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2,891,873

ASPHALT ADDITIVES

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6 Claims. (Cl. 106—273)

This invention relates to a bituminous composition comprising asphalt and an asphalt additive.

The application is a continuation-in-part of our copending application Serial No. 568,449, filed February 29, 1956, now abandoned.

The invention is particularly useful in improving the property of adhesion of asphaltic materials to oxygen-bearing surfaces, such as those of common mineral aggregates, masonry surfaces, and the like, this property being commonly referred to as "antistripping."

Numerous additives for use as antistripping agents in asphaltic paving composition, for improving the adherence of the asphalt to either wet or dry aggregates, have been proposed. One such additive in extensive use is an amidoamine soap. A representative amidoamine soap is that made from oleic acid and ethylene diamine. It may be written as

$$C_{17}H_{33}.CO.NH.C_2H_4.NH_3.OOC.C_{17}H_{33}.$$

The amine soap group, at the right end of this formula, may also be written

$$.C_2H_4.NH_2.HOOC.C_{17}H_{33}.$$

The present invention provides an additive composition that is adapted to retain its effectiveness on exposure in asphalt mixes, at high temperatures and in free communication with the atmosphere, for prolonged periods of time such as the temperature and time encountered in making, shipping, and applying asphalt cement in hot condition as a paving material.

Briefly stated, the invention comprises amidoamine soaps, constituting the base additive material for asphalt, in combination with a large excess of an amine.

With the combination including amidoamine soap and excess amine, we have been able to preserve the antistripping effect on heating an amidoamine soap in asphalt when vented to the air, the term amidoamine soap including the imidazoline form in the appreciable proportion that may result from heating the soap proper. Thus we have maintained the efficiency of the additive in asphalt in open containers at temperatures as high as 232° C. for periods up to 14 days, without loss of the antistripping property of the combination of the asphalt and additive when tested after application to wet paving aggregate.

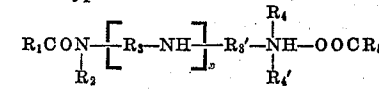
Once these results have been observed, an explanation may be advanced to explain the effectiveness of the excess amine. We consider that the free amine prevents or retards the heat decomposition of the amidoamine soap in contact with the asphalt and in communication with the atmosphere, the decomposition being considered otherwise to occur with escape of steam, as illustrated in the case of representative amidoamine soap of formula given above to an ineffective diamide, according to the equation

$$C_{17}H_{33}.CO.NH.C_2H_4.NH_3.OOC.C_{17}H_{33} \xrightarrow{\text{heat}} C_{17}H_{33}.CO.NH.C_2H_4.NH.OC.C_{17}H_{33} + H_2O$$

As to materials used, the asphalt is any one of the usual grades employed in making asphalt cements or

other asphaltic compositions, as for instance, the paving or roofing grades of either petroleum asphalt or mineral asphalt, in blown or unblown condition.

The base additive, that is the foundation additive, is an amidoamine soap. Examples of amidoamine soaps that may be improved by our excess of amine are those described in U.S. Patents 2,426,220, issued to Johnson on August 26, 1947 and 2,663,648, issued to Jelling on December 22, 1953. The soap, in other words, may be any one of the type formula



in which R_1 and R_5 each represents the same or a different C_{11}–C_{19} alkyl or the abietyl radical, R_2 hydrogen or any C_1–C_4 alkyl, R_3 and R_3' are alkylene radicals having from 2 to 18 carbon atoms and x is an integer from 0 to 4, and R_4 and R_4' hydrogen or any C_1–C_4 alkyl.

Examples of the meanings of various groups here and elsewhere herein are as follows:

R' and R_5: $C_{11}H_{23}$, $C_{15}H_{31}$, $C_{17}H_{33}$, $C_{17}H_{35}$, or the abietyl radical $C_{19}H_{29}$ as represented in the principal cyclic acid of tall oil.

R_2: H, CH_3, C_2H_5, C_3H_7, or the like.

