

1

2,877,129

ASPHALT COMPOSITION CONTAINING A FATTY ESTER AND A PROCESS OF MAKING IT

Harley F. Hardman, Lyndhurst, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application July 5, 1955
Serial No. 520,114

6 Claims. (Cl. 106—279)

This invention relates to an improved petroleum asphalt paving composition and to pavements comprising a mixture of such compositions and aggregate.

In this country today most asphalt pavements are prepared using petroleum asphalts. Petroleum asphalt is the residuum produced by distilling off the lighter fractions of petroleum, including gasoline, kerosene, and other oils which tend to disperse the heavier, less volatile asphalt. The product frequently is "blown," i. e., oxidized by blowing air through it at an elevated temperature, in order to increase its consistency to the desired value. Many physical modifications of petroleum asphalt residuum are available and are well known to those skilled in this art. Asphalt cement, cutback asphalt, and asphalt emulsions, which are aqueous emulsions of asphalt with emulsifying agents to assist in dispersing the asphalt, are those most usually encountered. Native asphalts which have been produced by natural processes from petroleum by evaporation of the lighter components usually are not used. They must be fluxed with lighter oils before they are suitable for paving purposes, and therefore present different problems. Some so-called asphalts also are obtained from the heavier distillates by solvent extraction. These too are somewhat different from the less volatile residuum. Neither of these are contemplated for use in this invention. Reference to "asphalt" hereinafter will be understood to refer to petroleum asphalt residuum only.

Over the years, through experience, a set of standards have been developed, prescribing the properties desired in petroleum asphalt for use as a paving material. These specifications do not, however, fully define a desirable petroleum asphalt paving material. It has been noted, for example, that many paving asphalts which have a ductility below the requirements give satisfactory pavements, some of which in fact may outwear pavements made with asphalts which do meet the ductility requirements. Many paving asphalts derived from certain crudes which meet all of the requirements are not satisfactory in cold climates, although they are fully satisfactory in warm climates. Asphalts derived from California A, West Texas, and Kansas cracked crude, for example, are unsatisfactory for use in northern states such as Ohio where the pavements have to endure winter temperatures as low as 0° F. and below.

Surfaces of bituminous pavements can reach minimum temperatures within a few degrees of minimum air temperatures unless the temperature rapidly drops from a high value and then rapidly rises again the next day. Moreover, gradients as high as about 10° F. exist through a 3 inch pavement, so that the pavement must withstand not only low temperatures but temperature differentials within it. It should be noted that in considering resistance of the pavement to breaking at low temperatures, account must be taken not only of resistance to stresses from the above due to the vehicles using it but also of strains caused by movement of the subsoil, particularly in early spring. These factors tend to show that flexibility of the pavement must be important. At the present time there is no way of measuring the ability of a paving asphalt to resist such stresses.

2

When a pavement slab is loaded, due to a stress from above or from below, it both decreases in thickness and deflects over a limited circular area, assuming a cupped shape in which the individual particles of aggregate must be spread somewhat farther apart in the horizontal direction, and somewhat closer together in the vertical direction. The particular segment of asphaltic pavement therefore must change its dimensions if it is not to break. Since the aggregate is not deformable, such movement requires movement of the asphalt between the aggregate particles. Obviously, if the pavement is to withstand cracking under these conditions, the asphalt must retain a certain minimum degree of flexibility, and this must be retained over the entire range of temperatures to which the asphalt will be subjected. This flexibility is not fixed by current standards established for petroleum paving asphalts.

Ductility is thought by some to measure flexibility, but actually it does not. It measures a flow property which is somewhat difficult to define (L. Kirschbraun, Ind. Eng. Chem. 6, 976 (1914)).

It is significant that those engaged in research on the problem of producing asphalts for use in cold climates have not reached an agreement on the contradictory observations of asphalt ductility. No explanation of the contradictions has been forthcoming. It is hard to understand how a pavement having a low ductility can withstand low temperatures, and yet some do. It is suggested here that low ductility pavements which outlast high ductility pavements in cold climates and elsewhere may do so because of a higher flexibility, and that this has gone unnoticed because flexibility has not been taken into account up until now, since ductility gives no indication of flexibility.

Asphalt is composed primarily of asphaltenes and petroleues, and is considered to be a colloidal system in which the asphaltenes constitute the dispersed phase and the petroleues the dispersing phase. The asphaltenes are defined herein as that portion of asphalt which is soluble in carbon disulfide and insoluble in 50 volumes of n-pentane per volume of asphalt. The petroleues are defined herein as that fraction of the asphalt which is soluble in 50 volumes of n-pentane per volume of asphalt. Asphalt can be defined in terms of other fractions, and some workers in the field have considered asphalt to be composed of asphaltenes, asphaltic resins, and oil fractions, with smaller quantities of waxes and other components. In this concept, the asphaltenes are considered as peptized by the asphaltic resins and thereby dispersed in the oil. The petrolene fraction as contemplated herein is inclusive of both the asphaltic resin and the oil fractions, together with the other components which remain in the oil phase when the asphalt is extracted with n-pentane.

Heretofore, it has been thought that the properties of the asphaltene fraction determined the suitability of the asphalt for paving, and that it was this fraction which had to be modified in order to improve the asphalt for paving purposes.

In accordance with the instant invention, it has been determined that the flexibility of the asphalt at low temperatures is determined by the properties of the petrolene fraction of the asphalt. The petrolene properties are modified, according to the invention, by incorporating in the asphalt a liquid organic ester of a monocarboxylic or polycarboxylic aliphatic fatty acid and a monohydric or polyhydric aliphatic or cyclic alcohol.

These esters can be defined by the formula



where R is an aliphatic hydrocarbon radical, which can

be saturated or unsaturated and have a straight or branched chain, having from about eight to about twenty carbon atoms, and R' is the residue of an aliphatic or cyclic alcohol whose molecular weight and structure are not critical but which will have an appreciable proportion of ether and/or hydroxyl groups to carbon atoms, usually at least one hydroxyl group or ether linkage for each six carbon atoms, or less. x and y are numbers corresponding to the number of carboxylic and/or hydroxyl groups of the acid and alcohol that are esterified. All of the carboxylic and hydroxyl groups of the polycarboxylic acids and polyhydric alcohols need not be esterified.

Thus, R can be derived from caproic acid, lauric acid, sebacic acid, palmitic acid, myristic acid, stearic acid, oleic acid, ricinoleic acid, linoleic acid, and the mixtures of fatty acids in naturally-occurring oils and fats, such as cottonseed oil, soyabean oil, tall oil, coconut oil and tallow. The iodine value of the oil or fat should be below about 140.

R' can be derived from any monohydric or polyhydric alcohol or ether alcohol, of which one or more hydroxyl groups are esterified, for instance, glycerol, ethylene glycol, erythritol, pentaerythritol, polyethylene glycols of varying molecular weights, e. g., 100, 200 and 400, tetrahydrofurfuryl alcohol, diethylene glycol, triethylene glycol, propylene glycol, butyl alcohol, and ethyl alcohol.

These esters are good asphaltene solvents and are miscible with the petrolenes in the amounts required to reduce the flexure limit of the asphalt to below 20° F.

The asphalt paving composition of the invention is as flexible at low temperatures, of the order of 20° F. and below, as the unmodified petroleum asphalts are at more elevated temperatures. The flexibility of the asphalt of the invention, and of the pavement mix obtained by combining such an asphalt with aggregate, may be as much as fifty times greater than a standard asphalt at the same temperature. This is a substantial difference, and, as might be expected, is accompanied by a high resistance to cracking at low temperatures.

This improvement in flexibility is evaluated with the aid of a special and novel test which determines the flexure limit, a characteristic determined herein for the first time, of the asphalt and of the asphalt pavement. This test is important in understanding the present invention. Without such evaluation heretofore it has been impossible to determine whether flexibility had to be improved. This test, applied to the asphalts of the invention, shows how much ester to add to reduce the flexure limit of the asphalt to 20° F. or less. The results of the test have been correlated with actual experience by application of pavements of the invention which pass the test to actual road construction.

The test in question, referred to hereinafter as the "flexure limit test," or, simply, "test," is applicable both to the asphalt and to mixtures of the asphalt with aggregate. It is carried out in the case of asphalt as follows: A sample bar of the asphalt is molded. The dimensions of the bar have been standardized at 1.25 x 1.25 x 11.5 cm. The bar is brought to the test temperature at which its flexibility is to be determined. One end is rigidly mounted in a rotatable quadrant, and the exposed end is brought sharply against the edge of an immovable object, for example, a mandrel, so placed in the path of the bar as to apply a shearing stress thereto, and so placed that if the bar can bend at an angle of 90° it will pass the object, but if it cannot bend that much it will break on contact with the object. Six samples of each asphalt are tested at a given temperature. The "flexure limit" is defined as the lowest temperature, in ° F., at which all six samples will pass the surface by bending without breaking, and the term is so used in the claims.

The test is based on the following theory. Intermediate between the solid and the gas states lie the liquid,

amorphous solid and gel states. At temperatures well above the softening points, asphalts are liquid. As temperature is decreased to below the softening point, they gradually depart from liquid behavior, and take on more and more a type of elastic behavior characteristic of gels. At still lower temperatures they become amorphous solids, incapable of flowing under stress except at very slow rates, and exhibiting brittle fracture when overstressed. In the case of asphalt, the transition from a gel-like liquid which retains appreciable flexibility to a brittle solid occurs within a relatively short temperature range. At successively lower temperatures, as the transition progresses, the tendency of the asphalt to break increases as it is forced to bend around the fixed radius, and eventually the asphalt reaches the flexure limit, at which fracture occurs. The test thus fixes the flexure limit at the temperatures at which the flexible gel-like state passes into the brittle state. The existence of this rather sharply defined flexure limit makes it possible to define rather precisely the low temperature properties of a paving asphalt.

The flexure limits of several of the most commonly met asphalts are given in the table below:

TABLE I

Asphalt from Crude	Flexure Limit, (°F.)	Penetration at 77° F.
California A.....	50	68
Illinois Cracked.....	55	58
Illinois N.....	33	64
Kansas Cracked.....	52	72
Smackover.....	33	63
Texas.....	31	59
Venezuelan.....	31	59
Kansas N.....	38	65
California B.....	35	68
West Texas.....	36	87
Panuco-Mexican.....	49	64
	31	83

These asphalts, which have known service records, show trends in the flexure limit which correspond to their performance at low temperatures. The Texas and Mexican asphalts are considered good paving asphalts in cold climates, and they have the lowest flexure limits in the group. The asphalts which are known to be worst in cold climates have the highest flexure limits; these are the West Texas, California A and the various cracked asphalts. It will be noted that the lowest limit is 31° F. In contrast, the paving asphalt compositions of the invention have flexure limits of 20° F., maximum, and preferably 15° F. or below.

In accordance with the invention a paving asphalt, such as any of the asphalts listed above, is blended with an ester as defined above having certain specified physical properties in an amount within the range from 10% to 40%, preferably from 15% to 30%, by weight of the asphalt blend sufficient to give the desired low flexure limit.

The ester must meet the following requirements:

(1) It must be a liquid at temperatures at least as low as the flexure limit required for the asphalt blend, preferably at least 5° F. less than the flexure limit, and in any event below 20° F.

(2) A flash point (Cleveland Open Cup) of at least 400° F., and preferably at least 440° F.

(3) A viscosity no higher than 20 poises at 77° F., and preferably less than 5 poises at that temperature.

(4) A viscosity index of not less than 40, and preferably at least 60.

Typical esters are glycerol monolaurate, glycerol monooleate, propylene glycol monolaurate, diethylene glycol dioleate, Cellosolve ricinoleate (ricinoleic acid ester of diethylene glycol), polyethylene glycol 200 monolaurate, polyethylene glycol di-2-ethyl hexoate, diisooctyl sebacate, tetrahydrofurfuryl oleate, butyl Cellosolve oleate (oleic acid ester of butyl ether of diethylene

glycol), polyethylene glycol 400 tallate, methyl tallate, and the naturally-occurring fats and oils having an iodine value below about 140, such as soyabean oil and cottonseed oil.

If desired, the ester can be used together with a hydrocarbon oil which is primarily paraffinic in nature, which has a viscosity index of at least 40, and which meets the other requirements mentioned for the ester. These are solvents for the petrolenes, and also are effective to lower the flexure limit.

The hydrocarbon oil can be solvent extracted and conventionally refined neutral oils, bright stocks, vacuum-distilled cylinder oils, gas oils, dewaxed gas oils, wax slops fractions, and the like.

The proportions of the oil and ester are not critical, inasmuch as both are effective for the same purpose. However, usually the ester will be in a major proportion, although mixtures containing as little as one-third ester and less are, of course, satisfactory.

It will be appreciated that the amounts of ester and mixtures thereof with the hydrocarbon oil depend upon the viscosity, softening point and other properties desired in the finished product, but the amount will be selected within the 10 to 40% range stated to produce an asphalt blend having the desired flexure limit of 20° F. or below.

After addition of the ester and/or hydrocarbon oil, the asphalt, if necessary, will be brought to a 77° F. penetration within the paving requirements. Of course, if the mixing is done after oxidation it will be necessary to oxidize the asphalt to a lower penetration than is desired in order to meet the final penetration requirement, inasmuch as the hydrocarbon oil and/or ester will increase the penetration. For paving purposes, the asphalt blend should have a 77° F. penetration within the range from 40 to 200.

As is well known, asphalts which are too soft can be brought to a higher consistency by blowing with air at a temperature within the range of 375 to 500° F. This is a standard procedure and is fully set forth in the literature. Oxidation is continued until penetration has increased to the desired value. The ester and the hydrocarbon oil do not interfere with the oxidation, although there is a possibility of some loss of the ester or hydrocarbon oil during oxidation if it has a low enough boiling point. To avoid this, the ester and/or oil can be added after oxidation of the asphalt, as has been stated.

The ester and/or mixture thereof with the hydrocarbon oil can be incorporated in the asphalt by any desired means. It is preferable that the asphalt be fluid, and that the blending be accompanied with sufficient mixing to insure uniform distribution therein. Conventional mixing equipment is satisfactory. If the ester and/or oil is added before the asphalt is air-blown, the air-blowing of the fluid asphalt at an elevated temperature will insure adequate mixing.

The asphalt composition of the invention is intended for use in the preparation of conventional asphalt-aggregate paving mixes. These are well known, and a detailed description therefore is unnecessary.

Asphalt pavements for road construction are prepared from 4 to 15% asphalt and the remainder mineral aggregate or filler. The mineral aggregate and filler is selected from materials such as limestone, slag, gravel, and the like. The aggregate must meet certain specifications as to the size range of the particles, depending upon whether the pavement is to be coarse or dense, and may range from coarse sizes of 3/8 inch in diameter down to dusts of 200 mesh and less. Details are given in chapters II and IV of the Asphalt Handbook (1947) published by The Asphalt Institute, College Park, Maryland, the disclosures of which are hereby incorporated by reference.

Asphalt paving mixes may be divided into two general classes, i. e., hot-mix and cold-mix. The cold-mix is prepared at ambient temperatures by the mixing of mineral aggregates with cut-back asphalts. "Cut-back asphalt" is a term used to describe conventional asphalt compositions to which a solvent such as petroleum naphtha has been added in order to render the asphalt fluid at ordinary temperatures. After application of cold-mix to a road, the solvent evaporates, leaving behind a hard asphalt surface. While cold-mix is satisfactory in certain specialized applications, it is believed by the paving industry that the most satisfactory roads are constructed with a hot-mix, and this invention is concerned particularly with the manufacture of a hot-mix.

Hot-mix asphalt paving mixtures are generally produced at an asphalt paving plant. Measured quantities of aggregate and asphalt cement, both at about a temperature of 300° F., are dumped into a mixer, and the mixing usually accomplished in a short time, on the order of two to five minutes. The hot-mix is then dumped from the mixer into trucks or into storage bins. The trucks are usually insulated so that the mix will not lose its temperature while being transported to the actual paving site.

The following examples are illustrative.

Examples 1 to 16

A sample of pipestill bottoms with a 77° F. penetration in the range of 200 to 280 was oxidized by heating while blowing with air at 450 to 460° F. to a viscosity of 132 Furol seconds at 300° F. This was used as a control. Additional samples of the same pipestill bottoms also were oxidized at 450 to 460° F. in the presence of the hydrocarbon oils and mixtures thereof with esters as identified in the table below, in the amounts indicated, to the viscosity stated in the table. Each of the additives had a viscosity, flash point and fire point within the ranges given heretofore.

TABLE IA

Example No.	Concentration, Percent	Ester	Ester			Asphalt						
			Vis., 77° F.	Flash, ° F.	Fire, ° F.	Vis., 300° F.	Flash, ° F.	Fire, ° F.	Penetration		Soft. pt. ° F.	Flexure Limit, ° F.
									77° F.	32° F.		
1		None			132	620	645	61	16	120	33	
2	25	Soyabean oil	0.55	565	650	146	630	665	220	80	102.5	7
3	20	Cottonseed oil	0.57	582	644	130			141	46	110	14
4	25	Diisooctyl sebacate		425	475	130.4	505	575	195	92	106	-3
5	25	Tetrahydrofurfuryl oleate	0.15	430	465	146.5			230+	188	102	-14
6	25	Polyethylene glycol di-2-ethyl hexoate				151			240+	134	104	-9
7	25	Diethylene glycol oleate	0.50			131			187	104	120	-11
8	25	Polyethylene glycol 200 monolaurate	0.39			129			285+	125	104	2
9	25	Butyl Cellusolve oleate				144.7			155	76	110	4
10	30	Glycerol monooleate	1.72			132			259	65.5	100	3
11	25	Propylene glycol monolaurate				133			153	69	109	7
12	25	Glycerol laurate S	6.75			129			140	48	114	12.5
13	20	Glycerol monooleate	1.72			130.8			180	65.5	106	8.5
14	30	Do	1.72			133			179	75.5	106	1.6
15	25	Polyethylene glycol 400 tallate	2.06	470	535	134	590	635	121	58	127	11
16	25	Polyglycol 300 tallate	1.39			133			145	65	114	12

7

The above data show that a wide variety of fatty esters are useful to adjust the flexure limit to below 15° F. and, in fact, a limit as low as -14° F. is obtainable (Example 5).

Examples 17 and 18

Two asphalts were prepared using the same pipestill bottoms employed in Examples 1 to 16. In one (Example 17) methyl tallate was added before oxidation of the pipestill bottoms. In the other, 27% methyl tallate (Example 18) was added after the pipestill bottoms had been oxidized to a penetration of 10 at 77° F. Example 18 had a flexure limit of 2° F., whereas Example 17 had a flexure limit of 30. This difference was due to volatilization of the methyl tallate during the oxidation in Example 17. The data show that in the case of more volatile esters it is necessary to incorporate the ester after the asphalt has been brought to the desired penetration. However, whether the ester is added before or after the oxidation is immaterial in obtaining the desired flexure limit, as Examples 1 to 16 show.

Examples 19 to 23

2900 gallons of conventionally-refined neutral oil, 300 SSU at 100° F., and 1400 gallons of soyabean oil were charged to a tank at about 60° F., and pipestill bottoms (viscosity at 300° F., 67 Furol seconds, penetration 77° F., 195; 19.9% asphaltenes; petroleum viscosity at 77° F. 2078 poises, and at 100° F. 368 poises; petroleum viscosity gravity constant 0.862) was added. The batch composition was 31.1 volume percent of the mixed neutral oil soyabean oil, and 68.9 volume percent of the pipestill bottoms. The mix was heated to 370° F., air-blowing was started, and the batch oxidized past the desired end point of 130 Furol seconds at 300° F., the viscosity going from 121 to 157 seconds in one hour.

275 gallons of the neutral oil-soyabean oil mixture were then added, followed by 880 gallons of the pipestill bottoms, and the batch finished by further oxidation to the viscosity given in Table II. The table compares the properties of this material with a standard 108 penetration asphalt and a standard 70/80 penetration asphalt.

TABLE II

	Example No. 19	Example No. 20	Example No. 21
Furol Viscosity at:			
350° F.	41.4	33.3	47.7
325° F.	68.4		
300° F.	126.8	88.2	136.5
275° F.	245.2		
250° F.	773.4	324.2	525
Softening Point (R & B), ° F.	127	110	118
Penetration:			
115°-50 g.-5 sec.	>270	>345	>340
110°-50 g.-5 sec.	161	269	201
77°-100 g.-5 sec.	110	111	80
32°-200 g.-60 sec.	69	42	18
Ductility:			
77°-5 cm./min.	22.7, 19.5	100+	100+
60°-5 cm./min.	8.5	100+	100+
Flexure Limit, ° F.	0	22.5	32.5
Thermal Expansion Transition Temp., ° F.	14	20	25
Coefficient, in./in./° F.	8.0×10 ⁻⁵	6.2×10 ⁻⁵	8.9×10 ⁻⁵
Standard Index, 140°-50 p. s. i., 72 hrs.	19	5	1
Flash Point (COC), ° F.	490	>600	>625
Fire Point (COC), ° F.	565	>600	>625
Loss on Heating, 325°-50 g., 5 hrs. percent.	0.14	0.004	0.013
Pen. on Residue.	101	70	70
Specific Gravity:			
77° F.	0.9904	1.002	0.996
60° F.	0.9972		
Olefinic	Homo	Homo	Homo
Percent Asphaltenes	29.9	22.0	16.8
Petroleum Viscosity at:			
100°	63.9	528	2,316
77°	224	1,960	17,585
Petroleum, 100° Viscosity, Gravity Constant	0.849	0.843	0.817

A fourth asphalt was prepared (Example 5) by vacuum distillation of Boscan crude having a penetration within the range of 85-100, and a fifth asphalt (Example

8

26) was prepared starting with a 107 penetration base containing 10 percent of Rubarite, a synthetic rubber additive. These asphalts had the following properties:

TABLE III

	Example No. 22	Example No. 23
Viscosity, Furol, at:		
350° F.	86	154
325° F.	146	310
300° F.	274	440
275° F.	577	986
250° F.	115	117.5
R & B Soft. Pt., ° F.		
Penetration:		
115°-50-5	202	190
100°-50-5	85	87
77°-100-5	25	25
32°-200-60		
Ductility:		
77°-5 cm./min.	100+	77
60°-5 cm./min.		
Flexure Limit, ° F.	30°	20
Stain Index, 140°	1	1
Flash Point (COC), ° F.	570	610
Specific Gravity, 77°	1.033	1.045
Loss on Heating, 325°-500-5 hrs.	0.054	0.008
Pen. on Residue	82	80
Percent Asphaltenes	28.3	23.4
Petroleum Viscosity:		
100° F.	391	1,330
77° F.	2,780	9,935
Petroleum, Specific Gravity, 100°	0.985	0.958
Petroleum, 100° Viscosity, Gravity Constant	0.914	0.828

These five asphalts (Examples 19 to 23) were subjected to rheological tests using test methods developed by the Franklin Institute Laboratories for Research and Development as part of the National Asphalt Research Center Program and described in NARC Reports R-1, R-2, R-4 and R-5. According to these tests the asphalt of the invention (Example 19) had a lower shear modulus of elasticity throughout the entire temperature range, was more easily sheared and behaved more like a liquid at low temperatures than Examples 22 and 23. The viscosity coefficient was not improved at the extreme low temperature but at above about 10° F. it is lower for the asphalt of the invention.

The asphalts were tested for variation in impact strength vs. temperature. All tests were made using ½" x ½" x 6" bars prepared by casting from the molten asphalt. The bars were supported on rounded supports separated by 1½", and a 50 gram striker guided by wires was allowed to fall from increasing heights until the approximate height for breaking was bracketed. The height was then increased until six successive samples were broken at the same drop height. The data showed that the asphalt of the invention was far superior in impact resistance to all of the others studied at all temperatures from -15° F. up.

The modulus of elasticity vs. temperature was measured using an American Instrument Co. "Modulimeter" mounted in a constant temperature box. Bars ½" x ½" x 6" were used as test specimens. The asphalt of the invention had a lower modulus of elasticity throughout the temperature range studied (0-40° F.) than any of the other asphalts.

In order to demonstrate that the same results are obtainable when the asphalts are mixed with aggregate, the above tests were repeated using pavement mixtures prepared as follows: 75 grams of 40-80 mesh lake sand and 15 grams of limestone dust were weighted out and each portion mixed and placed in a 325° F. oven along with a mold for a ½" x ½" x 5" bar and the asphalt to be used. When the asphalt was completely melted, 10 grams were added to the hot sand-limestone dust blend and the ingredients mixed well with a putty knife. 40 grams of the hot aggregate were placed in the mold and the mold subjected to 6000 p. s. i. g. hydraulic pressure in a Carver Laboratory press and allowed to come to room temperature.

In the Modulimeter test the asphalt of the invention

flexed the greatest at all temperatures and the changes in modulus elasticity from 35° F. to 0° F. were 1/20 that of the standard 108 penetration asphalt and 1/31 that of the others. The asphalt of the invention showed up well under impact and constant force deformation, as well. The sheet-asphalt mixture containing the asphalt of the invention will withstand an impact from a height 3 1/2 times greater than any other asphalt at 20 and 30° F.

Examples 24 to 29

A group of six asphalts were prepared in order to obtain weathering data. These were compared with the blank composed of the asphalt base without the additive. The same pipestill bottoms of Examples 1 to 16 were employed, and this was mixed with cottonseed oil, soyabean oil, solvent extracted neutral oil (300 SSU at 100° F.) and mixtures of solvent extracted neutral oil and cottonseed oil in the amounts indicated in Table IV below.

The test was carried out on a mixture obtained by heating a portion of the asphalt to 300° F. and thoroughly mixing it by hand with standard Ottawa sand heated to the same temperature in an amount such that the asphalt was 1.6% by weight of the mix. Each batch was divided into three portions and placed uncompacted in pans. One portion is retained as a control and the other two portions are placed on the roof of a building. One sample is examined after three months exposure and the other after twelve months. Extraction and recovery of the asphalt is carried out by the A. S. T. M. Abson method.

The weather and test results are given in the table below.

TABLE IV

Example No.	24	25	26	27	28	29
	Control	30% Cottonseed Oil	30% Soyabean Oil	15% Solvent extracted neutral oil, 140 SSU at 100° F., 10% Cottonseed Oil	20% Solvent extracted bright stock, 78 SSU at 210° F., 10% Cottonseed Oil	30% Solvent extracted neutral oil, 300 SSU at 100° F.
Penetration 77° F.:						
Original	50	135	135	102	110	98
After 3 months	41	111	127	88	100	72
After 12 months	31	69	103	82	60	56
Percent Decrease	38	49	24	20	45	43
Penetration 32° F.:						
Original	16	73	100	62	66	78
After 3 months	19	55	84	60	68	59
After 12 months	19	45	46	47	53	50
Percent Decrease	19	38	54	24	20	36
R & B Softening Point:						
Original	129	110	103	125	131	144
After 3 months	137	122	113	141	143	172
After 12 months	146	138	149	145	160	190
Percent Increase	13	26	43	16	22	32
Ductility, 77° F.:						
Original	100+	100+	100+	27	10	5
After 3 months	26.5	86	100+	11	6	3
After 12 months	5	30	36	9	4	3
Percent Decrease	95+	70+	64+	67	60	45

The data show that the mixture of solvent extracted neutral oil and cottonseed oil is quite satisfactory. The mixtures containing the solvent extracted neutral oil and solvent extracted bright stock change more slowly than the blank and the other samples. Softening points also increase for these materials but less rapidly than the others.

A blend of petroleum oil and fatty oil is the best from the standpoint of weathering.

All proportions and percentages in the specification and claims are by weight of the final asphalt composition.

I claim:

1. A paving asphalt composition having a "flexure limit" below 20° F. consisting essentially of a petroleum residuum asphalt having a "flexure limit" above 20° F.

and a liquid ester having an iodine value below 140 of an aliphatic fatty carboxylic acid having from about nine to about twenty-one carbon atoms and a saturated non-aromatic alcohol characterized by a softening point below the "flexure limit" of the asphalt composition, a flash point (Cleveland Open Cup) of at least 400° F., a viscosity at 77° F. below 20 poises, and a viscosity index above 40, the said ester being present in an amount within the range from about 10% to about 40% to reduce the "flexure limit" of the asphalt to below 20° F.

2. A paving asphalt composition having a "flexure limit" below 20° F. consisting essentially of a petroleum residuum asphalt having a "flexure limit" above 20° F. and a liquid ester having an iodine value below 140 of an aliphatic fatty carboxylic acid having from about nine to about twenty-one carbon atoms and a saturated non-aromatic alcohol, and a primarily paraffinic liquid mineral hydrocarbon oil, each characterized by a softening or pour point below the "flexure limit" of the asphalt composition, a flash point (Cleveland Open Cup) of at least 400° F., a viscosity at 77° F. below 20 poises, and a viscosity index above 40, the said ester and oil being present in a total amount within the range from about 10% to about 40% to reduce the "flexure limit" of the asphalt to below 20° F.

3. A process for preparing a paving asphalt composition having a "flexure limit" below 20° F., which consists essentially of the step of incorporating in a petroleum residuum asphalt having a "flexure limit" above 20° F., a liquid ester having an iodine value below 140 of an aliphatic fatty carboxylic acid having from about nine to about twenty-one carbon atoms and a saturated non-

aromatic alcohol characterized by a softening point below the "flexure limit" of the asphalt composition, a flash point (Cleveland Open Cup) of at least 400° F., a viscosity at 77° F. below 20 poises, and a viscosity index above 40, in an amount within the range from about 10% to about 40% to reduce the "flexure limit" of the asphalt to below 20° F.

4. A process for preparing a paving asphalt composition having a "flexure limit" below 20° F., which consists essentially of the step of incorporating in a petroleum residuum asphalt having a "flexure limit" above 20° F., a liquid ester having an iodine value below 140 of an aliphatic fatty carboxylic acid having from about nine to about twenty-one carbon atoms and a saturated non-aromatic alcohol, and a primarily paraffinic liquid mineral

11

hydrocarbon oil each characterized by a softening or pour point below the "flexure limit" of the asphalt composition, a flash point (Cleveland Open Cup) of at least 400° F., a viscosity at 77° F. below 20 poises, and a viscosity index above 40, the said ester and oil being present in a total amount within the range from about 10% to about 40% to reduce the "flexure limit" of the asphalt to below 20° F.

5. A process in accordance with claim 3 which includes oxidizing the asphalt to a penetration at 77° F. within the range of about 40 to about 200.

10. A process in accordance with claim 4 which includes oxidizing the asphalt to a penetration at 77° F. within the range of about 40 to about 200.

12

References Cited in the file of this patent

UNITED STATES PATENTS

	227,080	Warren	Apr. 27, 1880
	941,810	Phillips et al.	Nov. 30, 1909
	1,306,520	Burkley	June 10, 1919
	1,635,567	Weber	July 12, 1927
	1,883,683	Gardner	Oct. 18, 1932
	1,982,231	Parrett	Nov. 27, 1934
	2,028,922	Rose	Jan. 28, 1936
	2,392,813	Fewsmith	Jan. 15, 1946
	2,687,965	Schiermeier	Aug. 31, 1954

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,877,129

March 10, 1959

Harley F. Hardman

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 1, line 36, for "resium" read -- residuum --; column 6, line 36, after "mixing" insert -- is --; column 7, line 8, for "hethyl" read -- methyl --; column 8, line 65, for "weighted" read -- weighed --.

Signed and sealed this 7th day of July 1959.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents