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ASPHALT COMPOSITIONS

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The present invention relates to asphalt compositions of improved ductility especially useful for paving and industrial purposes and the like. More particularly, it is directed to asphalt compositions wherein the asphalt is contaminated with a naturally occurring hydrocarbon wax.

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 will be apparent to any experts in the petroleum field 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 deformtion, while waxes are normally employed where the crystalline character and related properties are desirable. The presence of crystalline waxes as an asphalt contaminant, such as occurs in the residues of mixed base crudes presents difficulty 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 asphalts emulsified in water or diluted with hydrocarbon solvents (cutback asphalts) are also used in road constructions. The base asphalts in these diluted materials should have the same qualities as a penetration grade asphalt. One of the primary requirements of such asphalts is that they possess 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, then it is indicated that the asphalt is unsuitable for paving purposes since it will lack proper flexibility and ductility, 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 which contain substantial amounts of wax are normally unacceptable for paving grade asphalts since the wax content results in low ductilities which do not meet the minimum requirements of many state highway specifications. This is true even when the wax content is in the order of 1–10% by weight of the asphaltic residue.

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 ductility and flexibility of residues from mixed base crudes. It is a further object of the present invention to improve the ductility and flexibility of waxy asphalts. It is a particular object of the present invention to improve the ductility and flexibility of asphalt without any appreciable increase in the cost of the product. Other objects will become apparent during the following description of the invention.

Now, in accordance with the present invention, the ductility and flexibility of paving grade asphalts contaminated with about 1–10% by weight of hydrocarbon waxes is unexpectedly improved by the synergistic combination of a polymerized linear ester of an acid of the acrylic acid series together with a hydrocarbon rubber, the proportions of this combination of improving agents being within the range from about 0.01% to about 0.5% by weight each.

It is known that each of these classes of additives has been employed in asphalts previously. However, each of the additives has been employed alone and in amounts greater than about 1% by weight of the asphalt. As the data given hereinafter will show, the individual additives employed in asphalt in the absence of the second additive either require excessively large amounts to produce the desired effect or result in a relatively minor improvement in ductility, regardless of the amount employed.

The remarkable improvement achieved by the combination of the two recited classes of additives is especially striking in view of the fact that such small amounts produce such a large effect, even when the proportion of wax present in the asphalt is in the order of 1–10% by weight of the waxy asphalt. It would appear that the action of the combined additives is substantially different from the known action of these same additives when they are present in such media as lubricating oils containing wax. Under such circumstances it is normally necessary to employ amounts in the order of 0.5–2.5% by weight of the polymethacrylate, for example, to achieve a substantial reduction in pour point or an appreciable increase in viscosity index of the oil. Neither of these properties enter into the alteration of asphalt properties or at least, the excellent improvement in ductility of an asphalt is not a factor taken into consideration with respect to lubricating oils.

The asphalts to which the present invention particularly applies have been outlined above and constitute normally waxy asphalts or, in other words, asphalts contaminated with hydrocarbon waxes. While this combination is primarily obtained in the refining of mixed base crudes, it may also be derived during the refining of paraffin base crudes and asphalt base crudes in the same refinery, the residues from these two crude refining operations being sent to a common residue tank.

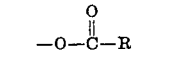
The elimination of contaminating amout of wax from

an asphalt in order to improve the ductility and flexibility properties of the latter is an uneconomic procedure due to the low cost of both of the components, namely, wax and asphalt. Consequently, it is necessary to utilize the waxy asphalt for some purpose where ductility and flexibility are not critical or to overcome economically the adverse effect of the presence of wax upon ductility. It is this latter alternative with which the present invention is concerned.

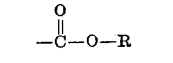
The esterified oil-soluble polymerization products are formed by polymerizing esters having the vinyl or substituted vinyl group having the following general formula:



wherein X represents a hydrogen, an alkyl or aromatic hydrocarbon group, and Y is



or



R representing a monovalent hydrocarbon radical containing more than 6 carbon atoms.

