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**PROCESS FOR PREPARATION OF IMPROVED ASPHALT COMPOSITIONS**

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This invention relates to an improved process for the preparation of asphalt compositions. More particularly, it is concerned with a process for the improvement in viscosity-temperature relationships of asphalt compositions and improvement in their weathering characteristics.

Asphalts have two major classes of components which are known as asphaltenes and maltenes. The division between these two classes of components is normally made in terms of their solubility. The asphaltenes constitute that fraction of an asphalt which is precipitated by the presence of lower aliphatic hydrocarbons such as gasoline, hexane, isopentane or the like. Maltenes, on the other hand comprise the portion fully soluble in the same medium employed for asphaltene precipitation. Asphaltenes are normally regarded chemically as high molecular weight polycyclic materials containing substantial proportions of heterocyclic rings wherein nitrogen, sulfur and oxygen are present in the ring structure.

Depending upon the source and previous history of asphalts relative to their isolation and preparation, they may vary widely in their response to thermal influences with respect to changes in viscosity. This is especially important in asphalts utilized for paving or roofing grade purposes. Moreover, there is a wide variation in the quality of an asphalt relative to its ability to withstand the adverse effects present during weathering, such as may particularly occur when the material is employed as a shingle coating or for other types of roofing and the like.

The change of viscosity with temperature should be kept within certain desired limits depending on the use to which the asphalt is to be put. The slope of the viscosity-temperature line should be, for many purposes, kept as flat as possible so as to maintain a relatively narrow range of viscosity difference upon changes in temperature of the asphalt composition. For example, if the asphalt is to be applied under low temperature conditions such as winter preparation of roads and the like, it is highly disadvantageous for the asphalt to stiffen to unworkable consistency wherein it is difficult or impossible to employ the usual road building equipment or where it is as stiff as to make satisfactory coating of an aggregate employed in road compositions impossible or incomplete. On the other hand, roofing asphalts which are applied while hot, should not be too fluid at such application temperatures. Likewise, it is necessary for an asphalt to withstand the adverse effects of weathering to a substantial extent if the material is to be employed for roofing or coating purposes. For example, it should not exhibit any abnormal tendency to form cracks or pin holes in the coating if it is to be employed for these purposes.

Asphalts obtained from naphthenic base crudes often have poor weatherability characteristics even after air blowing. Air blowing is known to cause coupling of maltenes with themselves and/or with at least part of the

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asphaltenes through ester linkages, most of which are formed during the blowing process. Naphthenic base crudes, however, contain maltenes which have a preponderance of naphthenic structures which, when coupled with the highly naphthenic polycyclic asphaltenes, form blown asphaltenes which exhibit relatively poor viscosity-temperature relationships, low squalane tolerance and relatively poor weatherability. Large quantities of these asphalts are being produced especially as the more desirable paraffinic base crudes are being exhausted. The latter type of crude result in asphalts having more desirable properties.

It is an object of the invention to improve the weathering characteristics of asphaltenes derived from naphthenic crudes. It is a further object of the invention to improve the viscosity-temperature relationship of these asphalt compositions. It is a particular object of the invention to improve the compatibility of naphthenic asphaltenes with more aliphatic cutter stocks or maltenes. It is a further object to provide a process for the preparation of improved asphaltenes wherein air blowing is either supplemented or replaced by a coupling reaction which does not take place by ester formation. It is a particular object of the invention to effect carbon-to-carbon coupling of asphaltenes with maltenes without airblowing and without any appreciable dehydrogenation.

Now, in accordance with this invention, it has been found that the weathering properties, the viscosity-temperature relationships and compatibilities of naphthenic asphaltenes can be substantially improved by coupling the naphthenic asphaltenes with maltenes from an aliphatic base crude, said coupled asphaltenes exhibiting surprisingly outstanding weatherability characteristics in asphalt compositions. More particularly, naphthenic asphaltenes having a carbon to hydrogen atomic ratio between about 0.85 and about 0.95 are improved in accordance with the present invention by coupling through carbon to carbon bonds with maltenes having a carbon to hydrogen ratio between about 0.60 and about 0.70, whereby coupled asphaltenes are obtained having an average molecular weight in excess of about 3500 and a carbon to hydrogen atomic ratio in the order of 0.73 to 0.88.

