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PREPARATION OF ASPHALTS WITH LOWER STAINING TENDENCIES

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This invention relates to a method of producing improved asphalt compositions. More specifically, this invention teaches the blending of asphalts to improve their staining properties.

In certain applications of industrial asphalts staining characteristics are of considerable importance. For example, asphalt is commonly used as a waterproofing and dampproofing medium in the manufacture of packaging, building papers and fiberboards. In these applications, the asphalt is described as laminating asphalt in which it acts as a moisture barrier as well as a binder between two or more layers of paper, fiberboard or other flexible material. In some cases it is a saturant since the paper or fiber material is hot soaked or dipped into the asphalt, while in other cases it is a coating, in which case a surface film or layer of asphalt is caused to be deposited on one face of the flexible material. When asphalt has a high staining propensity, undesirable characteristics are imparted to the asphalt-treated paper or fiberboard. This results in products that display an oily or greasy surface, and therefore are very unsatisfactory for most applications. Thus manufacturers desire and specify asphalts of low staining test properties. Also, in the manufacture of prepared roofing, coating asphalts of high staining properties impart a color discoloration to mineral granules; this too is highly undesirable.

To clarify the invention, a brief discussion of the composition of asphalt residuum is helpful. By use of nuclear magnetic resonance and conventional analytical test methods such as ebulliscopic molecular weight and ultimate combustion analysis each of five major components in asphalt have been characterized structurally. The five asphalt components may be described briefly as follows. The aromatic oils #2 and #3 are of particular interest in the invention.

Paraffins plus naphthenes—A mixture of pure paraffins and naphthenes with paraffin side chains.

Aromatic oil #1—A mixture of single ring aromatics with long paraffin side chains plus single ring aromatics with attached naphthene rings.

Aromatic oil #2—A mixture of monocyclic and polycyclic aromatics with paraffin side chains or attached naphthene rings.

Aromatic oil #3—A mixture similar in structure to aromatic oil #2 but definitely higher in molecular weight, and contains more nitrogen, sulfur and some oxygen.

Asphaltenes—A complex hydrocarbon of highly aromatic nature and high molecular weight, assumed to be a perinaphthalene type structure.

To further define the five components the following physical properties are given:

Component	Specific Gravity, 60/60° F.	Universal Viscosity, 210° F.	Viscosity Index	Color
Paraffin plus naphthenes.	.86-.90	50-125	75+	water white.
Aromatic oil #1.	.91-.95	100-300	25-100	yellow.
Aromatic oil #2.	.97-1.03	500-1500	25-75	yellow to red.
Aromatic oil #3.	1.04-1.08	10,000-500,000	[1] 0	black.
Asphaltenes	1.15-1.25	[2]		black-brown.

[1] Less than 0.
[2] Solid, infusible.

In addition all of the above components have high initial boiling points of 800° F.+ and a relatively high flash point (450° F.+ by the Cleveland Open Cup Method).

The average chemical structure of the components is shown in the following table:

Component	Formula	Molec. Wt.	C/H	BI	C/SC	AR
Paraffins+naphthenes.	$C_{43}H_{87}$	600	6.2	.36		
Aromatic oil #1	$C_{52}H_{90}$	674	6.9	.50	13.3	1.2
Aromatic oil #2	$C_{52}H_{81}S$	708	7.9	.55	6.7	5.1
Aromatic oil #3	$C_{66}H_{94}NSO$	956	8.4	.60	5.5	6.7
Asphaltenes	$C_nH_{2n-6}NSO$	3,000	10.6	.75	3.1	

Branchiness index indicated above by BI is the ratio of methyl to methylene hydrogens exclusive of hydrogens on the alpha carbon. Basically this is a measurement of the relative amount of hydrocarbon branching. Carbons per side chain (C/SC) sometimes referred to as the chain length is the average number of alkyl carbon atoms per side chain. Any carbon atom substituted on an aromatic ring is considered a side chain. This is a significant measure of the structure of a hydrocarbon as it portrays the length or size of the aliphatic derivative. Aromatic rings per molecule (AR) is the average number of individual unsaturated rings. It identifies the size of the basic aromatic nucleus around which the hydrocarbon structure is built.

A typical coating asphalt, specifically one obtained from a Tia Juana crude, contains the following percentages of the above five components respectively; 18%, 14%, 15%, 19%, and 34%.

In accordance with this invention, it has been found that by increasing the percentage of the aromatic oil #2 and/or #3 component by blending extraneous amounts of these materials in base asphalts improves their staining properties. The amount of these components blended with the base stock ranges from 2 to 25% by weight but preferably from 3 to 10%. The addition of the aromatic oil #3 component yields better results than the aromatic #2 component and is therefore preferred. As asphalt composition of maximum quality with respect to stain consists of 45–50% of the aromatic oil #2 and 3 combined, however an asphalt of satisfactory staining quality will consist of 35–45%.

