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ASPHALT COPOLYMER COMPOSITIONS

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The present invention relates to asphalt compositions. More particularly, it is directed to asphalt compositions wherein the adverse influence of wax is overcome by the use of a particular class of copolymers.

Asphalts constitute the residual fraction of petroleum crude oils. For the most part, petroleum crudes may be roughly divided into three classes with respect to these residual fractions. The "asphaltic crudes" are essentially non-waxy. The "paraffinic crudes" contain a preponderance of hydrocarbon waxes, both in the lubricating oil fractions and in the residues. The "mixed base crudes" are those with which the present invention is especially concerned, since the residual fractions of such crudes are mixtures of both asphalt and hydrocarbon waxes. It is known that the residues of mixed base crudes present technical and economic problems with respect to the disposal or utilization of the residues. Asphalts are utilized for purposes wherein plastic properties are necessary to prevent rupture of a bond or protective film when subjected to deformation, while waxes are normally employed where the crystalline character and related properties are desirable. The presence of crystalline waxes as an asphalt component or contaminant, such as occurs in the residues of mixed base crudes, presents difficulties with respect to the employment of the residue for asphaltic uses or for wax uses, since waxes reduce the plasticity of asphalt and asphalt degrades waxes for many purposes.

One of the important uses of asphalts is in paving compositions. The asphalts for this purpose are normally termed "paving grade asphalts" and generally are straight run asphalts having softening points from about 100 to about 130° F. and penetrations at 77° F. in the order of between about 50 and about 300 dmm. Paving grade asphalts emulsified in water or diluted with hydrocarbon solvents (cutback asphalts) are also used in road construction.

Waxy asphalts, which may be a mixture of residues from wax base crudes and from asphaltic crudes or a naturally occurring mixed base crude, inherently possess several physical disadvantages which should be overcome. This is becoming of increasing economic importance due to the larger amounts of such wax-containing asphalts which are being used commercially. The structure of crystallized wax in asphaltic residues promotes a relatively high consistency thereof at ambient temperatures. In other words, the asphalt has an undesirably low penetration at ordinary temperatures encountered in temperate climates. This is a substantial disadvantage since it is necessary to prepare carefully a relatively hard residue if the standard asphalt working equipment, such as paving machines and rollers, is to be employed. However, when waxy asphalts are utilized the high temperature properties thereof are undesirable, as reflected in the viscosity which is normally measured at 275° F. Asphalts containing wax, when heated to temperatures above the average melting point of the waxes contained therein, show a rapid drop in the viscosity at such elevated temperatures. This is undesirable since melted asphalts containing wax are too fluid for use in standard asphalt handling equipment and tend to run off of surfaces to which they are applied which are other than horizontal.

Further aspects of this problem concern the relatively poor properties of waxy asphalt with respect to "ductility."

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One of the indications of good future performance of such asphalts is a high ductility; that is, in the order of at least 100 centimeters at 77° F. as determined by the well-known ASTM Method D113–44. If the ductility of the asphalt is substantially lower than this figure, the asphalt may be unsuitable for paving purposes since it may possibly lack proper flexibility, thus resulting in cracking and fracturing of the paved surface under stress or change in temperature conditions. Most straight run asphaltic base crudes yield asphaltic residues having the desired high ductility. However, the mixed base crudes do not yield asphalts which meet the minimum requirements of many state highway specifications. This is especially true when the wax content is in the order of 5–10% by weight of the asphaltic residue and may be a matter of technical concern when as little as 1% of wax is present.

Many materials have been added to asphalts for the purpose of improving various properties thereof, including ductility and flexibility. However, the additives employed and the amounts utilized have normally been such as to result in uneconomic compositions. Asphalt, being a low cost material, is difficult to improve in any particular property by the addition of special additives without appreciably affecting the cost of the resulting composition. Many additives have been used in amounts between about 1 and 10% but quantities of most additives within this concentration range are substantially impractical since it is then economically possible for a consumer to find another source of asphalt having the properties he desires without the adverse cost factor. Hence, it is especially important to discover a means for improving the properties of asphalts without substantially adversely affecting the price structure of the product.

It is an object of the present invention to improve the physical properties of waxy asphalts. It is a particular object of the invention to raise both the room temperature penetration and the high temperature viscosity of waxy asphalts. It is an additional object of the present invention to improve the ductility and flexibility of asphalts containing wax. Other objects will become apparent during the following detailed description of the invention.

Now, in accordance with the present invention, asphalt compositions are provided comprising a major amount of asphalt containing a minor amount of a hydrocarbon wax and as an agent for overcoming the disadvantageous physical properties of such compositions an additive proportion of a copolymer of ethylene with an ester of a C_2–C_6 aliphatic alcohol and a C_2–C_8 aliphatic monocarboxylic acid, said ester containing one carbon-to-carbon double bond. The presence of limited amounts of such copolymers has been found to raise the penetration of waxy asphalts to an unexpected degree and at the same time to increase the high temperature viscosity of such asphalts. The increase in penetration at 77° F. of waxy asphalt by the addition thereto of high molecular weight copolymers according to the present invention is unexpected. Consequently, the proportion of the copolymers to be used in the compositions of this invention is limited between about 0.01 and 2.5% by weight and preferably between about 0.05 and 1.0%, optimum results being obtained with a preferred copolymer to be discussed hereinafter (0.075–0.3% by weight of the copolymer of ethylene with unsaturated ester is employed).