R_3: a bivalent group containing a C_2–C_{18} alkylene such as C_2H_4, C_3H_6, C_4H_8, $C_{18}H_{34}$, or $C_{18}H_{36}$; two or more of such alkylenes joined through one or more intermediate ·NH· groups, to give a structure such as $C_2H_4 \cdot NH \cdot C_2H_4$, $C_3H_6 \cdot NH \cdot C_3H_6$, $C_4H_8 \cdot NH \cdot C_4H_8$, $C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH \cdot C_2H_4$, etc.

R_4 and R_4': hydrogen or any C_1–C_4 alkyl as illustrated in connection with R_2 above.

When both R_4's are hydrogen, the amine represented in the amine soap is a primary amine. It is a secondary amine when one R_4 is hydrogen and the other R_4 an alkyl. It is a tertiary amine when both R_4's are alkyls. The variation of R_4 from all H to all alkyl is not an advantage in the functioning of the amidoamine soap in our composition.

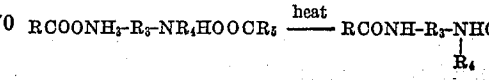
Examples of amidoamine soaps that illustrate the type formula above and that may be used are the oleylamidoamine oleate of formula first written above, the corresponding abietic acid compound of ethylene diamine $C_{19}H_{29} \cdot CO \cdot NH \cdot C_2H_4 \cdot NH_2 \cdot HOOC \cdot C_{19}H_{29}$, the stearic acid compound of diethylene triamine

$C_{17}H_{35} \cdot CO \cdot NH \cdot C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH_2 \cdot HOOC \cdot C_{17}H_{35}$

and compounds in which the NH_2 in these formulas is the residue of a tertiary amine, as for instance, $N(C_2H_5)_2$, $N(C_3H_7)_2$, and $N(C_4H_9)_2$. To provide the residue $N(C_2H_5)_2$, for example, in the amidoamine soap, the amine to be reacted with the selected higher fatty acid $R \cdot COOH$ is $H_2N \cdot R_3N(C_2H_5)_2$.

In all of these additives, the acid represented is organic and carboxylic, suitably a higher fatty acid or abietic acid. Examples of the fatty acids are those containing 12–20 carbon atoms to the molecule, such as lauric acid, oleic acid, red oil, tall oil, acids of soya or cottonseed oil, or mixtures thereof.

The amidoamine soaps constituting the foundation additive are made as described in the said patents to Johnson and Jelling. The process consists essentially of mixing the selected di- or other polyamine with approximately the stoichiometrical proportion of the selected organic acid or mixtures of acids, maintaining contacts of the mixed materials, to form a poly-soap, and then heating the soap until one of the soap groups is decomposed to amide, as by the equation



The polyamine used in admixture with the amidoamine soap is one of boiling point, at 760 mm., at least as high as about 115° C. We use to advantage aliphatic di- and other polyamines containing 2.18 and ordinarily 2–8 carbon atoms to the molecule. Examples of amines that meet the requirements and illustrate the class to be used are the alkylene polyamines including ethylene and propylene diamines, diethylene triamine, triethylene tetramine, tetraethylene pentamine; bis-3-aminopropylmethylamine sometimes known as 3,3′ (methylamino) bispropylamine of the formula

$$CH_3 \cdot N(CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2)_2$$

The selection of the amine depends in part upon the temperature to which the mix to be made is exposed during use, the amine being chosen in relation to said temperature so as to avoid loss of the amine by volatilization. The amine may be introduced originally as an amidoamine, an example being oleylamidoamine. In that case, it is unnecessary to heat the soap (that results with the fatty acid) to form an amide, since the amide group is already present. To obtain an amido-tertiary-amine soap, these amines are replaced by amines differing from the examples only in the replacement of one NH_2 group by $N(CH_3)_2$, $N(C_2H_5)_2$, $N(C_3H_7)_2$, or $N(C_4H_9)_2$ in the selected amine.

