of a highly naphthenic character such as a Mirando residuum and a straight run residuum of a more asphaltic character such as a heavy Eldorado residuum, I have been unable to produce a product that would meet the above specifications by any process other than the process of my invention. On the other hand, all the products produced by the process of my invention have had ductilities of at least fifty cm. at 77° F., and a penetration value at 32° F. of at least 22. Furthermore, the temperature susceptibility ratio for temperatures of 77° F. and 32° F., i. e., the ratio of the penetration at 77° F. to that at 32° F., has not been greater than 2.5 for a 50–60 penetration grade at 77° F.

In accordance with my invention the straight run residuum stock (or mixture of stocks) which it is known will produce the asphalt of higher ductility on conversion is charged to the converter and air-blown to approximately the desired melting point. At this point the straight run residuum stock (or mixture of stocks) which it is known will produce on conversion an asphalt of lower ductility but better temperature susceptibility is added intermittently or continuously, the air-blowing being continued so as to produce the desired melting point. The temperature susceptibility on sucessive samples withdrawn during the treat will then show improvement without serious loss of ductility, and the run is discontinued when the desired specifications have been met. The proportions of asphaltic residuum to Coastal residuum may vary widely depending upon various factors, such as the

specific nature of the residua and the exact properties desired in the finished asphalt.

The following specific examples are given in order to more clearly illustrate the invention, but it is to be understood that nothing therein is to be construed in a limiting sense as there may be variations therefrom without departing from the spirit of the invention.

The two charging stocks to be used in the examples are as follows:

	Flash, ° F.	Furol viscosity at 210° F.
		Seconds
Fire and steam reduced Mirando crude	455	42
Fire and steam reduced heavy Eldorado crude	515	89

EXAMPLE I

A charge of five parts of the reduced Mirando residuum is air-blown at 475° F. to fifty to sixty penetration at 77° F., the blowing rate being forty-eight cubic feet per hour per barrel. When fifty to sixty penetration at 77° F. is reached, the ductility is 110° F., but the penetration at 32° F. is only eighteen. At this point one part of the heavy Eldorado residuum is added and the blowing continued back to fifty to sixty penetration at 77° F. This is repeated until five parts of the heavy Eldorado has been added, samples being taken before each addition. Each of the last three samples taken meet the specifications listed above in Specification I, as can be seen from the following data in Table I:

TABLE I

Asphalt run #103

Charge: 5 parts Mirando residuum.

Converted to 50–60 penetration at 77° F., and added heavy Eldorado residuum at intervals as shown, continuing air-blowing down to 50–60 penetration at 77° F.

Total hours blown	Ratio of Mirando to Eldorado	Pen. at 77° F.	Pen. at 32° F.	Duct. at 77° F.	Melting point, ° F.
150	5-0	56	18	110+	124
ADDED 1 PART HEAVY ELDORADO RESIDUUM					
166	5-1	55	19	110+	125
ADDED 1 PART HEAVY ELDORADO RESIDUUM					
175½	5-2	73	23	110+	127
ADDED 1 PART HEAVY ELDORADO RESIDUUM					
192	5-3	57	23	110+	131
ADDED 1 PART HEAVY ELDORADO RESIDUUM					
200½	5-4	55	26	68	135
ADDED 1 PART HEAVY ELDORADO RESIDUUM					
208	5-5	60	29	54	135

In order to clearly show that the above specifications of Specification I cannot be met by other methods of blending, the following examples are included:

EXAMPLE II

The ratios of Mirando stock to heavy Eldorado stock in the last two samples of Table I are five to four and five to five. Mixes of these same ratios were made and then the mixtures were blown. The asphalts thus made did not meet the specifications. The results of these two tests are shown in Tables II and III.

TABLE II

Asphalt run #114

Charge {5 parts Mirando residuum / 4 parts heavy Eldorado residuum.

Hours blown	85½
Penetration at 77° F	54
Penetration at 32° F	25
Ductility at 77° F	32
Melting point	137° F.

TABLE III

Asphalt run #108

Charge {5 parts Mirando residuum / 5 parts heavy Eldorado residuum.

Hours blown	84½
Penetration at 77° F	54
Penetration at 32° F	26
Ductility at 77° F	16.5
Melting point	143° F.

EXAMPLE III

Furthermore, a run was made by first oxidizing the heavy Eldorado residuum and then adding the Mirando residuum intermittently while continuing oxidation. The above specifications of Specification I could not be met in this manner. The results of this test are shown in Table IV.

TABLE IV

Asphalt run #102

Charge: 5 parts heavy Eldorado residuum.

Converted to 50–60 penetration at 77° F., and added Mirando residuum at intervals as shown, continuing air-blowing down to 50–60 penetration at 77° F.

Total hours blown	Ratio of Eldorado to Mirando	Pen. at 77° F.	Pen. at 32° F.	Duct. at 77° F.	Melting point, ° F.
75	5-0	59	39	5	152
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
84	5½	58	35	6	149
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
101	5-1	57	36	6	148
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
116	5-1½	59	32	7	153
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
128½	5-2	60	35	9	147
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
144	5-2½	62	36	9	---
ADDED ½ OF ONE PART MIRANDO RESIDUUM					
161	5-3	56	28	11	---
ADDED 1 PART MIRANDO RESIDUUM					
184	5-4	52	25	12	144
ADDED 1 PART MIRANDO RESIDUUM					
205	5-5	56	25	15	142

EXAMPLE IV

A run was then made by charging five parts of Mirando residuum and converting same to the desired penetration and then adding five parts of heavy Eldorado residuum in one batch and continuing the oxidation to 50–60 penetration at 77° F. The following results of this run, which are listed below in Table V, show clearly that the desired blended asphaltic product of high ductility and low temperature susceptibility meeting the requirements of Specification I cannot be obtained by this method of operation.

TABLE V

Asphalt run #111

Charge: 5 parts of Mirando residuum.

Converted to approximately the desired penetration, added 5 parts of heavy Eldorado residuum in one batch, and continued the oxidation to 50–60 penetration at 77° F.

Total hours blown	Ratio of Mirando and heavy Eldorado	Pen. at 77° F.	Pen. at 32° F.	Duct. at at 77° F.	Melting point, ° F.
BEFORE ADDITION OF HEAVY ELDORADO					
169	5-0	41	16	110+	129
AFTER ADDITION OF HEAVY ELDORADO					
209½	5-5	57	27	25	136

What I claim is:

1. The method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility, which comprises oxidizing a straight run residuum of a highly naphthenic nature to approximately the desired penetration for the final blended asphalt, which residuum oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then gradually blending with said oxidized highly naphthenic residuum a desired amount of a straight run residuum of a more asphaltic nature, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

2. The method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility, which comprises oxidizing a straight run residuum of a highly naphthenic character to approximately the desired penetration for the final blended asphalt, which residuum when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then blending intermittently with said oxidized highly naphthenic residuum increments of a straight run residuum of an asphaltic crude, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

3. The method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility, which comprises oxidizing a straight run residuum of a highly naphthenic character to approximately the desired penetration for the final blended asphalt, which residuum when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then blending continuously with said oxidized highly naphthenic residuum a straight run residuum of an asphaltic crude, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

4. The method of producing a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration ratio at temperatures of 77° F. and 32° F. of not greater than 2.5 for a 50–60 penetration at 77° F. grade, which comprises oxidizing a straight run residuum of a highly naphthenic character to approximately the desired penetration for the final blended asphalt, which residuum when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then gradually blending with said oxidized highly naphthenic residuum a desired amount of a straight run residuum of a more asphaltic nature, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

5. The method of producing a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration ratio at temperatures of 77° F. and 32° F. of not greater than 2.5 for a 50–60 penetration at 77° F. grade, which comprises oxidizing a straight run Mirando residuum to approximately the desired penetration for the final blended asphalt, blending with said oxidized Mirando residuum an increment of a straight run residuum from an asphaltic crude, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, oxidizing said blend back to approximately the desired penetration value and continuing to add intermittently increments of said asphaltic residuum in a similar manner, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

6. The method of producing a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration value of 50–60 at 77° F. and at least 22 at 32° F., which comprises oxidizing a straight run Mirando residuum to approximately the desired penetration for the final blended asphalt and then gradually blending a substantially equal quantity of a heavy Eldorado straight run residuum with said oxidized Mirando residuum while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

7. As a new composition of matter, a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration ratio at temperatures of 77° F. and 32° F. of not greater than 2.5 for a 50–60 penetration at 77° F. grade, produced by oxidizing a straight run Gulf Coastal residuum of a highly naphthenic character to approximately the penetration point for the final blended asphalt, which residuum when oxidized

alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then gradually blending with said oxidized highly naphthenic residuum a desired amount of a straight run residuum of an asphaltic crude, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

8. As a new composition of matter, a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration ratio at temperatures of 77° F. and 32° F. of not greater than 2.5 for a 50–60 penetration at 77° F. grade produced by oxidizing a straight run Mirando residuum to approximately the desired penetration for the final blended asphalt, and then blending intermittently with said oxidized Mirando residuum increments of a straight run residuum from an asphaltic crude, which asphaltic residuum when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

9. As a new composition of matter, a blended asphaltic product possessing a ductility of at least fifty cms. at 77° F. and a penetration ratio at temperatures of 77° F. and 32° F. of not greater than 2.5 for a 50–60 penetration at 77° F. grade, produced by oxidizing a straight run Mirando residuum to approximately the desired penetration for the final blended asphalt, blending with said oxidized Mirando residuum an increment of a straight run residuum of a heavy Eldorado crude, oxidizing said blend back to approximately the desired penetration and continuing to add intermittently increments of said heavy Eldorado residuum in a similar manner while continuing the oxidation until the final blended asphalt is produced possessing the desired properties.

10. In a method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility the process which comprises oxidizing a petroleum residue of a highly naphthenic nature to approximately the desired penetration for the final blended asphalt, which residue when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then gradually blending with said oxidized highly naphthenic residue a suitable amount of a petroleum residue of a more asphaltic nature, which asphaltic residue when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until a blended asphalt of low temperature susceptibility is obtained which possesses a substantially higher ductility than can be obtained from said residues by any method of blending wherein said asphaltic residue receives at least as much oxidization as said naphthenic residue or wherein all portions of said asphaltic residue receive the same amount of oxidation.

11. In a method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility the process which comprises oxidizing a petroleum residue of a highly naphthenic nature to approximately the desired penetration for the final blended asphalt, which residue when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then blending intermittently with said oxidized highly naphthenic residue relatively small increments of a petroleum residue of a more asphaltic nature, which asphaltic residue when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until a blended asphalt of low temperature susceptibility is obtained which possesses a substantially higher ductility than can be obtained from said residues by any method of blending wherein said asphaltic residue receives at least as much oxidization as said naphthenic residue or wherein all portions of said asphaltic residue receive the same amount of oxidation.

12. In a method of producing a blended asphaltic product possessing a relatively high ductility and a relatively low temperature susceptibility the process which comprises oxidizing a petroleum residue of a highly naphthenic nature to approximately the desired penetration for the final blended asphalt, which residue when oxidized alone will produce an asphalt of relatively high ductility and relatively high temperature susceptibility, and then blending continuously with said oxidized highly naphthenic residue a petroleum residue of a more asphaltic nature, which asphaltic residue when oxidized alone will produce an asphalt of relatively low ductility and relatively low temperature susceptibility, while continuing the oxidation until a blended asphalt of low temperature susceptibility is obtained which possesses a substantially higher ductility than can be obtained from said residues by any method of blending wherein said asphaltic residue receives at least as much oxidation as said naphthenic residue or wherein all portions of said asphaltic residue receive the same amount of oxidation.

13. As a new composition of matter a blended oxidized asphaltic product of relatively high ductility and relatively low temperature susceptibility comprising an oxidized highly naphthenic petroleum residue, which residue when oxidized alone produces an asphalt of high ductility and high temperature susceptibility, and an oxidized asphaltic petroleum residue, which asphaltic residue when oxidized alone produces an asphalt of low ductility and low temperature susceptibility, all portions of said asphaltic residue being less oxidized than all portions of said naphthenic residue and various portions of said asphaltic residue being less oxidized than other portions thereof, said blended asphaltic product of low temperature susceptibility having a substantially higher ductility than oxidized blended asphaltic products of said residues wherein said asphaltic residue has received as much oxidation as said naphthenic residue or wherein all portions of said asphaltic residue have received the same amount of oxidation.

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