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ASPHALT COMPOSITIONS

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This invention relates to asphalt compositions. It is more particularly concerned with blown asphalts compounded with certain "sweating" preventatives.

Asphalt compositions have been prepared which have been subjected to oxidation. The principal reason for the use of oxidized asphalts, e. g., blown asphalts, is to obtain materials showing a relatively low response to thermal influences. It has been found that blown asphalts are particularly subject to exhibition of "sweating," by which is meant the property of exuding the oily constituents of the asphalt. In a number of applications this phenomenon is disadvantageous, especially when asphaltic bitumens are used for laminating paper or paper with other substances for the manufacture of products which are used as packing material. This sweating is also detrimental to the application of asphaltic bitumens in roofing materials which are covered with a mineral powder. The paper or the covering agent of the roofing material becomes spotted with oil given off by the asphalt and even the product contained in the packing material may be fouled by the oil.

While asphalts may be characterized by their asphaltene, malthene, resin and oil contents, the tendency to sweat is not necessarily characterized by any known combination of these ingredients. However, it has been observed that lightly blown asphalts having a low penetration index usually are subject to correspondingly low tendencies to sweat. In such materials the addition of small amounts (from a trace to about 5%) of any water insoluble soap is usually sufficient to suppress the sweating phenomenon. However, it has been found that with increasing oxidation and correspondingly high penetration indices the colloidal nature of asphalt changes to a marked degree. Hence, for asphalts having penetration indices of about +4 the addition of even 5% water insoluble soaps no longer suppresses oil exudation. Moreover, many soaps are incompatible with asphalts having high penetration indices.

It is an object of the present invention to provide improved asphaltic compositions. It is another object of this invention to reduce the sweating tendencies of strongly blown asphalts. It is a specific object of this invention to suppress the sweating of asphalts having a penetration index of greater than about +4. Other objects will become apparent during the following discussion.

Now in accordance with the present invention the sweating of asphalts having a penetration index greater than about +4 may be substantially depressed by the addition thereto of at least 7.5% by weight of an alkaline earth metal soap of naphthenic acids, said acids having an average molecular weight above about 250. Still, in accordance with this invention even further improvements may be obtained in this respect without adverse effect upon other properties of the asphalt by the additional incorporation of a lubricating oil.

The term "penetration index" as used throughout the specification has been defined by J. P. Pfeiffer and P. M. Van Doorman in National Petroleum News, February 23, 1948, pages R–78 to 84. The penetration index is a mathematical expression of the relationship between the penetration and softening point of an asphalt. When softening points are referred to during the following discussion, the figures refer to those obtained by the use of ASTM method D–36–26, under the group "Standards on Petroleum Products and Lubricants," ASTM Committee D–2. Penetrations referred to are those obtained by ASTM method D–25–25.

The change in the colloidal structure of highly blown asphalts is such that most water insoluble soaps are no longer compatible with the asphalt. This is illustrated by Table I below which shows the effect of such incompatibility as reflected in the penetration and softening point of modified asphalts. As this table shows, aluminum naphthenate, when added in an amount of 15% by weight of asphalt, caused nearly a 40% drop in penetration and increased the softening point 29° C. Hence, it will be seen that even if sweating tendency had been reduced the other desirable properties of the blown asphalt were drastically altered so as to make the asphalt unsuitable for its originally designated purpose. In comparison with the undesirable effect of aluminum naphthenate on penetration and softening point, Table I also includes the data on an asphalt modified by the use of 15% calcium naphthenate, a composition falling within the scope of the present invention. As the data show, this particular type of alkaline earth metal naphthenate had substantially no adverse effect upon either the penetration or softening point of the asphalt.

Table I

	Penetration, 25° C.	Ring and Ball Softening Point, ° C.
Blown asphalt, no additive	42	86
Blown asphalt+15% Al naphthenate	24	115
Blown asphalt+15% Ca naphthenate	40	85

While small amounts of various soaps may be beneficial in asphalts of low sweating tendency they are ineffective for depressing this property in asphalts such as those considered here, which have high penetration indices and also high sweating tendency. Table II illustrates the ineffectiveness of small amounts of various soaps as compared with the amount of 15% utilized in accordance with the present invention. As this table shows, 5% of a calcium naphthenate only reduced the sweating tendency by one point, while aluminum naphthenate in the same proportion had a similar effect. However, addition of 15% of calcium naphthenate (according to the present invention) doubled the effective reduction in the sweating tendency.

