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3,202,621 ASPHALT-EPOXY COMPOSITIONS AND METHOD OF MAKING THE SAME

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No Drawing. Filed July 27, 1960, Ser. No. 45,547
4 Claims. (Cl. 260-18)

This invention relates to improved asphaltic compositions and, more particularly, to thermohardenable compositions comprising asphalts, the reaction product of epoxy resins and polymeric fatty acids, and relatively small or minor amounts of compatibilizing agents as compared with the total weight of the composition or blend. The invention also relates to the foregoing compositions used wherever resistance toward hydrocarbon fuels and lubricating oils, as well as a high heat softening point and a low penetration value, are required, such as on asphaltic roads, toll gate pavings, airport runways, floors, etc.

Heretofore, difficulty has been experienced in providing an asphaltic material suitable as a surfacing material for the construction of asphaltic surfaces that have to withstand automotive vehicle traffic. It has been found that common asphaltic surfaces are seriously damaged by spillage of hydrocarbon fuels and lubricating oils. This disadvantage limits the use of asphaltic materials in service station pavings, garage floors, airport runways, pavements for plane warming-up aprons, hangars, etc.

Although it has been previously suggested to incorporate certain additives, such as polyethylene, natural rubber, unsaturated nitriles, etc., in order to overcome these shortcomings, and, although such additives do improve the performance of asphalts, none of them solve the problem of providing thermohardenable asphaltic compositions.

An object of this invention is to provide improved thermohardenable, homogeneous asphaltic compositions that possess improved physical properties after being heat cured.

Another object is to provide a method of curing asphalt-epoxy compositions characterized in that compatibilizing agents, as described below, are employed for achieving homogeneous compositions. Still another object is to provide a method of increasing the resistance of asphalts toward hydrocarbon fuels and lubricating oils by blending said asphalts with epoxy esters and compatibilizing agents, and curing the resulting blends at elevated temperatures.

These and other objects will be apparent from the following specification and the claims appended thereto.

It has been discovered that these and other objects of the invention are attained by adding monoesters of polyalkylene glycols an unsaturated higher fatty acids as compatibilizing agents to blends comprising asphalts and the reaction products of polymeric fatty acids containing at least 24 carbon atoms and epoxy resins, and curing the resulting mixtures at elevated temperatures. The monoesters may be obtained by esterifying polyalkylene glycols with unsaturated higher fatty acids at a mol ratio of approximately one to one. The polyalkylene glycol component includes polyethylene glycols, such as diethylene glycol, triethylene glycol, tetraethylene glycol and other polyethylene glycols up to a molecular weight of about 1000. It also includes polypropylene glycols having molecular weights between about 134 to about 1000. The unsaturated fatty acid component includes fatty acids which contain at least 12 carbon atoms and at least one carbon-to-carbon double bond, such as dodecylenic acid, palmitoleic acid, oleic acid, ricinoleic acid, petroselinic acid, vaccenic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, parinaric acid, gadoleic acid, arachi-

donic acid, cetoleic acid, erucic acid, selacholeic acid, nervonic acid, etc. Instead of the pure fatty acids, mixtures that occur in natural fats and oils, wherein the unsaturated acids predominate, may be used. Examples of such mixtures are linseed oil fatty acids, soy bean fatty acids, dehydrated castor oil fatty acids, tung oil fatty acids, etc. Although all monoesters of these glycols and fatty acids described above may be used as compatibilizing agents, particularly good results were obtained with monoesters of oleic acid and polyethylene glycols having molecular weights up to about 600. The amount of compatibilizing agents that may be added to blends of asphalts and the reaction products of polymeric fatty acids and epoxy resins depends upon the weight ratio of the two components in said blends but in any event is relatively small in comparison with the total weight of the blend and preferable ranges from about 1.0 percent up to about 14 percent by weight. For most practical purposes, however, it is preferred to use between about 3 and about 5 percent by weight.

The asphalts contained in the blends constitute the semi-solid or solid residual fractions of petroleum crude oils and may have been subjected to any of the commonly known refining or treating processes, such as distillation, steam reduction, air blowing, or other oxidizing treatments. Any asphalt may be used regardless of its geographical occurrence. In accordance with common usage, the asphalts used in the present invention were characterized by their penetration values.

The reaction product of polymeric fatty acids containing at least 24 carbon atoms and epoxy resins may be obtained by reacting the ingredients with or without the addition of an amine catalyst at elevated temperatures, until the reaction mixture remains homogeneous when cooled to room temperatures. The polymeric fatty acids are usually available as mixtures containing both dimerized and trimerized fatty acids. They are usually made by polymerizing fatty acids having at least one carbon-to-carbon double bond and at least 12 carbon atoms, such as dodecylenic acid, palmitoleic acid, oleic acid, ricinoleic acid, petroselinic acid, vaccenic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, parinaric acid, gadoleic acid, arachidonic acid, cetoleic acid, erucic acid, selacholeic acid, nervonic acid, etc. Although any of the fatty acids may be polymerized, those having 18 carbon atoms and being readily available from animal and plant fats and oils, either in pure form or as mixtures, are generally preferred from a standpoint of economics and performance. They may also be made by polymerizing monohydric alcohol esters of such fatty acids, saponifying the resultant polymeric ester and isolating the free polymeric fatty acids. The polymerization may be effected by heat or by anionic catalysts, or by both, whereby mixtures result that contain both dimer and trimer fatty acids as well as unreacted starting material. The latter is usually removed by distillation at reduced pressures. Although both the dimer and the trimer fatty acids, as well as mixtures of both, may be used in the reaction with epoxy resins, the trimer fatty acids gave particularly good results.

The epoxy resins used in the present invention are polyglycidyl ethers of polyhydric phenols and are usually made by etherification of polyhydric phenols with an epihalohydrin in alkaline medium. The polyhydric phenols include p,p'-dihydroxy diphenyl dimethyl methane (Bisphenol A), resorcinol, hydroquinone, catechol, condensation products of mono and polyhydric phenols with aldehydes, particularly with formaldehyde (novolacs and resols), etc. Depending upon the mol ratio of epihalohydrin to the phenolic hydroxyl and further depending upon processing, resins of various molecular weights may

be obtained. It is customary, however, to identify the resins by their epoxy equivalent weights. The epoxy resins that may be used in the invention have epoxy equivalent weights up to about 300. To achieve optimum results, resins having epoxy equivalent weights between about 175 and 220 are generally preferred.

The reaction product of polymeric fatty acids and epoxy resins may be obtained by reacting the two ingredients in approximately stoichiometric amounts so that about one carboxylic group is employed per each epoxy group. The reaction may be conducted at elevated temperatures and may be controlled by checking the reaction mixture for homogeneity when cooled to room temperature, homogeneity indicating a sufficient extent of the reaction. Once this homogeneity is achieved, the reaction mixture is cooled to room temperature in order to prevent it from becoming infusible and insoluble. Reaction temperatures may be varied within a very wide range. Although lower temperatures may be employed, it is generally preferred to choose temperatures not below 95° C., as then difficulties might be encountered in obtaining homogeneous mixtures. On the other hand, substantially higher reaction temperatures may be employed, thereby speeding up the rate of reaction. However, the top temperatures should not be so high as to cause decomposition. A convenient temperature range is between about 95° C. and about 120° C.

As mentioned above, the reaction may be catalytically sped up by adding catalysts to the reaction mixture. Suitable catalysts include amine compounds and, more particularly, tertiary amines, such as triethanolamine, benzyl dimethyl amine, etc. While the amine catalyst may be omitted altogether, up to five percent by weight, based on the combined weights of polymeric fatty acids and epoxy resins, may be added. Usually it is preferred to use between about 0.5 percent and about 1.0 percent by weight.

The weight ratios of the components contained in the blends of asphalts and the reaction product of polymeric fatty acids and epoxy resins may range from about 1 to 28 to about 3 to 1. For economical reasons, however, a range from about 1 to 8 to about 3 to 1, and particularly from about 3 to 1 to about 2 to 1 is generally preferred, the asphalts as the cheapest component being used in major amounts.

The following examples are presented to better illustrate and describe the invention; and only such limitations as are imposed by the appended claims are hereby intended.

EXAMPLES

I. Preparation of starting materials and intermediates

In order to better identify the materials used, the preparation of some of them is given below.

A. EPOXY RESIN

Bis-phenol A was dissolved in epichlorohydrin in the proportion of 5,130 parts (22.5 mols) of bis-phenol in 20,812 parts (225 mols) of epichlorohydrin and 104 parts of water. The solution was prepared in a kettle provided with heating and cooling equipment, agitator, distillation condenser and receiver. A total of 11,880 parts of solid 97.5% sodium hydroxide, corresponding to 2.04 mols of sodium hydroxide per mol of bis-phenol (2% excess) was added in installments. The first installment of 300 parts of sodium hydroxide was added and the mixture heated with efficient agitation. The heating was discontinued as the temperature reached 80° C. and cooling was started in order to remove the exothermic heat of reaction. The temperature control, i.e. cooling, prevented the temperature from rising to more than 100° C. When the exothermic reaction had ceased and the temperature had fallen to 97° C., a further addition of 316 parts of sodium hydroxide was made and similar further additions were effected at successive intervals. An exothermic reaction took place after each caustic addition.

Sufficient cooling was employed to cause a gentle distillation of epichlorohydrin and water, but the temperature was not allowed to go below about 95° C. No cooling was necessary after the final addition of sodium hydroxide. After the last addition of sodium hydroxide and with completion of the reaction, the excess epichlorohydrin was removed by vacuum distillation with use of a kettle temperature up to 150° C. and a pressure of 50 mm. Hg. After completion of the distillation, the residue was cooled to about 90° C. and about 360 parts of benzene added. Cooling dropped the temperature of the mixture to about 40° C. with precipitation of salt from the solution. The salt was removed by filtration and carefully washed with about an additional 360 parts of benzene to remove polyether therefrom. The two benzene solutions were combined and distilled to separate the benzene. When the kettle temperature reached 125° C., vacuum was applied and distillation continued until the kettle temperature was 170° C. at 25 mm. pressure. The resulting glycidyl polyether of bis-phenol had a Durrans' Mercury Method softening point of 9° C., an average molecular weight of 370 by ebullioscopic measurement in ethylene dichloride, and an epoxide value of 0.50 epoxy equivalents per 100 grams. It had an epoxide equivalent weight of 200 and a 1,2-epoxy equivalency of 1.85.

B. REACTION PRODUCT OF EPOXY RESIN AND POLYMERIC FATTY ACID

To an 800 ml. beaker was charged:

200 gms. (equivalent to 1.0 mol epoxy groups) of the epoxy resin described above, and

322 gms. (equivalent to 1.08 mol carboxyl groups) of a commercial trimer acid which will be further identified below.

The beaker was heated on a hot plate, and the mixture was stirred occasionally. The temperature was brought up to and maintained at 100° C., whereupon 0.66 gms. of benzyl dimethyl amine was added as a catalyst. Every minute a sample of the reaction mixture was drawn in order to check compatibility at room temperature. Fifteen minutes after the catalyst had been added, test samples remained clear when cooled to room temperature. At this point, the beaker was placed into a 25° C. water bath and the reaction product cooled to room temperature. The yield was almost quantitative. The product will be referred to hereinunder as "Epoxy-Trimer."

The trimer acid used was obtained commercially and was further identified as follows:

"Polymerized C-18 fatty acid containing about 91 percent by weight of trimer acid and about 5 percent by weight of dimer acid. Molecular weight approximately 900. Acid number 183 to 188, corresponding to a neutralization value of 299 to 306. Saponification number 192 to 198."

II. Thermohardenable asphalt-epoxy compositions

Having described above the preparation of the resinous constituent of the thermohardenable blends of the present invention, the following experimental results illustrate the unique performance of monoesters of polyalkylene glycols and higher fatty acids as compatibilizing agents for said thermohardenable blends. The results show further the superior characteristics of the hardened compositions.

The compositions were prepared by heating separately the epoxy-trimer to about 100° C. and the asphalt to about 150° C., mixing both components and adding the compatibilizing agent. Thereupon the mixture was heated at 160° C. for about one hour or more to effect cure. Proper cure was indicated by a rubber-like consistency at

both 150° C. and at room temperatures, while insufficient cure or total lack of it left the mixture more or less fluid. Table I lists compositions of widely different weight ratios and their behavior under curing conditions.

TABLE I

Dependency of curing characteristics on composition

Test Number-----	1	2	3	4	5	6	7
Composition (parts by weight):							
Asphalt-----	90	70	70	50	50	10	10
Epoxy-Trimer-----	10	30	30	50	50	90	90
Triethylene glycol monooleate-----	0 to 5	0	1 to 5	0	1 to 5	0	1 to 5
Stage of Cure-----	(1)	(1)	(2)	(1)	(2)	(1)	(2)

¹ Not cured.

² Cured.

Tests 1, 2, 4 and 6 showed that mixtures of asphalts and epoxy-trimer could not be cured without a compatibilizing agent. It was observed that in these cases the components separated leaving the asphalt as a liquid residue.

Test 1 showed further that, even with substantial amounts of a compatibilizing agent, compositions high in asphalt content cannot be cured.

Test 3 gave optimum results both from a standpoint of performance and economy, utilizing a relatively large proportion of asphalt, the latter being a very inexpensive constituent.

Three different grades of asphalt were used in each of the above tests, so that actually 21 tests were conducted. The asphalts were characterized by their penetration values as follows:

Asphalt A----- 33-40 penetration.
Asphalt B----- 85-100 penetration.
Asphalt C----- 500 flash stock.

To further identify and describe cured compositions comprising asphalts and epoxy-trimer, some physical properties were determined and compiled in Table II.

TABLE II

Physical properties of cured asphalt-trimer compositions

	1	2	3
Composition (parts by weight):			
Asphalt, 85-100 Penetration-----	100	50	25
Epoxy-Trimer-----		50	75
Triethylene Glycol Monooleate-----		3	3
Physical Properties:			
Tensile Strength, p.s.i. ¹ -----	(2)	400	480
Elongation, percent-----		170	140
Shore A Hardness-----	0	35	50

¹ Pounds per square inch.

² Not measurable.

In Table II, the physical properties of the cured asphalt-epoxy-trimer composition were contrasted with those of straight asphalt and demonstrate the superior performance of the former.

For a study of the penetration values, compositions of 70 parts by weight asphalt, 30 parts by weight epoxy-trimer and 3 parts by weight of triethylene glycol monooleate were cured for one hour at 160° C. Employing an asphalt of 105 penetration, the value of the cured material was lowered to 95 and, hence, also shows substantial improvement in regard to this property.

I claim:

1. A method of preparing cured asphalt-epoxy compositions having high resistance to hydrocarbon fuels and lubricating oils comprising mixing (1) a monoester of a polyalkylene glycol having a molecular weight not exceeding 1000 and a monocarboxylic fatty acid which contains at least 12 carbon atoms and at least one double bond per molecule, (2) asphalt and (3) the reaction product of a polymeric carboxylic fatty acid of at least 24 carbon atoms containing the dimer and trimer as major constituents and stoichiometric amounts of a polyglycidyl ether of a polyhydric phenol having an epoxy equivalent weight of up to 300, and heating the resulting blend at elevated temperatures to form a cured rubber-like product, the weight ratio of asphalt to said reaction product being between about 1 to 28 and about 3 to 1, the amount of said monoester ranging from about 1 to 14% based on the weight of asphalt and said reaction product.

2. The method of claim 1, wherein the monoesters of the polyalkylene glycols are monoesters of polyethylene glycols, the polyglycidyl ethers of polyhydric phenols are polyglycidyl ethers of p,p'-dihydroxy diphenyl dimethyl methane having epoxy equivalent weights of about 175 to about 300, and the weight ratios of the asphalt to said reaction product are between about 1 to 8 and about 3 to 1.

3. The method of claim 1, wherein the monoesters of the polyalkylene glycol are monooleates of polyethylene glycols, the glycol components having molecular weights up to about 600, the polyglycidyl ethers of polyhydric phenols are polyglycidyl ethers of p,p'-dihydroxy diphenyl dimethyl methane and have epoxy equivalent weights of about 175 to about 200, and the weight ratios of the asphalt to said reaction products are between about 3 to 1 and about 2 to 1.

4. The cured product produced according to claim 1.

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