The blending of an asphalt using any base asphalt stock, either straight run, air blown or propane precipitated, can be accomplished by straight forward blending in most cases. It has been found that the paraffin plus naphthene and the three aromatic oil components blend completely and homogeneously by raising the blend mixture to a temperature in the range of 100° F. to 400° F. and providing a moderate amount of intimate mixing or stirring. The temperature for mixing depends in general upon the viscosity of the final blend or that of the base asphalt. Softening point is another indication of the proper mixing temperature, and it has been found that a mixing temperature of 100° F. or more above the softening point of the blend or base ingredients is sufficient to accomplish the blend. The best mixing temperature is determined by the desired viscosity. That is, a viscosity of 10 poises or less lends itself to ready mixing and blending. With most asphalts and/or blends, this viscosity will be reached at 100° to 200° F. above its softening point. Temperatures above this give greater fluidity and slightly greater ease of mixing; however, for practical reasons these greater fluidities are not necessary.

Staining properties are directly related to two empirical test characteristics. The Barber stain test (Ind. Eng. Chem. An. Ed. 9, 563–65, 1937) and the ASTM stain test (Method D 1328–54T) are both applicable in determining this property, but differ in the technique involved and in the reference standards used. Both tests involve the placement of a sample of asphalt next to layers of a specified grade of cigarette paper. This is submitted to an elevated temperature for a given period after which the stain number is determined by reading the number of papers that have actually been stained. In the Barber test, the stains will normally be measured from 1 to 8 with a number of 4 or less being desirable, depending upon the application. ASTM stains are measured from 8 to 30 with a number of 20 or less being desirable.

One mode of separation which may be used to obtain the desired aromatic oil #2 and #3 components from an asphalt residuum is as follows: Firstly, the asphaltenes are separated by precipitation and filtration using normal hexane as a solvent. The soluble portion called petrolenes is then submitted to chromatographic separation eluting first the paraffin plus naphthene and the aromatic oil #1 components with a solvent composed of 90% n-heptane and 10% benzene. Remaining behind is a cut containing predominantly aromatic oil #2 and #3 component. These are separated by first treating with benzene to remove the aromatic oil #2 component, and then treating with pyridine to obtain the aromatic #3 component.

The modified or reconstituted asphalts described above have improved staining characteristics over blends of asphalt with conventional petroleum refining processes. This is shown in the examples which follow. The base stocks with which the aromatic oils #2 and 3 are blended are similar to those used in the examples and may be characterized as follows:

Crude Source	Softening Point, ° F. (B&R)	Penetration at 77° F. (100 g., 5 sec.)
Tia Juana Med	258	11
Redwater	243	16

The following examples further show the advantages of the instant invention:

EXAMPLE I

The aromatic oil #2 and #3 components used in the instant invention were obtained by the following procedure:

400 grams of Tia Juana flux asphalt were mixed with 400 grams of normal hexane. The insoluble portion, asphaltenes, was removed from the solution by filtration. The soluble portion, petrolenes, containing 350 grams of deasphaltened asphalt in normal hexane was then subjected to a chromatographic separation at a temperature from 70–120° F. under atmospheric pressure. A 3" x 10' column filled with 30 pounds of 20–60 mesh dried Porocel was used. The paraffin plus naphthenes fraction was subsequently eluted with 25 liters of normal heptane at 2–4 liters/hour. 68 grams of paraffins plus naphthenes were obtained. Subsequently, the aromatic oil #1 component was eluted with 25 grams of solvent composed of 90% heptane and 10% benzene. 62 grams of the aromatic oil #1 were obtained. 90 grams of the aromatic #2 were then removed by the elution with 25 liters of benzene. The final component, aromatic oil #3, was eluted with 30 liters of pyridine. 120 grams were obtained. Each of the last four components were separated from the Porocel as an eluate from which the oils were recovered by stripping off the solvent. Since, as the subsequent data show, both the aromatic oil #2 and #3 give improved stain properties, it is unnecessary to elute them separately. Actually they may be removed as one fraction and still be used to gain the object of the invention.

The aromatic oil components as separated above are then blended with a base asphalt such as one of the two examples listed above. Since these oils will lower the softening point of a base asphalt, it will be customary to select a base with a softening point higher than that desired in the end product. Such a blend is accomplished by simple mixing at a temperature about 100° F. higher than the softening point of the base. Homogeneity will normally be obtained within a few minutes with mixing. Mixing or blending may also be accomplished in the presence of a mutual solvent such as benzene, petroleum naphtha, etc. By use of a mutual solvent the temperature of mixing may be reduced but final stripping of the solvent will be necessary.

The softening point of the blend is always lower than that of the base asphalt, and the softening point of the blend is a near linear function of the percent of aromatic oil fraction added. Thus the choice of the base asphalt is largely governed by the softening point desired in the end product and the percentage of oil that is added. A few trial blends will clearly indicate the selection and the percentage of materials to be blended.