One aspect of the invention comprises addition of naphthenic asphaltenes to a straight run asphalt of more paraffinic character. Another aspect of the invention comprises isolating the asphaltenes from a naphthenic asphalt, isolating the maltenes from a paraffinic asphalt, combining the two components and thereafter coupling in accordance with the invention to achieve the above-stated purposes.

The type of asphalt from which naphthenic asphaltenes are to be obtained is typified by certain California Valley crude asphalts, particularly from the Poso-Coalinga fields. While these may be straight-run, blown or cracked asphalts or mixtures thereof, it is preferred that straight-run asphalt be employed for the purpose of isolating naphthenic asphaltenes therefrom.

The more paraffinic asphalts which constitute the source of the desired maltenes later to be coupled with the naphthenic asphaltenes are typified by the West Texas straight-run asphalts.

The term "asphaltenes" is defined in Abraham, 5th edition, of "Asphalts and Allied Substances" on pages 1165-6 as being the non-mineral constituents remaining

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insoluble in petroleum naphtha, thus differentiating them from the maltenes (ptrolenes) which dissolve in the same medium and under the same conditions. As the test is made at room temperature (65–75° F.), this latter would constitute a further limitation. A still further limitation might comprise the portion of petroleum naphtha or specific lower alkane employed for the purpose of causing the separation. According to the standardized method, 50 volumes of petroleum naphtha are employed, the test temperature normally being ambient room temperature. While this standard procedure defines the term, it will be understood that the asphaltic fraction insoluble at room temperature in any aliphatic hydrocarbon having 5–12 carbon atoms per molecule may be regarded as "asphaltenes" for the purposes of defining the present invention. The preferred alkane if a single one is employed is isopentane.

The asphalts of naphthenic character may be introduced into the aliphatic hydrocarbon precipitant by several alternative means, dependent upon their physical characteristics. For example, hard asphalt having a penetration at 77° F. of less than about 10 are preferably introduced by first dissolving them in a minimum amount of aromatic hydrocarbon solvent. In order to minimize the effects of the solvent upon the precipitation of the asphaltenes, it is preferred that the proportion of solvent be restricted to about 0.5 and 2 volumes for each volume of the asphaltic residue. The aromatic solvent is preferably one predominating in aromatic hydrocarbons having less than 10 carbon atoms per molecule of which benzene and toluene are typical members. Preferably, the aromatic solvent contains at least about 70% by weight of such aromatic hydrocarbons and more desirably contains 85% or more of such hydrocarbons. The solution may take place at room temperature or, preferably, at reflux temperatures in order to hasten the process. Softer asphalts such as those having penetrations greater than about 10 at 77° F. may be dispersed sufficiently for the present purpose in a limited amount of the precipitating aliphatic hydrocarbon, although the aromatic solvent may be used in addition to or in place of the aliphatic medium for this dispersion purpose. The proportion again is preferably limited to about 0.5 and 2 volumes of the refluxing medium for each volume of the asphalt, regardless of whether or not the refluxing medium comprises entirely aliphatic hydrocarbons having 5–12 carbon atoms per molecule or additionally contains aromatic hydrocarbons as well.

The maltene solution and the precipitated asphaltenes are separated by any suitable means such as filtration, centrifuging, sedimentation, decantation or similar treatment. Following separation of the asphaltenes they may then be suspended in the more aliphatic maltenes with which they are to be coupled, preferably in the presence of a suitable solvent.

