June 25, 1963 J. C. MUNDAY ETAL 3,095,314

ASPHALT CONTAINING MIXED METAL SALTS

Filed Dec. 20, 1961

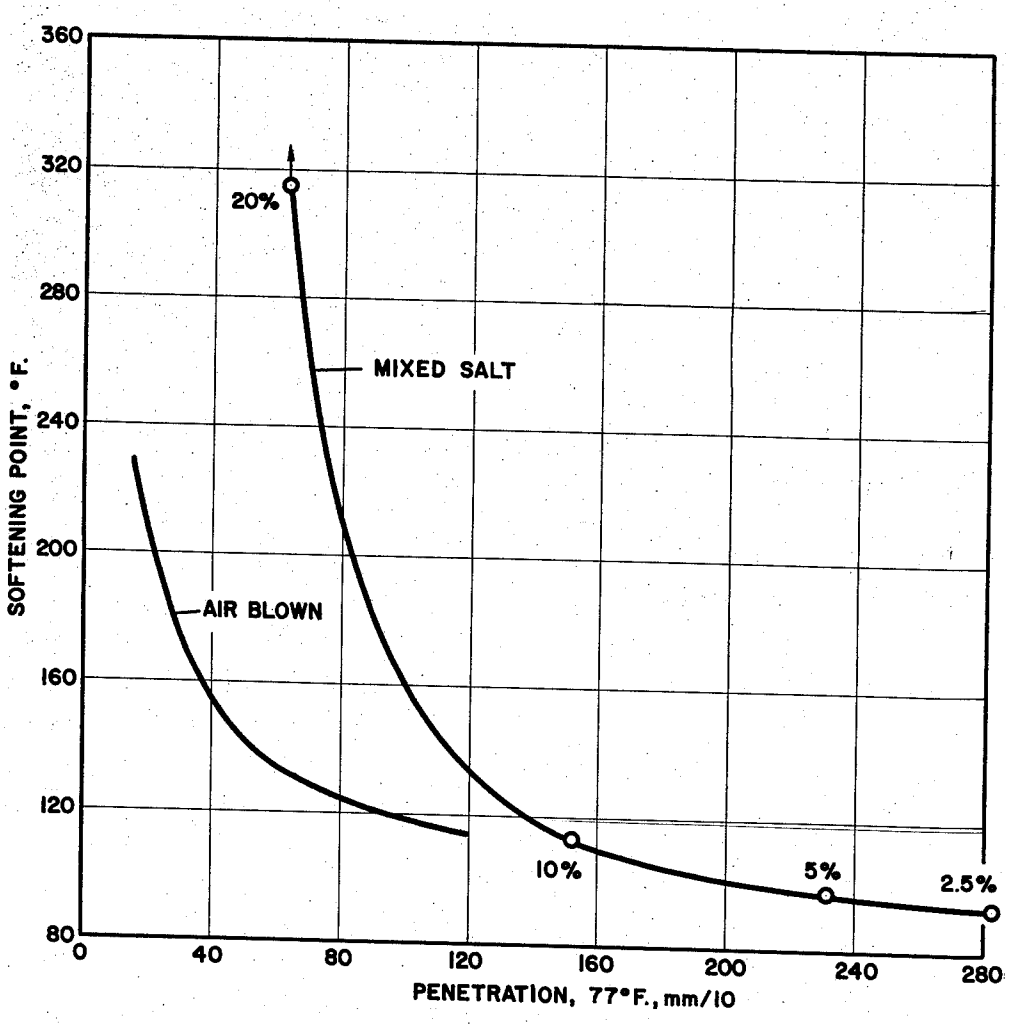


FIG. - 1

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United States Patent Office 3,095,314 Patented June 25, 1963

3,095,314

ASPHALT CONTAINING MIXED METAL SALTS

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Filed Dec. 20, 1961, Ser. No. 160,786
7 Claims. (Cl. 106—269)

This invention relates to improved asphalt containing a minor amount of mixed metal salts. Particularly, the invention relates to an asphalt whose stability is improved, and whose viscosity and softening point are increased, by the incorporation therein of mixed calcium salts of low and high molecular weight carboxylic acids.