In this example an aromatic oil #2 and an aromatic oil #3 component were added separately to asphalts derived from a Tia Juana crude. The table below shows the staining characteristics of asphalts blended with these components compared with an asphalt of the same softening point made by normal processing methods.

Table II

Component	Percent Added	Softening Point, ° F.	Barber Stain	ASTM Stain
	0	210	3½	22
AO-2	4	210	3	18
	0	246	4	23
AO-2	5	246	3½	22
	0	231	3½	22
AO-2	10	231	2½	18
	0	251	4½	25
AO-3	3	251	2	13
	0	202	3½	22
AO-3	10	202	2	14

The above data clearly show the improved staining properties of the blended asphalt. All of the samples showed improvement, and, with the exception of the sample with the 246° F. softening point, all met the target level of less than 4 on the Barber stain test and less than

20 on the ASTM test. Even the 246° F. sample, after the addition of 5% of the aromatic oil #2 components was within acceptable limits on the Barber stain test.

It is also readily apparent that the aromatic oil #3 gave a better result than the aromatic oil #2. Both asphalts to which the aromatic oil #3 was added were well within the proper target area.

EXAMPLE II

Samples were prepared in the same manner as in the previous example with the exception that the asphalt was from a Redwater (Canadian) crude. The following results were obtained.

Table III

Component added	Percent Added	Softening Point, ° F.	Barber Stain	ASTM Stain
	0	194	8	30
AO-2	15	194	3	19
	0	204	8	30
AO-3	10	204	5	26
	0	218	3½	21
AO-3	15	218	2	17

The above data further shows the improved staining properties obtained by reconstitution. In all cases considerable improvement in staining properties resulted.

EXAMPLE III

To show the advantage of blending with the components of this invention over conventional refinery streams, stain test comparisons were made. The conventional refining stream selected was a bright stock extract which is the conventional refinery fraction closest in composition to the aromatic oils #2 and #3 of this invention. The following data were obtained:

Table IV

Crude Source	Component Added	Wt. Percent Added	Softening Point	Barber Stain	ASTM Stain
Tia Juana			246	4	23
Do	Bright stock extract	10	246	5	25
Do	Aromatic oil #2	5	246	3½	22
Do			231	3½	22
Do	Bright stock extract	10	231	4½	23
Do	Aromatic oil #2	10	231	2½	18
Do			210	3½	22
Do	Bright stock extract	10	210	4½	22
Do	Aromatic oil #2	4	210	3	18
Redwater			218	3½	21
Do	Bright stock extract	15	218	8	30
Do	Aromatic oil #3	15	218	2	17
Do			194	8	30
Do	Bright stock extract	15	194	7½	30
Do	Aromatic oil #2	15	194	3	19

The above data clearly show that a conventional refinery stream does not effect the improvement in staining characteristics obtained by blending with the aromatic oil #2 and 3 components. As a matter of fact, when the bright stock extract was added to asphalt of certain penetrations the staining characteristics were even further impaired.

EXAMPLE IV

In order to further show the advantages of blending aromatic oils #2 and #3 fractions as compared to conventional refinery streams, an asphalt from a Tia Juana medium crude was blended with a propane precipitated stock from a West Texas crude. The Barber stain and ASTM stain were compared with the unblended asphalt and asphalt blended with the aromatic oils #2 and #3. The following table shows the results:

Table V

Component Added	Wt. Percent	S.P., ° F.	Barber Stain	ASTM Stain
None	0	218	3½	23
Propane ppt. stock from W. Texas crude	10	218	3	17
Aromatic oil #3	10	218	2	14
Aromatic oil #2	10	218	2½	15

It will be noted that while some improvement was obtained with the propane precipitated stock, both of the aromatic oils gave better improvement in the staining properties. These data further show that the aromatic oil #3 gives better results than the aromatic oil #2.

The foregoing examples should not be construed as limitations on the invention as they are merely illustrative.

What is claimed is:

1. A process for preparing an asphalt having low staining properties which comprises separating asphaltenes from a base asphalt and recovering a petrolene fraction containing a first fraction having a viscosity of less than about 1500 SUS at 210° F. and a specific gravity at 60/60° F. of less than about 1.03 and an oil fraction comprising polycyclic aromatics and having a viscosity of above about 10,000 SUS at 210° F. and a specific gravity at 60/60° F. between about 1.04 and about 1.08, separating said first fraction from said oil fraction and blending said oil fraction with a base asphalt.

2. A process for reducing the staining properties of a base asphalt which comprises deasphalting a first base asphalt and withdrawing a petrolene fraction containing an aromatic oil fraction comprising polycyclic aromatics, having a viscosity above about 10,000 SUS at 210° F., a specific gravity at 60/60° F. between about 1.04 and about 1.08 and boiling above about 800° F.; paraffins; naphthenes and aromatic components of lower molecular weight than said aromatic oil fraction, separating said aromatic oil fraction from said paraffins, said naphthenes, and said aromatic components of lower molecular weight and blending said aromatic oil fraction with a base asphalt.

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