Table II

	Sweating tendency
Blown asphalt, no additive	3
Blown asphalt+5% Al naphthenate	2
Blown asphalt+5% Ca naphthenate	2
Blown asphalt+15% Ca naphthenate	1

The "sweating tendency" referred to throughout this specification is determined as follows:

A copper ring with a height and inside diameter of 25 mm. is placed on a metal plate covered with a mixture of glycerol and talc and filled more than brimful with the bitumen to be tested, which has been liquefied by heating. The ring and its contents are left to cool for 30 minutes and the excess of bitumen is then cut even with the rim of the ring by means of a hot knife. After 15 minutes the ring plus contents is turned upside down on a filter paper (Whatman No. 40) having a diameter of 9 cm. In this position, in which the bitumen is in contact with the filter paper, the ring is kept on a glass plate in a drying stove for 24 hours at a temperature of 60° C.

After the ring has been cooled to room temperature the discoloration of the filter paper is tested visually. The sweating tendency (expressed as a figure as indi-

cated in the table below) of the asphaltic bitumen is stronger, the greater the discoloration of the filter paper.

Discoloration of the filter paper	Tendency to sweating
none	0
slight	1
moderate	2
strong	3
very strong	4

In order to standardize the results of the various experiments, the discoloration occurring is compared to the discoloration brought about by two standard samples, to which a certain value for the sweating tendency has been assigned.

By the data given in Table II it will be seen that asphalts prone to excessive sweating are not sufficiently improved by the addition of only 5% of soaps even if the soap is an alkaline earth metal naphthenate. In order to reduce the sweating tendency to a satisfactory degree, larger amounts of alkaline earth metal naphthenates are necessary.

The naphthenates suitable for use in the present compositions are those derived by the saponification of naphthenic acids with alkaline earth metals including especially calcium, barium and magnesium. The most effective member of this group is the calcium soap of naphthenic acids. The naphthenic acids which may be used in the preparation of the subject soaps are those having average molecular weight of at least 250 and preferably between about 250 and about 600. Naphthenic acids having these limitations are usually obtained by extraction from mineral lubricating oils and preferably from heavy lubricating oils. Ordinarily, these acids are obtained by distilling a crude oil into desired fractions and subsequently redistilling the lubricating oil fraction obtained thereby over a base such as lime. In this case, the residue remaining from the redistillation operation comprises 20–70% of calcium naphthenates and the remainder is a heavy lubricating oil. Such a residue is especially desirable for use in the present compositions.

Naphthenic acids of the type under consideration are illustrated by those described by Harkness and Brunn in Industrial and Engineering Chemistry, vol. 32, pages 449–502, April 1940. As these authors indicate, naphthenic acids from lubricating oil fractions appear to be polycyclic acids having from 2 to 5 rings as indicated by the carbon to hydrogen ratio. Naphthenic acids appear to be analogs or homologs of substituted cyclopentene alkane carboxylic acids. Within the present molecular weight range of 250–600 they have empirical formulae varying between about $C_nH_{2n-4}O_2$ and $C_nH_{2n-10}O_2$.

In arriving at the compositions of the present invention the suitability of other types of soaps was also investigated. Among these were the soaps of higher fatty acids used either in unmodified form or in the presence of added lubricating oils. Table III given hereinafter illustrates the ineffectiveness of aluminum stearate in an amount of 15% when used together with an equal amount of oil and also shows the undesirable effect of aluminum stearate when used in these amounts but in the absence of added oil.

Table III indicates that aluminum stearate is largely incompatible with highly blown asphalts since it causes a marked reduction in penetration and resulted in 40° C. increase in the ring and ball softening point. The undesirable shift in these properties was of such magnitude that the partial reduction in sweating tendency did not result in the preparation of a desirable asphalt composition.

This table also shows that these undesirable changes were not overcome by the addition of lubricating oil. This addition, in fact, caused the sweating tendency of the composition to become excessive and at the same time did not improve the softening point of the mixture. Hence, it can be seen that aluminum stearate either in the presence or absence of added lubricating oil is ineffective for causing a satisfactory reduction in sweating tendency and at the same time causes undesirable changes in penetration and softening point.

For the purpose of comparison, Table III also includes data obtained on a blown asphalt composition containing 15% calcium naphthenate and 15% mineral lubricating oil. It will be noted that the sweating tendency was drastically reduced while at the same time there was substantially little effect upon either the penetration or softening point of the asphalt.

Table III

	Penetration, ° C.	Ring and Ball, ° C.	Penetration Index	Sweating
Blown asphalt, no additive	42	86	+4.7	3.
Blown asphalt, 15% Al stearate	31	126	+7.8	1½.
Blown asphalt, 15% Al stearate + 15% Lubricating oil	45	123	+8.4	Greater than 4.
Blown asphalt, 15% Ca naphthenate + 15% lubricating oil	45	93	+5.6	½.

The lubricating oils which may be incorporated in the asphalt together with the alkaline earth metal naphthenates are preferably obtained from mineral lubricating oils and still more preferably from petroleum lubricating oils.

The lubricating oil which is added preferably has a viscosity of between about 200 and about 2000 SSU at 100° F. Suitable oils are those obtained from the heavier (500–2000 SSU at 100° F.) varieties of petroleum lubricants. The lubricating oil may be used in an amount varying from about 20 to about 200% based on the weight of the added alkaline earth metal naphthenate. The ratio is preferably confined to between 25 and 100% based on the weight of the naphthenate. The effective amount of added alkaline earth metal naphthenate is between 7.5 and about 20% and preferably is between about 10 and 15% based on the weight of the asphalt.

While aluminum soaps as shown by Table III were unsuitable for use in the present compositions it was thought possible that alkaline earth metal soaps of higher fatty acids might be effective in the same order as the alkaline earth metal soaps of the subject naphthenic acids. However, as Table IV shows, such was not the case. This table indicates that the addition of calcium stearate together with lubricating oil caused substantially no decrease in sweating tendency but resulted in an increase of 39° C. softening point and also caused about a 25% reduction in penetration. These data prove that calcium stearate was unsuitable for use in highly blown asphalts due to its negligible effect on sweating tendency and because of its adverse effect upon penetration or softening point. Hence, it can be seen that the only class of soaps which were found to be suitable for the suppression of sweating without adversely affecting the other properties of highly blown asphalts was the class of alkaline earth metal soaps of certain naphthenic acids.

Table IV

	Penetration, 25° C.	Ring and Ball, ° C.	Penetration Index	Sweating
Blown asphalt, no additive	42	86	+4.7	3
Blown asphalt+15% Ca stearate+13% lubricating oil	32	125	+7.6	2½
Blown asphalt+15% Ca naphthenate+15% lubricating oil	45	93	+5.6	½

In order to determine the effect of other members of this same class, samples were tested which contained barium naphthenates. Table V presents the data resulting from these tests. It will be seen that in comparison with calcium naphthenate, barium naphthenate is substantially equally effective in reducing sweating tendency without causing any substantial change in either penetration or softening point. These data, therefore, indicate the suitability of alkaline earth metal soaps of naphthenic acids to be suitable as a class for the purpose of the present invention.

Table V

	Penetration, 25° C.	Ring and Ball, ° C.	Penetration Index	Sweating
Blown asphalt, no additive	42	86	+4.7	3
Blown asphalt+15% Ca naphthenate	40	85	+4.5	1
Blown asphalt+15% Ca naphthenate+15% oil	45	93	+5.6	½
Blown asphalt+15% Ba naphthenate+4% oil	44	87	+4.9	1

The calcium naphthenate and lubricating oil distillate may be added prior to, during or after the blowing of the asphaltic bitumen. They may be incorporated in the asphaltic bitumen by stirring the components together at a temperature at which the asphaltic bitumen is liquid. If the substances are added subsequent to the blowing of the asphaltic bitumen, higher mixing temperatures will, as a rule, be required than when the additives are incorporated in the asphaltic bitumen prior to blowing. It may generally be stated that the asphaltic bitumen may be mixed with the additives at temperatures varying from room temperature to 300° C., and preferably between 125 and 250° C.

The subject class of alkaline earth metal naphthenates are added in the stated amounts to asphalts having penetration indices of at least +4 and preferably at least +4.5 since it has been found that such asphalts exhibit unusually pronounced tendencies to sweat. Maximum improvement is obtained with asphalts having a penetration index above +4 and a king and ball softening point below 93° C., and preferably less than 90° C. Asphalts of this character are generally residual asphalts obtained as residues from petroleum fractionation and especially from petroleum crude oil distillation or extraction. They may be oxidized by the usual procedure of air blowing which may take place either in the presence or absence of certain catalysts. Suitable catalysts which may be used for the production of asphalts having high penetration indices are ferric chloride, phosphoric acid and monofluoro phosphoric acid. The conditions for air blowing asphalt are well known but generally include oxidation of the asphalt by means of blowing with air at temperatures between about 425 and 550° F.

All of the experiments from which the data contained in the tables were obtained were carried out with the same blown Venezuelan asphalt having a ring and ball softening point of 86° C. and a penetration of 42 at 25° C. The lubricating oil added as indicated in examples given in the tables was a lubricating oil distillate of a Venezuelan crude oil and had viscosity of 41 SSU at 100° C.

The addition of lubricating oil to the present compositions when using alkaline earth metal naphthenates extends the composition without causing any adverse effect upon the desirable properties thereof. Table VI illustrates the change in properties caused by the addition of 15% calcium naphthenate as compared with similar compositions also containing 3 and 15% lubricating oil, respectively. It will be noted that the addition of oil within these limits caused no adverse effect upon either penetration or softening point and even appears to have unexpectedly improved the sweating tendency of the composition.

Table VI

	Penetration, 25° C.	Ring and Ball, ° C.	Penetration Index	Sweating
Oxidized asphalt, no additives	42	86	+4.7	3
Oxidized asphalt+15% Ca naphthenate	40	85	+4.5	1
Oxidized asphalt+3% lubricating oil+15% Ca naphthenate	47	83	+4.6	1
Oxidized asphalt+15% lubricating oil+15% Ca naphthenate	45	93	+5.6	½

I claim as my invention:

1. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4, and a ring and ball softening point below 93° C., from about 10 to about 20% by weight based on the asphalt of a barium soap of naphthenic acids, said acids having an average molecular weight between about 250 and about 600 and from about 25 to about 100% based on the weight of said soap of a mineral lubricating oil.

2. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point between about 83° C. and about 90° C., from about 10 to about 15% by weight of said asphalt of a calcium soap of naphthenic acids, said naphthenic acids having a molecular weight between 250 and about 600 and from about 25% to about 100% based on the weight of the soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F., the presence of said naphthenate having substantially no effect upon the penetration and softening point of the composition.

3. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point between about 83° C. and about 90° C., from about 10 to about 15% by weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having a molecular weight between about 250 and about 600, and from about 20% to about 200% based on the weight of said soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F. the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

4. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point between about 83° C. and about 90° C., from about 10 to about 15% by weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having a molecular weight between about 250 and about 600, and from about 20% to about 200% based on the weight of said soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F., the presence of said naphthenate having substantially no effect upon the penetration and softening point of the composition.

5. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4.5 and a ring and ball softening point lower than 90° C., from about 10 to about 15% by weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having a molecular weight between about 250 and about 600, and from about 20% to about 200% based on the weight of said soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F., the presence of said naphthenate having substantially no effect upon the penetration and softening point of the composition.

6. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4, from about 10% to about 15% by weight based on the asphalt of an alkaline earth metal soap of naphthenic acids, said acids having an average molecular weight between about 250 and about 600 and from about 20% to about 200% based on the weight of the soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F., the presence of said naphthenate having substantially no effect upon the penetration and softening point of the composition.

7. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4, from about 10% to about 20% based on the weight of the asphalt of an alkaline earth metal of naphthenic acids, said acids having a molecular weight between about 250 and about 600 and from about 20% to about 200% based on the weight of the soap of a mineral lubricating oil having a viscosity of between about 200 and about 2000 SSU at 100° F., the presence

of said naphthenate having substantially no effect upon the penetration and softening point of the composition.

8. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point lower than 90 C. and about 10% to about 15% based on the weight of the asphalt of a calcium soap of naphthenic acids, said acids having an average molecular weight between about 250 and about 600 the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

9. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point not more than 93° C. and from about 10% to about 15% based on the weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said acids having an average molecular weight between about 250 and about 600 the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

10. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and from about 10% to about 15% based on the weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having an average molecular weight between about 250 and about 600 the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

11. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and a ring and ball softening point below 90° C. and from about 10% to about 15% based on the weight of said asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having an average molecular weight between about 250 and about 600 the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

12. An asphalt composition having reduced sweating tendency consisting essentially of a major amount of an oxidized asphalt having a penetration index greater than about +4 and from about 10% to about 20% based on the weight of the asphalt of an alkaline earth metal soap of naphthenic acids, said naphthenic acids having an average molecular weight between about 250 and about 600 the presence of said naphthenate having substantially no effect upon the penetration and softening point of said composition.

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