In asphalt manufacture, it is common practice to subject the asphaltic residua from asphalt-bearing crude petroleum oils to various treatments in order to modify the properties of the asphalt. These treatments include straight reduction, steam distillation, and vacuum flashing, all of which remove oils from the residua and produce harder asphalts of higher softening point. Another widely practiced treatment is oxidation by air-blowing at elevated temperature, which through polymerization increases the asphaltenes content. Oxidation by air-blowing generally increases softening point, viscosity, and ductility, and decreases penetration and staining tendency, although with soft base stocks ductility and staining tendency may be adversely affected. Through these treatments, the asphalt refiner modifies the properties of asphalts so that they will be more suitable for various uses, such as in paving, roofing materials, paper laminants, joint and crack fillers, protective coatings, briquette binders and canal membrane linings.

There has been a need for additional methods of modifying asphalt to afford the refiner greater latitude in the properties of the asphalts which can be produced. One such property which needs to be improved is resistance to hardening and subsequent cracking of asphalts on ageing. Another such property is temperature susceptibility, i.e. the relation between softening point and penetration. Still other properties in need of improvement are staining tendency, i.e. the tendency to bleed into unimpregnated paper or into paint, and resistance to attack by ozone.

According to the present invention, these and other improvements are achieved by incorporating in the asphalt a minor amount of mixed calcium salts of low and of high molecular weight carboxylic acids. Specifically, the low molecular weight acid is formic, acetic or propionic. Acetic acid, or its anhydride, is preferred. The high molecular weight acid is C_6 to C_{30} acid. The naturally occurring straight chain fatty acids are entirely suitable, but either straight or branched chain acids produced synthetically, as by oxidation, can also be used.

Mixed metal salts of the above type are already known as thickeners for lubricating oils to form both fluid lubricants and grease compositions and have been described in various patents, e.g. U.S. Patents 2,846,392, 2,844,536, 2,909,485, and 2,976,242. However, the present invention is directed to mixed salts in normally solid asphalts instead of oil.

The asphaltic materials which are operable in the concept of this invention may be any of the asphalts obtained from petroleum crude oils, or from tar sands, by processes known to the art. For example, those petroleum crudes having high asphaltic contents such as those of: South America, e.g. Lagunillas; California, such as San Joaquin; or Mid-Continent crudes; can be used as the source for the asphalt. These petroleum crude oils are treated for removal of the lighter fractions by well-known

methods, for example, steam distillation, vacuum flashing, or by solvent separation, e.g., butane or propane deasphalting, etc.

In addition to the petroleum asphalts mentioned above, natural asphalts, such as Trinidad, Bermudez, gilsonite, grahamite, or Cuban may be used. Blends of these natural-occurring asphalts with petroleum asphalts may also be used.

The asphaltic material operable in the concept of this invention may be any of the above-described natural or petroleum asphalts having Saybolt Furol viscosities in the range of from 25 to 5,000 seconds at 300° F. Preferred, however, are those petroleum asphaltic materials having Saybolt Furol viscosities from about 50 to 3,000 seconds at 300° F. These ranges cover what is known in the asphalt trade as fluxes, binders, and coating asphalts. The softer fluxes have softening points (ASTM—ball and ring) less than 100° F., and needle penetrations at 77° F. (ASTM—100 g., 5 sec.) of 300 mm./10 or more, while the harder coating asphalts have softening points as high as 300° F., and penetrations as low as 5 mm./10 at 77° F. All of these asphalts useful in the invention, even the softer fluxes, have asphalt contents of 80% or more of 100 mm./10 penetration at 77°F./100 g./5" asphalt.

The mixed salt-asphalt compositions of the invention comprise a major amount of asphalt and about 1 to 40, preferably 2 to 20 wt. percent, based on the total weight of the composition, of the mixed salt. In the mixed salt, the mole ratio of lower molecular weight acid to the higher molecular weight carboxylic acid is in the range from 1/1 to 100/1, preferably 5/1 to 30/1. In general, the higher the relative mole ratio, the harder the final product.

The mixed salts can be prepared by reacting calcium base, such as the hydroxide or carbonate, with the mixture of C_1 to C_3 fatty acid and the higher molecular weight C_6 to C_{30} fatty acid.

The higher molecular weight C_6 to C_{30} fatty acid can be considered as two general types, namely C_6 to C_{12} fatty acids and C_{13} to C_{30} fatty acids.

The C_6 to C_{12} fatty acids are preferably straight chain, saturated acids such as capric, caprylic, pelargonic acid, lauric acid, etc., although branched chain or unsaturated acids can also be used.

Examples of the C_{13} to C_{30} fatty acids include stearic, 12-hydroxy stearic, oleic, tallow, elaidic, hydrogenated fish oil acids, etc.