The polymers of esters having this general formula are colorless, odorless, and stable towards oxidation or storage. The polymerization is controlled so that oil-insoluble polymers are not formed. The oil-soluble polymers that are used according to this invention are the esters of acrylic acid or of its alpha-alkyl or alpha-aryl substitution products and monohydric alcohols containing more than 4 carbon atoms, such as octyl, nonyl, decyl, lauryl, myricyl, cetyl, or octadecyl, corresponding esters of alpha-methacrylic acid, alpha-phenylacrylic acid, and other alpha-substituted homologues of acids of the acrylic acid series. These esters are preferably those of the normal primary saturated aliphatic alcohols, but the analogous esters of the corresponding secondary or of the branched-chain alcohols can also be used. The esters of the above acids of the acrylic series with monohydric aromatic, hydro-aromatic, or ether alcohols may also be used, such as the benzyl, cyclohexyl, amylphenyl, n-butyloxyethyl esters. Also the vinyl esters of valeric, keptoic, lauric, palmitic, stearic, n-amyl-benzoic, naphthenic, hexahydrobenzoic, or of n-butyloxybutyric acid can be used. Copolymers of the various esters may likewise be used.

Specific commercial products exemplifying suitable polymethacrylates include those sold by Rohm and Haas under the generic trade name "Acryloid" and include Acryloid 150 and 860. These various Acryloids differ with respect to the specific monohydric aliphatic alcohols used as the esterifying group. For example, Acryloid 150 is understood to be polylauryl methacrylate, while Acryloid 860 is understood to be a copolymer of octyl methacrylate and decyl methacrylate.

The rubbers which are to be used in combination with the polymerized esters may be either natural or synthetic hydrocarbon rubbers including especially those of the butadiene-styrene type, of which the preferred variety comprises the family of Buna S (GR–S) rubbers; and the butyl rubbers, which are polymers of isolbutylene with small amounts of isoprene, butadiene, or dimethyl-butadiene, wherein the "small amount" of the copolymerizing olefin is usually between about 1.5 and 4.5%.

The rubber may be plasticized for ready dispersal in asphalt by the presence of aromatic rubber plasticizers (such as petroleum aromatic resinous fractions) and is most easily incorporated in asphalt by heating the rubber and asphalt to form a concentrated rubber-asphalt solution or dispersion and thereafter dispersing the concentrate in the main body of the asphalt together with the polymerized ester. Another means for incorporation of rubber in the asphalt comprises dispersion of a rubber latex in the asphalt and subsequent elimination of water therefrom by evaporation or boiling. The incorporation may take place when the asphalt is in the form of an emulsion but under such circumstances it is normally necessary to subject the latex and asphalt emulsion to a sufficient amount of milling so that the rubber will be colloidally dispersed within the main body of the asphalt.

It is normally unnecessary to employ amounts of each of these two additives, when they are used in combination, greater than about 0.1% by weight each, based on the asphalt. This is especially true when the amount of contaminating wax is between about 2 and about 7.5% by weight, based on the asphalt. As the proportion of wax increases or as the percentage, especially, of paraffin waxes increases, it may be necessary to raise the proportion of each of the two additives to as much as 0.5%. Beyond this figure, however, substantially no improvement in ductility occurs. Hence, the broadest range economically and technically feasible for each of the two additives is between about 0.01% and about 0.5% by weight, and preferably, is between about 0.025% and 0.1% each.

The data given hereinafter shows that when the polymerized ester is utilized as the sole additive in a waxy asphalt, it is necessary to employ at least about 0.15% by weight thereof to achieve a ductility of 110, which is above the normal minimum ductility required by state highway specifications. Also, when rubber is utilized as the sole additive in the same waxy asphalt, a maximum effect is obtained at about 0.12% of the rubber, but this maximum is lower than the minimum ductility requirement. However, when only about 0.03% of the polymerized ester and 0.04% of the rubber are combined in the same waxy asphalt, the resulting asphaltic composition has a ductility higher than the minimum ductility required by state highway specifications.

The following examples support the above remarks.

Example I

The asphalt employed for these tests was the residue from an Alberta crude having a penetration of 250 to 77° F. and containing about 6% by weight of wax. The unmodified waxy asphalt had a ductility at 77° F. of 50–55 centimeters. Addition of a polymerized C_{12}–C_{18} methacrylate ester in an amount of 0.15% gave a ductility of 110 centimeters. It will be noted, however, that this amount of the polymethacrylate would excessively increase the cost of the modified asphalt. The addition of 0.12% of a GR–S rubber increased the ductility from 60 to a maximum of 80 centimeters, and further quantities of rubber did not improve the ductility of the modified product. However, modification of the same waxy asphalt with 0.03% of the same polymethacrylate and 0.04% of the same rubber gave an asphaltic composition having a ductility of 105 centimeters at 77° F.

Example II

When a waxy asphalt containing about 7% by weight of wax is modified by 0.1% by weight of butyl rubber, the ductility of the modified product does not meet the minimum ductility highway specification, since it has a ductility at 77° F. of only 55 centimeters. The addition of a polymerized tetradecene methacrylate in an amount less than about 0.5% does not produce an asphalt composition meeting the minimum ductility specification. However, combination of 0.1% by weight each of the two additives, namely, the polymethacrylate and the butyl rubber produces an asphalt having a ductility of 110 centimeters at 77° F.

We claim as our invention:

1. An asphalt composition comprising a major amount of an asphalt, a contaminating minor amount of a hydrocarbon wax, said wax being present in an amount be-

tween about 1% and about 10% by weight of the combined asphalt and wax, and between about 0.01% and about 0.5% by weight each of a hydrocarbon rubber of the group consisting of natural rubber, butadiene-styrene rubbers, and isobutylene copolymerized with 1.15–4.5% by weight of a di-olefin and a polymerized ester of an acrylic acid and an aliphatic monohydric alcohol having between 8 and 24 carbon atoms per molecule, said polymerized ester having a molecular weight between 5,000 and 500,000.

2. An asphalt composition comprising a major amount of a waxy asphalt, said waxy asphalt comprising a major proportion of asphalt and 1–10% by weight, based on the waxy asphalt, of hydrocarbon wax, said waxy asphalt having a ductility less than about 75 centimeters at 77° F. having added thereto between about 0.02% and about 0.5% by weight each of a butadiene-styrene rubber and of a linear polymerized ester of an acrylic acid having an average molecular weight between about 5,000 and about 500,000.

3. An asphalt composition comprising a major amount of a waxy asphalt, said waxy asphalt comprising a major propotion of asphalt and 1–10% by weight, based on the waxy asphalt, of hydrocarbon wax, said waxy asphalt having a ductility less than about 75 centimeters at 77° F. having added thereto between about 0.02% and about 0.5% by weight each of a natural hydrocarbon rubber and of a linear polymerized ester of an acid of the

acrylic acid series having an average molecular weight between about 5,000 and about 500,000, said composition having a ductility at 77° F. greater than about 95 centimeters.

4. An asphalt composition comprising a major amount of an asphalt contaminated with between about 1% and about 10% by weight of a hydrocarbon wax and having dispersed therein between about 0.02% and about 0.2% by weight each of a rubbery copolymer of isobutylene with 1.5–4.5% by weight of a low molecular weight diolefin and of a polymerized linear ester of methacrylic acid having an average molecular weight of between about 5,000 and about 500,000.

5. A paving grade asphalt composition having a penetration at 77° F. of between about 50 and about 300 contaminated with between about 2% and about 7.5% by weight of a petroleum hydrocarbon wax and having dispersed therein between about 0.025% and about 0.1% by weight each of a synthetic hydrocarbon rubber and an oil-soluble polymerized aliphatic monohydric alcohol ester of methacrylic acid in which the average alcohol radical contains from 12 to 24 carbon atoms.

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