Another aspect of the present invention comprises the possibility of employing relatively harder asphalts, which naturally have higher high temperature viscosity, in conjunction with the copolymers of the present invention, since the latter cause an increase in ambient temperature penetration and at the same time result in a desirable increase in viscosity at high temperatures. The results obtained in this respect are entirely different from those experienced from many other types of additives, such as ester waxes and many polyolefins.

The asphalts to which the present invention particularly applies have been outlined above and constitute normally waxy asphalts or, in other words, asphalts containing hydrocarbon waxes. While this combination is primarily obtained in the refining of mixed-based crudes, it can also be derived during the refining of paraffin-base crudes and asphalt-base crudes, the residues from these two crude refining operations being sent to a common residue tank. The elimination of naturally occurring or contaminating waxes from asphalt in order to improve their physical properties is an uneconomic procedure since both components, namely wax and asphalt, are such low cost products. Consequently it is necessary on a commercial basis to utilize the waxy asphalt, if possible counteracting the adverse effect of the wax present therein. Otherwise the utility of waxy asphalts is limited to situations in which the adversely affected properties are of minor importance.

The class of ethylene-ester copolymers to be utilized in accordance with the present invention is prepared by known procedures from ethylene and vinyl esters of low molecular weight fatty acids or from ethylene copolymerized with lower alcohol esters of an acrylic acid.

The vinyl esters are those formed between vinyl alcohol and lower fatty acids having an average of from 2–6 carbon atoms per molecule and include especially acetic, propionic, butyric, valeric and caproic acids as well as mixtures of the same. In order to be the most effective in the manufacture of waxy stocks, it is preferred that the copolymers are those containing only between about 15 and 40% by weight of ester units, the balance being ethylene units. More particularly, the preferred copolymers comprise those in which the ester is vinyl acetate and the proportion of the latter in the copolymer is between 20 and 35% by weight. The average molecular weight of such copolymers determined by light scattering methods is normally between about 10,000 and 1 million, preferably 20,000 to 100,000.

The preferred copolymers of the present invention are those formed between ethylene and vinyl acetate, particularly when the vinyl acetate portion of the copolymer is between about 25 and 35% by weight and the average molecular weight thereof is between 2.5 and 5×10^5. Expressed in other terms, the molecular weight can be specified by means of its intrinsic viscosity at 30° C. in 0.25% toluene solution. This is preferably between 0.75 and 0.90 dl./g. Esters formed between C_{2-6} alcohols and C_{3-6} acids of the acrylic acid series may be used in place of or in addition to the vinyl esters in preparing the copolymers with ethylene. These are preferably acrylates or methacrylates, including ethyl acrylate, propyl, acrylate, butyl acrylate, ethyl methacrylate, propyl methacrylate and mixtures of the same. The proportion of acrylic ester in the copolymer is preferably 5–30%, with average molecular weights of 10,000–1 million.

In accordance with the present invention, it has been ascertained that the addition of the copolymers of the

present invention to asphalts containing wax (particularly those containing at least about 1.0% of wax, and up to about 20% wax based on the combined wax and asphalt) results in a substantial increase in penetration at temperatures below the melting point of the wax (such as the usual test temperature of 77° F.) as long as the amount of copolymer is restricted to between 0.01% and 2.5% by weight of copolymer based on the waxy asphalt. If the amount of copolymer is increased beyond this point, the room temperature penetration of the waxy asphalt actually decreases. In other words, the asphalt becomes "harder" at room temperature. The most effective range of copolymer concentration in waxy asphalt is between about 0.05 and 1.0% by weight of copolymer, still more preferably 0.075 to 0.3%.

As stated hereinbefore, the presence of the critically limited proportion of copolymer causes a softening of the asphalt at ambient (room) temperatures, while at the same time causing an increase in the viscosity of the waxy asphalt at elevated temperatures, usually above the melting point of waxes present in the asphalt. The extent of this high-temperature viscosity effect may be as much as 25–35 seconds Saybolt-Furol viscosity at 275° F. The ductility of waxy asphalt compositions is substantially increased by the presence of the subject copolymers.

The following examples illustrate the benefits to be obtained by the present invention and demonstrate that the amount of copolymer which may be employed is strictly limited when the aim is to increase penetration at ambient temperatures.

Example I

A waxy asphalt (containing about 10% by weight of wax), obtained by distillation of a waxy Canadian crude oil, was blown to 178° F. softening point and 17 dmm. penetration and blended with a Midcontinent aromatic short residue extract in appropriate proportions of each component. The blended asphalt so prepared was heated to a temperature of 400° F. for 16 hours and then cooled to 77° F., at which point the penetration of the cooled waxy asphalt was determined at 275° F.

In order to determine the effect of the subject copolymers upon the room temperature penetration and the high temperature viscosity of the asphalt, varying proportions of a copolymer of ethylene and vinyl acetate were added in the amounts given in the table below. The copolymer was dispersed in the waxy asphalt by heating the copolymer-waxy asphalt mixture to a temperature of 400° F. for 16 hours. The same properties were then obtained on the copolymer-waxy asphalt compositions and are given in the table below.

TABLE I

Sample	Composition	Pen., dmm.	Visc. at 275° F., SSF	Ductility at 77° F., cm.	Oliensis Spot Test
A	Base Blend	131	115	65	Fail.
B	Same + 0.25% Polymer B.[a]	156	124	111+	Pass.[c]
C	Same + 0.25% Polymer C.[b]	153	124	90	Pass.[c]

[a] Polymer B: Copolymer of 67% ethylene and 33% vinyl acetate, average mol wt. ca. 30,000.
[b] Polymer C: Copolymer of 95% ethylene and 5% ethyl acrylate, average mol wt. ca. 30,000.
[c] The effect of the polymers on the Oliensis test is noteworthy and unexpected.

While the polymers may be incorporated directly in the asphalt, better dispersion is obtained by blending the polymers and an aromatic oil (such as a short residue extract) and dispersing this blend in asphalt.

We claim as our invention:

1. An asphalt composition comprising a major amount of an asphalt, a minor amount of a hydrocarbon wax, said wax being present in an amount between about 1.0 and about 20% by weight of the combined asphalt and wax, and between about 0.01 and 2.5% by weight of a copolymer of ethylene with an ester of vinyl alcohol and

a C_{2-6} fatty acid, said copolymer having an ester content of 15–40% by weight and an average molecular weight of 1×10^4 to 1×10^6.

2. An asphalt composition comprising a major amount of an asphalt, a minor amount of a hydrocarbon wax, said wax being present in an amount between about 1.0 and about 20% by weight of the combined asphalt and wax, and between about 0.05–1.0% by weight of a copolymer of ethylene with an ester of vinyl alcohol and a C_{2-6} fatty acid, said copolymer having an ester content of 20–35% by weight and an average molecular weight between 2.0×10^4 and 1×10^5.

3. An asphalt composition comprising a major amount of an asphalt, a minor amount of a hydrocarbon wax, said wax being present in an amount between about 1.0 and about 20% by weight of the combined asphalt and wax, and between about 0.075–0.3% by weight of a copolymer of ethylene with vinyl acetate, said copolymer having a vinyl acetate content of 25–35% by weight and an inherent viscosity of 30° C. in 0.25% toluene solution of 0.75–0.90.

4. A paving grade asphalt composition comprising asphalt containing 2–7.5% by weight petroleum hydrocarbon wax, said asphalt-wax mixture having a penetration at 77° F. of 50–300 dmm., and 0.075–0.3% by weight of a copolymer of ethylene with vinyl acetate, said copolymer having a vinyl acetate content of 25–35% by weight and an inherent viscosity at 30° C. in 0.25% toluene solution of 0.75–0.90.

5. An asphalt composition comprising a major amount of an asphalt, a minor amount of a hydrocarbon wax, said wax being present in an amount between about 1.0% and 20% by weight of the combined asphalt and wax, and between about 0.01% and about 2.5% by weight of a copolymer of ethylene with an ester of a C_{2-6} fatty alcohol and a C_{3-6} acrylic acid, said copolymer having an ester content of 5–30% by weight and an average molecular weight of 1×10^4–1×10^6.

6. An asphalt composition comprising a major amount of an asphalt, a minor amount of a hydrocarbon wax, said wax being present in an amount between about 1% and 20% by weight of the combined asphalt and wax, and between about 0.01% and 2.5% by weight of a copolymer of ethylene with an ester of a C_{2-6} aliphatic alcohol and a C_{2-6} aliphatic monocarboxylic acid, said ester containing one carbon-to-carbon double bond, said monocarboxylic acid being a C_{3-6} acrylic acid when the carbon-to-carbon double bond is contained in the acid portion of said ester, said aliphatic alcohol being vinyl alcohol when the carbon-to-carbon double bond is contained in the alcohol portion of said ester, said copolymer having an ester content of from 5 to 30% by weight when the double bond is in the acid portion of said ester and an ester content of from 15–40% by weight when the double bond is in the alcohol portion of said ester, said copolymer having an average molecular weight of 1×10^4 to 1×10^6.

References Cited by the Examiner

UNITED STATES PATENTS

2,610,956	9/1952	Derksen et al.	260—28.5
2,848,429	8/1958	Woodruff et al.	260—28.5
2,871,212	1/1959	Thayer	260—28.5
2,877,196	3/1959	Reding	260—28.5

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