It will be understood that known asphalt additives such as wetting agents, anti-stripping agents, etc., may be added to the compositions (e.g. 0.1 to 10.0 weight percent based on the total weight of the composition), without departing from the spirit of the invention.

The compositions of the invention may be prepared in several ways. In one method, all of the acids are dispersed in the molten asphalt and neutralized with the calcium metal base. Alternatively, the metal base is dispersed in the molten asphalt and the mixed acids added thereto. Following evaporation of water of neutralization, the product is then preferably heated to about 350° to 550° F., preferably 400° to 500° F. This heat treatment, although not always necessary, is desirable because higher viscosities in the final product are obtained, probably through higher conversion of the mixed salt into a complex salt.

The invention will be further understood by the following examples.

In carrying out the following examples, various asphaltic materials were used, whose properties are summarized in the following Table I:

TABLE I

Asphalt Inspections Using ASTM Approved Methods

Grade Crude source Method	Flux Tia Juana Pipestill	Binder Mixed Venezuelan Pipestill	Coating Ti Juana Oxidized flux
Spec. grav. at 60° F.	1.004	1.024	1.022
Flash (Cleveland O.C.), ° F.	570	545	575
Soft. point, ° F.	Soft	116	213
Pen., 32° F./200 g./60"	Soft	21	10
Pen., 77° F./100 g./5"	Soft	89	18
Loss 325° F. (50 g., 5 hr.), percent	0.06	0.02	0.02
Soluble in CCL_4, percent	99.7	99.7	99.6
Insol. in 86° naph., percent	16.4	20.8	39.6
Viscosity, Furol at—			
210° F.	601	1,770	
275° F.	93	174	
300° F.	54	84	
350° F.			1,045
400° F.			261
Asphalt content 100 Pen., percent	90		

EXAMPLE I

A series of asphalt compositions were prepared containing various amounts of calcium acetate and calcium stearate formed in situ in the asphalt.

The asphalt was a flux derived from Tia Juana crude. The inspections of this asphalt using ASTM-approved methods, are shown in the preceding Table I.

The mixed salt was prepared by heating the asphalt to 175° F. in order to melt it, stirring lime into the molten asphalt, and then adding a mixture of glacial acetic acid and stearic acid dissolved therein, into the hot asphalt-lime dispersion with stirring. The mixture was heated further, and after water of neutrilization had been evolved, the temperature was raised to 400° F. and maintained at this temperature for about one-half hour. The resulting composition was then cooled and subjected to a series of tests. The amount of lime was sufficient to neutralize all the fatty acid added, while the relative molar ratio of the acetic acid and stearic acid, used in forming the mixed salt, was 10 moles of acetic acid per mole of stearic acid.

EXAMPLE II

A series of compositions were prepared in the same general manner as in Example I except that the binder grade of asphalt derived by pipestill reduction of mixed South American crude oils was used. The mole ratio of acetic to stearic acid used in preparing the mixed calcium salt was 10/1, and the maximum temperature was 400° F.

Inspection data obtained on the compositions of Examples I and II are shown in Table II, where it will be seen that the mixed salts increased both the softening point and the penetration of the flux, and of the binder. Also shown in Table II are the results of the Thin Film Oven Test (AASHO T–179) which was carried out on various compositions of Examples I and II. This test is carried out by heating a thin (⅛") film of the asphalt in an oven for five hours at 325° F. The penetration of the residue at 77° F. (100 g./5 sec.) is then determined and this is reported per se and also as a percentage of the original penetration. The test results are an indication of the hardening which can be expected in long-time service, higher numbers indicating better stability. It can be seen from the test results that high stability is imparted to both types of asphalts by the mixed salts.

Another useful criterion of asphalt quality is the Penetration Index (Highway Engineers Handbook, McGraw-Hill, New York, 1960, pages 18–22), which is a measure of temperature susceptibility or loss of structure on heating. As shown in Table II, the mixed salt compositions

have improved Penetration Indices over those of the base asphalts.

TABLE II

EXAMPLE I (FLUX)

Weight percent mixed salt	0	2.5	5.0	10.0	20.0
Soft. point, ° F. ASTM D-36	Soft	94	98	113	315+
Pen. 77° F.	Soft	283	231	152	63
Thin film oven test:					
Residue, pen. 77° F.		195	167	106	
Percent orig. pen. 77° F.		69	72	70	
Pen. index	−2	0	−0.6	1.2	10

EXAMPLE II (BINDER)

Weight percent mixed salt	0	2.5	5.0	10.0
Soft. point, ° F.	[1] 116 (113)*	132	138	152
Pen. 77° F.	[1] 89 (80)*	57	51	42
Thin film oven test:[2]				
Residue, pen. 77° F.	60	44	41	32
Percent orig. pen. 77° F.	67	77	80	76
Pen. index	[1]−0.6 (−1.4)*	0.5	1.0	1.8

[1] After heating to 400° F.
[2] 325° F., 5 hours (AASHO T-179).

EXAMPLE III

(*a*) A calcium acetate/calcium stearate mixed salt (20 wt. percent) was prepared in situ in the coating grade asphalt. The asphalt was dissolved in 1.5 volumes of toluene, and acetic acid and stearic acid were added in a 10/1 relative mole ratio. The solution was heated to 175° F., and sufficient calcium oxide was added to neutralize the acids. The product was heated further to evaporate off the toluene. The resulting composition had a softening point of 300° F. and a penetration at 77° F. of 10, whereas the base asphalt had a softening point of 213° F. and a penetration at 77° F. of 18. The Penetration Index of the composition was 7; that of the base asphalt was 4.3.

(*b*) A similar preparation was made by dispersing calcium oxide in molten (300° F.) coating grade asphalt, and adding sufficient of a 10/1 acetic acid/stearic acid mixture to neutralize the lime. Some acetic acid was lost by vaporization. The product was further heated to 450° F. and then cooled. The resulting composition containing 20% of the mixed salt had a softening point of >315° F., a penetration at 77° F. of 9, and a penetration index of >7.3.

EXAMPLE IV

A mixed salt composition was prepared in the same binder used in Example II by heating the asphalt to 200° F. where hydrated lime was then stirred into the asphalt in order to obtain a smooth dispersion. Then, in an amount sufficient to neutralize the lime and to provide a small excess, a mixture of acids comprising Emery 787–97–D acid and Wecoline AAC acid in a 10:1 molar ratio was added, following which the temperature was raised to evaporate the water of neutralization. Finally, the temperature was raised to 450° F. for about one hour to ensure high complex formation of the mixed salts.

The Emery 787–97–D acid is a commercial mixture of synthetic acids, mostly formic and acetic, but with small amounts of higher acids. The Wecoline AAC acid is a mixture of fatty acids derived from coconut oil and consists of about 26 wt. percent caprylic acid, 56 wt. percent of capric acid, and about 18 wt. percent of lauric acid.

In Table III, the resulting composition containing 5 wt. percent of the mixed salts is compared with the binder per se, with two asphalts produced by steam reduction, and with one asphalt produced by oxidation, using in each case the same residiuum as that used in producing the binder by pipestill reduction.

The properties of the various above compositions was summarized in the following Table III:

TABLE III

	5% mixed salt in binder	Binder	Steam reduced binder		Oxidized binder
Soft. pt., ° F. ASTM D-36	154	116	136	130	150
Pen. 39.2° F., ASTM D-5	19	36	20	24	24
Pen. 77° F., ASTM D-5	39	89	35	43	30
Pen. ratio, 39.2°/77° x 100	49	40	57	56	80
Pen. index	2.0	−0.6	−0.2	−0.5	1.0
Ductility 77° F. ASTM D-113	42	100+	100+	100+	12
Thin film oven tests:					
Pen. 77° F	36	60			
Percent orig. Pen. 77° F.	92	67			
Barber stain	1				Ca. 3
Spot test, oliensis	Pos.	Neg.	Neg.	Neg.	
Vis. Furol:					
275°		247	421	384	
300°	1,800	121			308
350°	560	45			98
400°	130	21			46

As seen from Table III, the addition of 5 wt. percent of the mixed salt raised the softening point of the asphalt from 116° F. to 154° F. while reducing the penetration at 77° F. from 89 to 39. In addition, the addition of the mixed salt resulted in a very considerable improvement in resistance to hardening as measured by the Thin Film Oven Test. Here the resistance to hardening was increased from 67% to 92%, an exceptionally high value. Also, the Barber Stain test value of one (1) was very good for a composition of such a penetration. It is also seen that the preparation had a very high viscosity, e.g. 1800 Furol seconds at 300° F. and 560° Furol seconds at 350° F. This high viscosity is important in resistance to slumping when coating roofs, paper, metal panels, and the like.

Compared with the steam reduced asphalts at approximately the same penetration level, and with the oxidized asphalt at approximately the same softening point level, the composition containing the mixed salt had better 39.2°/77° Penetration Ratio, better Penetration Index, better Thin Film stability, better stain characteristics, and, of course, higher viscosity.

Strips of blotter paper were impregnated with the binder alone and also with the binder containing 5% of the mixed salt. These strips were placed in an atmosphere containing 0.2 wt. percent ozone. The blotter paper containing the binder alone immediately developed cracks and after two hours in the ozone containing atmosphere was severely cracked. The strips impregnated with the binder plus the calcium mixed salt had only a few long fine cracks after two hours in the ozone.

EXAMPLE V

The flux of Example I was air-blown using standard procedure in order to reduce its penetration and increase its softening point to various degrees. The resulting penetrations and softening points are plotted in FIGURE 1 along with the variation of softening point and penetration with increasing amounts of mixed salt obtained with the compositions of Example I.

As seen by FIGURE 1, the asphalt compositions containing the mixed salt are markedly different from asphalt obtained by air-blowing. The figure also shows the lower temperature susceptibility of the products of the invention, in that the products of the invention have higher penetrations at the same softening point, indicating higher asphalt quality.

What is claimed is:

1. A normally solid asphaltic composition comprising a major amount of asphalt and a minor hardening amount, within the range of about 1 to 40 wt. percent, of calcium mixed salt of C_1 to C_3 fatty acid and C_6 to C_{30} fatty acid, in a molar ratio of C_1 to C_3 fatty acid salt to C_6 to C_{30} fatty acid salt of about 1/1 to about 100/1, wherein said asphalt has a Saybolt Furol viscosity of 25 to 5,000 seconds at 300° F., and contains at least 80 wt. percent based on the total weight of said asphalt, of asphalt having an ASTM needle penetration of 100 mm./10 at 77° F., under a 100 gram load for five second.

2. A normally solid asphaltic composition comprising a major amount of asphalt, and about 2 to 20 wt. percent, based on the total weight of the composition, of calcium mixed salts of C_2 fatty acid and C_{13} to C_{30} fatty acid in a relative molar ratio of salt of said C_2 fatty acid to salt of said C_{13} to C_{30} fatty acid of 5/1 to 30/1, wherein said asphalt has a Saybolt Furol viscosity of 25 to 5,000 seconds at 300° F., an ASTM ball and ring softening point of about 100° F. to about 300° F., an ASTM needle penetration at 77° F. under a 100 gram load for five seconds of about 5 to 300 mm./10, and contains at least 80 wt. percent based on the total weight of said asphalt, of asphalt having an ASTM needle penetration of 100 mm./10 at 77° F., under a 100 gram load for five seconds.

3. A composition according to claim 1, wherein said C_1 to C_3 acid is acetic acid.

4. A composition according to claim 1, wherein said molar ratio is about 5/1 to 30/1.

5. A composition according to claim 1, wherein said C_6 to C_{30} fatty acid is a C_{13} to C_{30} fatty acid.

6. A method of preparing a hardened asphalt which comprises heating said asphalt to its melting point, adding to said asphalt calcium base, C_1 to C_3 fatty acid and C_6 to C_{30} fatty acid, wherein the amount of said base is sufficient to neutralize said acids and the molar equivalent ratio of said C_1 to C_3 fatty acid to said C_6 to C_{30} fatty acid is about 1/1 to about 100/1, followed by further heating said mixture to a temperature in excess of 350° F., and then cooling said composition to thereby obtain an asphalt composition having substantially increased hardness, and wherein said asphalt has a Saybolt Furol viscosity of 25 to 5,000 seconds at 300° F., an ASTM ball and ring softening point of about 100° F. to about 300° F., an ASTM needle penetration at 77° F. under a 100 gram load for five seconds of about 5 to 300 mm./10, and contains at least 80 wt. percent, based on the total weight of said asphalt, of asphalt having an ASTM needle penetration of 100 mm./10 at 77° F., under a 100 gram load for five seconds.

7. A method according to claim 6, wherein said metal base is lime, wherein said C_1 to C_3 fatty acid is acetic acid, wherein said molar ratio is about 5/1 to 30/1, wherein said heating is carried out in the temperature of about 400° F. to about 600° F. and said composition is heated to a temperature of about 400° F. to about 600° F.

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