The naphthenic asphaltenes so obtained are characterized by their relatively high carbon-hydrogen atomic ratio which indicates their naphthenic (or even aromatic) character and relatively short alkyl branches. The asphaltenes to be improved in accordance with the process of this invention by coupling with more aliphatic maltenes have a carbon to hydrogen atomic ratio in the range between about 0.85 and 0.95 and usually between about 0.88 and 0.93 and an average molecular weight range of 1500–2000.

The asphalts constituting the source of relatively aliphatic maltenes differ especially in the carbon to hydrogen ratio of the latter as compared with the carbon to hydrogen atomic ratio of maltenes normally associated with the naphthenic asphaltenes described above. Maltenes to be coupled with the relatively naphthenic asphaltenes preferably have carbon to hydrogen atomic ratios between about 0.60 and 0.70, usually between about 0.62 and 0.68, indicating relatively long alkyl chains. Such maltenes are normally found in residues from crudes having high viscosity index lubricating oil fractions.

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The relatively aliphatic maltenes are generally obtained from West Texas crudes and may be straight-run, cracked or blown, but preferably are straight-run asphalts. The maltenes may be separated from the asphaltenes naturally associated therewith (such as by distillation or precipitation) or the whole aliphatic asphalt may be utilized in the process of this invention.

The relatively naphthenic asphaltenes are combined with the relatively aliphatic maltenes in weight ratios between about 1 part of asphaltenes to 4 of maltenes and about 3 parts of asphaltenes to 2 parts of the maltenes. Preferably, however, the proportions are in the order of about 1 to 4 and to about 1 to 1.

The maltenes may be isolated from physically associated asphaltenes by the simple asphaltene precipitation procedure previously described with respect to the naphthenic asphaltene isolation. In the present instance, however, if such is utilized, the solution of the aliphatic hydrocarbon will contain the maltenes which may be recovered if desired by distillation of the aliphatic hydrocarbon.

Coupling may be effected by several desired means of which treatment with peroxides is highly preferred. Treatment may be with hydrogen peroxide, alkyl hydroperoxides, aryl hydroperoxides, dialkyl peroxides or diaryl peroxides. However, dialkyl peroxides are preferred, particularly those in which each alkyl radical contains between about 3 and 8 carbon atoms per molecule. Specific peroxides to be utilized in this process include: tertiary butyl hydroperoxide, normal hexyl hydroperoxide, diisopropyl peroxide, di-normal butyl peroxide, di-tertiary butyl peroxide, dioctyl peroxide and their homologues.

The coupling process comprises heating the mixture of asphaltenes and maltenes at a preferred temperature between about 110 and 160° C. for a period between about 2 and about 8 hours, preferably while maintaining a peroxide content in the reaction mixture of between about 3 and 7.5% by weight based on the combined weight of the naphthenic asphaltenes and the relatively aliphatic maltenes. The concentration of peroxide is readily maintained by incremental addition thereof during the reaction period. Preferably the peroxide coupling reaction is carried out for a period of 4–6 hours at a temperature in the order of 140–160° C. while maintaining a peroxide concentration of about 4–6% by weight. Temperature control is conveniently achieved by selection of an inert solvent of a predetermined boiling point, such as aromatics (tert-butyl benzene) or halogenated aromatics (dichlorobenzene).

The treatment with peroxide is one way of causing coupling of the relatively naphthenic asphaltenes with the relatively paraffinic maltenes. This has been found to result in a coupled product having surprisingly improved weatherability characteristics. While the result may be likened to that which is obtained with air blowing, it has been found that coupling through a carbon-to-carbon linkage as with peroxides results in a product having far greater weatherability than most blown asphalts. Moreover, the coupling of the relatively aliphatic maltenes with the naphthenic asphaltenes has been found to unexpectedly improve the weathering characteristics of the latter material. This cannot be obtained by coupling the naphthenic maltenes which naturally occur together with the naphthenic asphaltenes.

The asphaltenes coupled with the aliphatic maltenes result in a coupled product having asphaltenic properties insofar as solubility and C<sub>15–12</sub> alkanes is concerned. Consequently, they may be separated, if desired, from the reaction product and blended with any cutter stock to form a particular product. However, in many instances it is possible to utilize the reaction product without such isolation.

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The asphaltene-maltene coupled product so produced is characterized by having a carbon to hydrogen ratio of about 0.72-0.89, preferably 0.73-0.85. The molecular weight of the product appears to have significance in that many of the coupled products so produced have much higher molecular weights than ordinary air blown asphalts having the same penetration and softening point characteristics. Molecular weights are of the asphaltene-maltene coupled product over 3500 and preferably are in the order of 5000-15,000.

The coupled product has been found to have surprisingly increased solubility in squalane, or, in other words, to have a higher squalane tolerance. Possibly because of this compatibility improvement, asphalt compositions containing the coupled product have a surprisingly reduced tendency to crack upon aging and if the asphaltene-maltene coupled product is separated, such as by precipitation with C<sub>6-15</sub> alkanes, from the total reaction product it may be utilized as such or may be further modified by incorporation of cutter stocks to reach particular physical properties desired.

The coupled product may be precipitated and then combined with a cutter stock to more closely control the physical properties of the end product. Cutter stocks are preferably hydrocarbon mixtures from the lubricating oil boiling range. They may be aromatic extracts or lubricating oil raffinates or even reclaimed motor oil and mixtures of these. Ordinarily, a cutter stock preferably comprises 0 to 15% by weight of lubricating oil aromatic extract and 10 to 60% by weight of lubricating oil raffinates, the reclaimed motor oil normally falling in the latter general classification. For most coating grade asphalt products compositions cutter stocks of this character are employed in amounts of between about 30% and about 65% by weight, the remainder being the coupled product. Of course, it is possible to combine the coupled product with other asphalts such as straight-run, blown or cracked if such is desired to obtain particular physical properties.

The following examples illustrate the advantages to be gained by the use of the present invention, emphasis being placed upon improvement in the weatherability of relatively naphthenic asphaltenes when coupled with relatively paraffinic maltenes.

The naphthenic asphaltenes were precipitated from this asphalt by addition of 40 parts isopentane thereto. These asphaltenes had a C/H mol ratio of 0.92 and a molecular weight of about 1600. Maltenes were left in the isopentane and were recovered by distillation of isopentane to yield a maltene product of naphthenic character having a C/H ratio of 0.68 and a molecular weight of 735. The maltenes were treated with ditertiary butyl peroxide at 150° C. for 8 hours, a peroxide content of about 4% being maintained in the reaction mixture, and the isopentane-insoluble product precipitated from the reaction product. This product had a carbon to hydrogen ratio of 0.78, a molecular weight of 5470, squalane tolerance of 45.

The asphaltenes were subjected to the same type of treatment with ditertiary butyl peroxide and the isopentane-insoluble product obtained by precipitation had a carbon to hydrogen ratio of 0.93, a molecular weight of 2680 and a squalane tolerance of 20. This product failed in less than one cycle in a standard weatherometer test.

A mixture of one part of the asphaltenes and 4 parts by weight of the maltenes was treated with ditertiary butyl peroxide and the isopentane-insoluble coupled product separated from the reaction mixture. This product had a carbon to hydrogen ratio of 0.83, an average molecular weight 3660, a squalane tolerance of 40 but failed in one cycle in a standard weatherometer test.

In comparison, the following data were obtained to demonstrate the advantage of coupling the naphthenic asphaltenes with relatively paraffinic maltenes: the latter was obtained by precipitating the asphaltene from a

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West Texas short residue from a high viscosity index lube crude. The maltenes recovered has a C/H mol ratio of 0.70 and molecular weight of 745. One part by weight of the relatively naphthenic asphaltenes and 4 parts by weight of the paraffinic maltenes were treated with ditertiary butyl peroxide at 150° C., maintaining a concentration of about 4-6% peroxide in the reaction mixture during a heating period of 4-6 hours. The isopentane-insoluble coupled product of this treatment was separated by precipitation and mixed with 47% by weight of industrial lubricating oil raffinate to obtain an asphalt composition having a penetration of 20 and a softening point of 220° F. This composition had a weatherability life of 20 in a standard weatherability test.

A substantial reduction in peroxide requirement can be gained by air-blowing prior to the peroxide treatment. Substantially improved results are obtained by isolating the isopentane insolubles from the peroxide treated product and subjecting the remaining maltenes to one or more additional peroxide treating periods.

I claim as my invention:

1. The process for the preparation of asphalt compositions having improved weatherability which comprises isolating isopentane-insoluble asphaltenes having a C/H atomic ratio of 0.88-0.93 from a naphthenic asphalt having relatively poor weatherability, isolating isopentane-soluble maltenes having a C/H atomic ratio of 0.62-0.68 from a paraffinic asphalt, blending the asphaltenes with the maltenes in a weight ratio between 1:4 and 3:2, treating the mixture so formed with a peroxide at a temperature sufficient to effect coupling of asphaltenes and maltenes to form a coupled asphaltene product, isolating therefrom the isopentane-insoluble fraction thereof having a C/H atomic ratio of 0.78-0.89 and blending it with a cutter stock whereby an asphalt composition of improved weatherability is formed.

2. The process for the preparation of an asphalt having improved weatherability which comprises isolating isopentane-insoluble asphaltenes from a naphthenic asphalt of poor weatherability, said asphaltenes having a C/H ratio between about 0.88 and about 0.93, isolating isopentane-soluble maltenes from a paraffinic asphalt, said maltenes having a C/H ratio between about 0.62 and about 0.68, combining the asphaltenes and maltenes in a weight ratio between about 1:4 and about 3:2, heating the mixture so formed with an alkyl peroxide at a temperature between about 110 and about 160° C. for 2-8 hours, whereby a coupled product is formed, isolating the isopentane-insoluble fraction of the coupled product and blending it with a cutter stock, whereby an asphalt composition of improved weatherability is formed.

3. A process according to claim 2, wherein the peroxide is a dialkyl peroxide and wherein the peroxide concentration is maintained in an amount between about 3 and about 7.5%, based on the weight of asphaltenes and maltenes.

4. The process for the preparation of an asphalt composition of improved weatherability which comprises precipitating isopentane-insoluble asphaltenes having a C/H atomic ratio of about 0.92 from a naphthenic asphalt by addition of a lower alkane thereto, isolating isopentane-soluble maltenes having a C/H atomic ratio of about 0.64 from a paraffinic asphalt by solvent precipitating and removing asphaltenes therefrom, combining about 1 part of the naphthenic asphaltenes with about 4 parts by weight of the paraffinic maltenes, heating the mixture so formed for 4-6 hours at 140-160° C. while maintaining a concentration of about 4-6 weight percent di(tert-butyl) peroxide therein, whereby an asphaltene-maltene coupled product is formed in the reaction mixture, precipitating said coupled product from the reaction mixture, said coupled product having a C/H atomic ratio of about 0.79, and combining 53 parts by weight of the coupled product with 47 parts by weight of a lubricating oil

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raffinate, whereby an asphalt composition of improved weatherability is formed.

5 The process for the preparation of an asphalt composition of improved weatherability which comprises isolating naphthenic asphaltenes from a naphthenic asphalt, said asphaltenes having a C/H atomic ratio of about 0.85-0.95, combining said asphaltenes with paraffinic maltenes having a C/H atomic ratio of about 0.60-0.70, the asphaltene to maltene weight ratio being between 1:4 and 3:2, heating the mixture so formed with a peroxide at 110-160° C. for 2-8 hours, whereby a reac-

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tion product comprising a carbon-to-carbon coupled asphaltene-maltene product is formed, said product having substantially improved weatherability characteristics.

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