As to proportions, it is essential that the amine be present in the final product in large excess of the amount required theoretically to form the amidoamine soap of the foundation additive.

Proportions that meet these requirements are such as to provide total amine content equivalent of 4.5 (2.25 moles of a diamine and 1.5 of a triamine) for 1 mole of the organic acid. For maximum benefit, we increase the amine ratio up to 15 equivalents of the amine. Additional amine may be used but is unnecessary and uneconomical. Stated differently, we admix, with the preformed amidoamine soap, at least 2.5 and ordinarily not over 10 equivalent weights of the added amine for each mole of the acid represented in the preformed amidoamine or its soap. With the amidoamine soap of the kind described in the said patent to Johnson we use to advantage 20–100 parts of ethylene diamine or diethylene triamine to 100 of the heated soap.

The invention will be further illustrated by description in connection with the following specific examples of the practice of it. In these examples and elsewhere herein parts are expressed by weight unless specifically stated to the contrary.

EXAMPLE 1

15 parts of diethylene triamine, containing 85% of diethylene triamine and 15% of higher polyamines and having an equivalent weight as an amine of about 111÷3, or 37 (ca. 0.13 mole or 0.39 equivalent) are mixed with 40 parts of crude tall oil of equivalent weight about 330 (ca. 0.12 mole). After the initial reaction period, the mixture is heated until sufficient water is lost (from the amine soap first formed) to correspond to approximately 0.5 mole for each mole of tall oil fatty acid used and thus leave an amidoamine soap.

$$R \cdot CO \cdot NH \cdot C_2H_4 \cdot NH \cdot C_2H_4 \cdot NH_3 \cdot OOC \cdot R'$$

in which the organic acids represented in the R·CO and OOC·R′ groups are those of the tall oil.

The reaction product so produced is then mixed with additional diethylene triamine in the amount of 40 parts (ca. 0.36 mole) so as to provide a large excess of the diethylene triamine in the finished composition. The total amine used is approximately 0.13+0.36 or 0.49 mole (1.47 equivalent) for the 0.12 mole of organic acid in the tall oil.

EXAMPLE 2

Red oil in amount to provide 1 mole of higher fatty acids is mixed with 1 mole of 3,3′ (methylimino)-bis-

propylamine. The whole is then heated until the amine and acid have reacted and approximately 0.5 mole of of water has been removed for each mole of the amine soap first formed.

The product is an amido-tertiary-amine soap as described in the patent to Jelling.

More amine is then added in amount to provide 50 parts by weight of the amine for 100 parts of the reaction product after loss of the said water.

EXAMPLE 3

We give the following example of a preparation using an amine containing a primary and a tertiary amine group as described in the said patent to Jelling.

1 mole of dimethylaminoethylamine and 1 mole of oleic acid are mixed and heated slowly at 150° C. and with continuous agitation for 4 hours. To this additive so made, there was added 2 moles of diethylenetriamine.

Such amidoamine soap, heated alone, retains its antistripping effect when subsequently incorporated into asphalt. When, however, the amidoamine soap is mixed into asphalt and the mixture then heated in communication with air, antistripping properties are largely destroyed. We find now that we can decrease this instability or loss in antistripping effect by incorporating, into the amidoamine soap first formed, a large excess of the originally used amine containing a primary and also a tertiary amine group or of any one of the other amines listed earlier herein.

In a modification of this example, we replace the 2 moles of diethylenetriamine added to the initial reaction product by 1.5 moles of the 3,3′ (methylimino)-bispropylamine or an equivalent weight of any of the other amines listed herein.

EXAMPLE 4

The procedure of Example 1, 2 or 3 is followed with the substitution of the amine there used by any one or ones of those listed earlier herein, on an equimolecular weight basis.

EXAMPLE 5

The additive compositions made as described in Examples 1–4 are mixed with petroleum asphalt in the proportion of 0.1–3 parts of the additive composition for 100 of the asphalt. The whole may then be heated in either a closed or a vented vessel, to a temperature of 135°–180° C. for a period of 1–14 days.

Use as antistripping agents

Mixtures of the additive composition with the asphalt, when stirred with either limestone or siliceous aggregates such as used in asphalt paving compositions, give good adhesion whether the aggregate as mixed is in dry or wet condition. In laboratory tests the mixed asphalt and additive compositions meet the requirements of standard specifications for heat stable antistripping additives for asphalt.

Products containing the excess of free amine and made as described in Examples 1–4 retain their effectiveness as antistripping agents in asphalt cement during the prolonged exposure to high temperatures normally encountered in the shipping, storage, and use of asphalt cements, even in vented containers. These periods of time may exceed 2 weeks and the temperatures may range up to about 450° F. (232° C.) The additives made from the primary amines are more effective after completion of this exposure than those made from tertiary amines.

Materials for heat stability

TESTS

We have applied the standard heat stability test to unheated cut back asphalt and additive composition and observed the approximate percentage of the total surface of the stones (aggregate) that remains coated with the asphalt after the stripping test is completed. This test is

the control test. We have repeated the test with the same asphalt and additive composition and the same aggregate, the asphalt and additive composition having been heated to a temperature of approximately 176° C. for 24 hours in a vented container before application to the aggregate.

For comparison we have tested also an asphalt additive that is no part of this invention, namely, an amidoamine which contains substantially no soap.

The specific additive compositions tested were prepared as follows:

(*a*) Amidoamine was made by mixing 69 parts of tall oil (0.12 equivalent) with 58.5 parts of technical diethylenetriamine (1.58 equivalents). The mixture was heated for 5 days at 150°–200° C. to give a substantially constant acid value and to decompose the mono-amine soap, first formed, to an amidoamine including here a very large excess of free diethylenetriamine.

(*b*) The amidoamine soap and additive composition of the present invention was made by first reacting 15 parts of diethylenetriamine with 65 parts of tall oil for 1 hour at 130°–133° C. A mixture of 15 parts of the diethylenetriamine and 55 of roleic acid (crude acid from castor oil, eq. wt. 282) were separately heated for the same time and at approximately the same temperature. Then the two di-soaps so formed were blended together and heated to 176° C. for 1 hour, to cause conversion of the di-soap to amidoamine soap by loss of approximately 1 molecule of water for each molecule of the di-soap. To the amidoamine soap so made there was then admixed additional diethylenetriamine in the proportion of 56 parts for 100 of the amidoamine soap.

(*c*) The amido-tertiary-amine soap used in this test is that sold commercially as "Pave 100" and understood to be made in accordance with the said patent to Jelling and to be the amido-tertiary-amine soap of tall oil acids with N-dimethylaminopropyl oleamide.

Tests of heat stability

The test for antistripping effect of the additive when incorporated into asphalt includes applying the asphalt and admixed additive composition to small stones or aggregate such as used in road paving while the aggregate is submerged in distilled water at room temperature. The whole is then agitated and the proportion of the surface of the aggregate that remains coated with the asphalt is noted after a standard period of time all as stated in detail later herein.

The several products (*a*), (*b*), and (*c*) were mixed with cutback asphalt in various proportions of the additive (including the excess amine) and the stripping properties were determined (1) without any heating of the asphalt and additive mixture and (2) after heating the mixture, to determine the heat stability as shown by the antistripping properties retained after the heating. The results follow.

Additive used, Free Amine +	Additive, Percent of Cutback Asphalt	Percent of Immersed Stone Surfaces Remaining Coated	
		Control Not Heated	Heated 24 hrs. at 176° C. (Vented to Air)
Amidoamine (*a*)	0.25	70+	Practically 0.
Do	0.35	80+	Do.
Do	0.45	90	Do.
Amidoamine Soap (*b*)	0.25	65	65.
Do	0.5	85	85.
Do	0.75	100	100.
Amido-tert. amine soap (c)	0.5	85	20.
Do	0.75	100	40.

In view of the great differences noted, it is not important that the observation of the percentage of the surface of the aggregate that remained coated, after the water immersion and agitation test, is only visual and that small differences are not significant. What is important is that good coating is obtained with an adequate amount of our additive (*b*) composition including the excess poly-amine and that there is no visible stripping from the coated aggregate during the antistripping test. It is important also that the test temperature of 176° C. is approximately the highest temperature at which the asphalt and additive compositions are in contact during blending, storing, shipping or use of such mixes in commerce.

Details of heat stability test

The test for heat stability was made as specified below.

Reference aggregate: The stone used as a reference aggregate shall be selected as being representative and suitable for the purpose. It shall be graded to pass a ⅜" sieve and be retained on a No. 4 sieve. Before use it shall be washed with distilled water until free from dust, and air dried.

Preparation of asphalt: Asphalt from a single source shall be designated as the reference asphalt. The additive shall be blended into 85–100 penetration asphalt at a temperature of 200 to 250° F., and the resultant blend poured into a 3-ounce seamless tin box, filling it nearly to the brim. A vented cover shall be placed on the tin box, and no attempt shall be made to seal or otherwise preclude air from entering the box. The box and its contents shall be placed in an oven maintained at 350° F. for 24 hours, then removed and cooled to approximately 200° F. A cutback shall be prepared by diluting 75 parts of the treated asphalt with 25 parts of Varnish and Paint Maker's Naphtha.

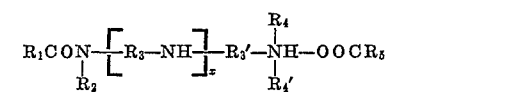
Stripping test: 200 grams of the washed and dried reference aggregate shall be weighed into a pint Mason jar and covered with 200 cc. of distilled water at room temperature. Twelve grams of the treated bituminous material, prepared as above, shall be added to the contents of the Mason jar. The jar shall be tightly sealed and rotated end over end by mechanical means at 60 r.p.m. for 15 minutes. After the rotation period the lid of the Mason jar shall be removed and the contents dumped into a clean 600 ml. beaker and allowed to stand undisturbed at room temperature for 1 hour.

Evaluation of test result: At the conclusion of the stripping test the sample shall be examined under a strong light and the result, as determined by visual observation, shall be reported in terms of percent of the total surface of the aggregate that remains coated.

It is to be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What we claim is:

1. A bituminous composition comprising asphalt and an asphalt additive in an amount of from 0.1 to 3% by weight of the asphalt, the additive consisting of an amidoamine soap of the formula



in which R_1 and R_5 are selected from the group consisting of alkyl radicals having from 11 to 19 carbon atoms and abietyl, R_2, R_4 and R_4' are selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms, R_3 and R_3' are alkylene radicals having from 2 to 18 carbon atoms and x is an integer from 0 to 4; and an amine having a primary amino group and from 2 to 18 carbon atoms, said amine being present in the proportion of from 2.5 to 15 equivalent weights for each equivalent weight of the acid represented in the R_1CO and $OOCR_5$ groups in the amidoamine soap.

2. The bituminous composition of claim 1 in which the $[R_3NH]_xR_3'$ radical is derived from diethylene triamine.

3. The bituminous composition of claim 1 in which the amine having a primary amino group is diethylene triamine.

4. The bituminous composition of claim 1 in which the amine having a primary amino group is 3,3'-(methylimino)-bispropylamine.

5. The bituminous composition of claim 1 in which x is 0.

6. The bituminous composition of claim 1 in which the asphalt is a blown asphalt.

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CERTIFICATE OF CORRECTION

Patent No. 2,891,873 June 23, 1959

Charles W. Falkenberg et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 22, for "R′" read -- R_1 --; column 3, line 10, for "(methylamino)" read -- (methylimino) --.

Signed and sealed this 10th day of November 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents