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ASPHALT EMULSIONS AND METHOD FOR MAKING SAME

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ABSTRACT OF THE DISCLOSURE

Asphalt emulsions useful in paving, resurfacing and coating are prepared employing an anionic emulsifier formed by solvent refining a heavy cycle oil with a solvent selective for aromatic hydrocarbons, reacting the aromatic hydrocarbon extract with alkali metal and carboxylating the product to form the emulsifier.

This invention relates to a method for making an emulsion and the product thereof.

Heretofore when heavy cycle oils produced by cracking operations have been solvent extracted in order to separate out nonaromatic hydrocarbons, the aromatic hydrocarbon extract, which is an exceedingly complicated mixture of complex compounds, has been regarded as a waste product. Because no profitable method for disposing of these compounds is generally applicable, extraction is rarely employed and the compounds are generally recycled to extinction in a cracking operation, wherein they are substantially completely converted to coke, or are blended off in burning stocks, which they degrade.

Quite unexpectedly, it has been found that effective anionic emulsifiers for the preparation of asphalt emulsions are produced when the above aromatic hydrocarbon extract is treated by known methods to form partially hydrogenated alkali metal salts of the complex polynuclear, high molecular weight, aromatic and alkylaromatic hydrocarbons and heterocyclics present in the extract.

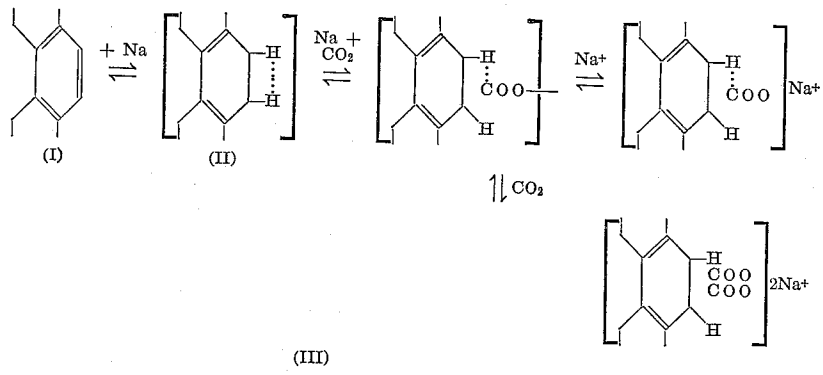
Accordingly, it is an object of this invention to provide a new and improved method for making emulsions. It is another object of this invention to provide effective anionic emulsifiers from heretofore waste hydrocarbons and heterocyclics.

Other aspects, objects and the several advantages of the invention will be apparent to those skilled in the art from the description and the appended claims.

According to this invention a heavy cycle oil is solvent refined with a solvent selective for aromatic hydrocarbons which extracts the predominantly aromatic hydrocarbons and heterocyclics from the paraffinic and naphthenic hydrocarbons and thereby forms a raffinate containing the paraffinic and naphthenic hydrocarbons

which raffinate is a preferred cracking stock and a complex polynuclear, aromatic hydrocarbon extract which extract was heretofore characterized as a waste product. The aromatic hydrocarbon extract is then reacted with an alkali metal, mixtures of alkali metals and amalgams of alkali metals to form alkali-aromatic hydrocarbon adducts. The adducts are then subjected to a carboxylation operation to add carboxyl groups to the alkali aromatic hydrocarbons thereby forming partially hydrogenated alkali metal salts of complex polynuclear, aromatic polycarboxylic acids. The alkali metal salts of the above complex aromatic polycarboxylic acids can be used as an anionic emulsifier or it can be acidified with a mineral acid to give partially hydrogenated carboxylic acids corresponding to the salts, which acids can then be utilized with an alkali metal base such as NaOH to form the metal salts in situ during the asphalt emulsion formulation operation.

Although not completely understood and therefore not desiring to be bound thereby it appears at present that what occurs in the above sequence of operations is represented by the following equation:



(I) Represents a portion of the complex polynuclear, aromatic hydrocarbons in the oil extract.

(II) Represents the adduct.

(III) Represents the carboxylated adduct, i.e. the alkali metal salts of complex polynuclear, aromatic polycarboxylic acids.

The emulsifiers of this invention can be utilized as a sole emulsifying agent wherein such use results in an anionic-type emulsion, i.e. one in which the dispersed droplets bear a negative charge. The emulsifiers of this invention can also be utilized in conjunction with other anionic emulsifiers, e.g. alkylaryl sulfonates, nonionic emulsifiers, e.g. the octylphenoxypoly(ethyleneoxy)ethanols, and amphoteric emulsifiers, e.g. N-substituted amino acid derivatives and mixtures of these emulsifiers. Other suitable emulsifiers are set forth in U.S. application Ser. No. 404,967, filed Oct. 19, 1964 and assigned to the same assignee.

The heavy cycle oils which can be utilized in the practice of this invention are generally those which can be extracted with a solvent selective for aromatic compounds to produce an aromatic hydrocarbon extract. More specifically, the cycle oils have the following properties: 400 to 1000° F. boiling range, 3 to 40° API gravity, −20 to 100° F. pour point, 1.460 to 1.630 refractive index, 0 to 2 weight percent sulfur, 20 to 100 Bureau of Mines Correlation Index (BMCI), and 130 to 400 molecular weight.

The general process of treating mineral oils to form solvent extracts of aromatic hydrocarbons is well known

in the art and generally comprises successive, countercurrent contacts of the mineral oil with at least one aromatic selective solvent. Examples of such solvents include liquid sulfur dioxide, dimethylsulfoxide, phenol, nitrobenzene, chlorophenol, trichloroethylene, cresylic acid, pyridine, furfural, 2,2'-dichloroethylether, liquid propane, cresol and mixtures thereof.

The aromatic hydrocarbon extracts utilized to form the emulsifiers of this invention have the following general properties and characteristics:

Properties and characteristics:	Range of values
Gravity, ° API	—5 to 20.
Molecular weight, average	130 to 300.
Boiling point (Initial), ° F.	400.
Sulfur, weight percent	0 to 4.
Sulfur Compound, weight percent	0 to 5.
Aromatics and thio compounds	70 to 100.
Thio compounds, volume percent	0 to 30.
Average number of rings/mean aromatic mol.	1.3 to 3.5.
H/C atom ratio, aromatic portion	1.5/1 to 1/0.8.
BMCI	70 to 120.

Although the preparation of the alkali metal aduct from the aromatic hydrocarbon extract can be achieved by methods known in the art since the preparation merely requires the reaction of the extract with an alkali metal, a preferred procedure is the reaction of from about 1 to about 40 weight percent of alkali metal based upon the amount of extract, with said extract at a temperature of from about —70 to 90° C., under pressures sufficient to keep the reactants liquid, and in the presence of a solvating organic reaction medium inert to alkali metal at reaction conditions. The alkali metal can be at least one metal selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, but is preferably sodium or potassium. Representative reaction solvents include dimethyl ether, methyl alkyl ethers, dialkyl glycol ethers, dialkyl polyethylene glycol ethers, tetrahydrofuran, methyl ethyl ketone, methylal, dioxane and trimethylamine. As a general rule water-soluble ethers are effective solvating media.

The formation of the alkali metal adduct is promoted by providing a high shear action, e.g. agitation, providing an excess of alkali metal with respect to that necessary to form the adduct, using a preformed dispersion of alkali metal in an inert organic solvent to provide a high alkali surface area, or using a performed dispersion of the alkali metal in a portion or all of the solvent extract. These techniques promote the formation of the adduct by overcoming the slowing of the reaction which results from initially formed adduct, coating the alkali metal and thereby preventing, at least for a certain amount of time, reaction of the alkali metal with the aromatic hydrocarbons present in the extract. Generally, any shearing device such as colloid mills, mullers, ball mills and the like, can be employed.

The color changes of the mixtures of extract, alkali metal and reaction solvent, for example from brown to black, indicate the progress of the reaction towards the formation of the alkali metal adduct.

The alkali metal adduct thus formed is then either separated from the unreacted oil in the extract or left therein and the mixture treated to a carboxylation operation.

Generally, any operation which will add carboxyl groups to the aromatic hydrocarbons which have reacted with the sodium to form the adduct can be employed. A preferred operation is treating the adduct either per se or in mixture with the unreacted oil, with an excess of gaseous or solid carbon dioxide at temperatures ranging from about —10° to —90° C. thereby causing a decrease in color, i.e. from black to tan. This operation forms the alkali metal salts of the complex polynuclear, aromatic polycarboxylic acids which can then be used as such as the emusifier of this invention.

It should be noted that the above alkali metal salt of the polycarboxylic acids can be acidified with a mineral acid, preferably HCl, to give an acid corresponding to the salt, which acid can then be employed together with an alkali metal base, such as an alkali metal hydroxide, during an asphalt emulsion formulation, thereby forming the metal salt emulsifier of this invention in situ. Of course, the acid can be reacted subsequently with an alkali metal base to again form the metal salt which salt can then be used in an emulsion formulation.

Generally, the emulsifiers of this invention can be employed in any emulsion employing a mixture of two immiscible liquids, one dispersed in the other in very fine droplet form, the most common of which relating to asphalt is the oil-in-dispersing liquid type. In the case of the oil-in-dispersing liquid type, asphalt is dispersed in an external, dispersing liquid phase. Although any type of dispersing liquid is applicable to this invention, the more common and the preferred dispersing liquid is water.

Although this invention is applicable to any type of asphalt that has been heretofore utilized in the preparation of emulsions including both natural asphalts and those derived from petroleum refining such as a steam refining and the like, the invention is particularly and preferably applicable to asphalts characterized by penetrations (ASTM D 5–61) from 0 to about 500, preferably from about 40 to about 300, and by softening points (ASTM D 36–26) in the range of from about 90 to about 250° F., preferably from about 100 to about 150° F.

The general process of emulsification involves controlled mixing of water, asphalt and emulsifying agent. The order of mixing or of premixing of the three materials and other additives if desired, such as naphtha solvent to add stability to the emulsion, does not now appear to be critical. With the aid of a high shear action the asphalt is broken up into fine droplets and dispersed in the water. Suitable shear actions are provided by simple mixers, centifugal pumps, homogenizers, colloid mills, mullers, ball mills, and the like.

The amount of emulsifier added will vary greatly and depend upon the type and amount of asphalt employed, the type and amount of dispersing liquid employed, the type of emulsion desired, e.g. rapid-, medium-, and slow-setting types, additional additives present, and conditions under which the emulsion is to be formed. Generally, all that is required is an amount of emulsifier effective to produce the desired emulsion. Generally, from about 0.5 to about 3.5 weight percent, preferably from about 0.9 to about 2.5 weight percent, of emulsifier can be employed.

The asphalt emulsions of this invention can be applied in paving, resurfacing, coating, etc., and will produce good uniform and smooth coatings. The emulsion can be mixed with siliceous aggregate, for example in the ratio of 0.5 to 5 parts emulsion to 4 to 10 parts siliceous aggregate, and the resulting slurry applied to the surface desired to be treated. After such application, the slurry sets in the usual manner to provide an adhering coating. The aggregate to be used preferably has a moisture content in the range of 5 to 20 percent, and dry aggregate can be prewet to provide this moisture content. In the "slurry seal" technique, the moist sand can be mixed with the asphalt emulsion to form a slurry of a consistency similar to that of a Portland cement mix. This slurry can be continuously dumped from a revolving drum mixer or other suitable mixing device onto a road surface, and as the paving vehicle proceeds along the road a rubber drag apron can be used to smooth the slurry to a uniform thickness. For this purpose, a graded sand aggregate containing more than 10 percent fines passing a 20 mesh sieve is preferred. At least 1½ to 2 minutes will be usallly required to mix the emulsion with the aggregate and spread the resulting slurry on the road surface before the emulsion breaks. In another application, the asphalt emulsion, sand, and Portland cement or diatomaceous earth can be applied to surfaces as a mixture by the "gunnite" method,

which is especially suited for coating canals, reservoirs, water ponds, dam facings, etc. Such application can be made with pneumatic-type spray equipment, such as a REFRACT-ALL GUN. Glass wool, rock wool, hemp, cotton, and other fibers can be added to the slurry or emulsion to provide coatings having higher tensile strength and which will not crack with shifting of the base or surface to which the cating is applied.

Example

A mixture of partially hydrogenated complex polynuclear, aromatic polycarboxylic acids was prepared by dispersing 50 grams of sodium in 220 grams of a complex polynuclear, aromatic extract separated from a heavy cycle oil having the following characteristics: API° gravity of 33.6, refractive index of 1.488, BMCI of 32.7, and molecular weight of 242. The extract was prepared from the above heavy cycle oil by continuous countercurrent extraction of the oil with sulfur dioxide followed by continuous countercurrent extraction of the sulfur dioxide extracted oil with dimethylsulfoxide. The dispersion of sodium in the extract was effected by mixing at about 220° F., i.e. slightly above the melting point of sodium. To 22.2 grams of the dispersion cooled to room temperature was added 220 ml. of tetrahydrofuran. The dispersion and tetrahydrofuran were mixed thoroughly to promote the formation of the sodium-aromatic adduct.

The solution of dispersion and tetrahydrofuran was chilled to about −80° F. and treated with a mixture of nitrogen-carbon dioxide which contained about 50 mol percent carbon dioxide to effect carboxylation and to form sodium salts of complex polynuclear, aromatic, polycarboxylic acids. Water was added to form an aqueous solution of the sodium salts of the aromatic, polycarboxylic acids and the resulting mixture of the aqueous solution of the sodium salts and unreacted aromatics was extracted with benzene to remove the unreacted aromatics and allow separation of the aqueous solution of the sodium salts.

The benzene was removed from the unconverted aromatics by heating and the thus-separated unconverted aromatics were dissolved in 220 ml. of tetrahydrofuran and cooled to −80° F. To the cooled solution 7.4 grams of a 1:1 sodium-xylene dispersion was added to form additional sodium-aromatic adduct, and the adduct was carboxylated with a nitrogen-carbon dioxide mixture to form additional sodium salts of complex polynuclear, aromatic, polycarboxylic acids. These additional sodium salts were separated from the remaining unreacted aromatics by the addition of water to form an aqueous solution of sodium salts and extraction with benzene as above and the second aqueous solution of sodium salts was added to the first aqueous solution of sodium salts to form a composite product. From the 22.2 grams of dispersion of sodium in polynuclear aromatics separated from the heavy cycle oil 16.4 grams, 78 percent conversion, of complex polynuclear, aromatic, polycarboxylic acids was recovered by acidifying the composite product with dilute aqueous hydrochloric acid.

The complex polynuclear, aromatic, polycarboxylic acids prepared above were used to prepare an emulsion, using the following recipe:

Emulsion components—	Parts by weight
Asphalt, ASTM D 5–61 penetration 85 to 100	62.3
Anhydrous sodium hydroxide	0.2
Complex polynuclear, aromatic, carboxylic acids prepared above	1.1
Soy flour (KAYSOY 220 D) (stabilizer)	0.2
Water (dispersing liquid)	36.2

The emulsion was prepared by adding a water solution of all ingredients except asphalt to the charge tank of a Manton-Gaulin colloid mill. The asphalt was heated to about 250° F. and added slowly while recirculating the aqueous phase through the mill. After asphalt addition was completed the stator-rotor spacing was adjusted to about 0.005 inch and milling was continued at about 190° F. for 3 to 4 minutes. The emulsion was stored in a capped container at 80° F. for 24 hours prior to use in aggregate mixing tests.

Aggregate mixing tests were made in a 4-inch diameter 6-inch deep container equipped with a 3-blade paddle stirrer powered by a variable speed motor. A 100-gram portion of Kenoyer sand was placed in the container and wetted with about 20 ml. of water while being stirred at low speed, after which stirring speed was increased to about 100 r.p.m.

The Kenoyer sand employed had the following characteristics:

Source	(1)
Sieve analysis, wt. percent:	
No. 10+	2.2
No. 20+	17.3
No. 40+	33.0
No. 60+	18.8
No. 100+	15.3
No. 200+	6.1
No. 200—	7.3
Surface area, No. 100— fines, $m.^2/gm.$	<5
Composition (X-ray diffraction, 100— fines):	
α-Quarts, SiO_2	+++
Dolomite, $CaMg(CO_3)_2$	+
Calcite, $CaCO_3$	+
Calcium in total aggregate as percent $CaCO_3$	3.6

[1] Baxter Springs, Kans.

From 18 to 20 grams of the asphalt emulsion was added rapidly to the wet sand, and a timer was started at the instant the emulsion contacted the sand. Mixing time was recorded at the time the mix could be stirred before the emulsion broke, as evidenced by solidification of the mix. By code standards the mixing time should be at least 100 seconds in order to permit adequate time for mixing and applying the mix to the working surface such as a road surface. Mixing time for the emulsion so prepared was greater than 200 seconds and the slurry appearance was excellent.

Reasonable variations and modifications of this invention can be made, or followed, in view of the foregoing without departing from the spirit or scope thereof.

We claim:

1. A method for making an asphalt emulsion comprising contacting asphalt, an aqueous dispersing liquid and an effective emulsifying amount of an emulsifying agent comprising partially hydrogenated alkali metal salts of complex polynuclear, aromatic, polycarboxylic acids prepared by reacting an aromatic hydrocarbon extract produced in the solvent refining of heavy cycle oils produced from cracking fractions of crude mineral oils with a solvent selective for aromatic compounds, with at least one alkali metal to produce alkali metal adducts and carboxylating said adducts, mixing said contacted materials to form an emulsion, and recovering said emulsion.

2. A method for making an asphalt emulsion comprising contacting asphalt, an aqueous dispersing liquid and an effective emulsifying amount of an emulsifying agent comprising alkali metal salts of complex polynuclear, aromatic, polycarboxylic acids prepared by extracting a heavy cycle oil having the characteristics of 400 to 1000° F. boiling range, 3 to 40° API gravity, −20 to 100° F. pour point, 1.460 to 1.630 refractive index, 0 to 2 weight percent sulfur, 20 to 100 Bureau of Mines Correlation Index (BMCI), and 130 to 400 molecular weight with a solvent selective for aromatic compounds to form an extract having the characteristics of −5 to 20° API gravity, 130 to 300 molecular weight, 400° F. initial boiling point, 0 to 4 weight percent sulfur, 0 to 5 weight percent sulfur compound, 70 to 100 aromatics and thio compounds, 0 to 30 volume percent thio compounds, 1.3 to

3.5 average number of rings/mean aromatic mol, 1.5/1 to 1/0.8 aromatic portion H/C atom ratio, 70 to 120 Bureau of Mines Correlation Index (BMCI), reacting the aromatic hydrocarbon extract thus formed with an alkali metal to form alkali metal adducts and carboxylating the adducts, mixing said contacted materials to form an emulsion, and recovering said emulsion.

3. The method of claim 2 wherein said dispersing liquid is water.

4. The method of claim 2 wherein there is also present an effective emulsifying amount of at least one emulsifying agent selected from the group consisting of anionic, nonionic and atmphoteric emulsifying agents, and the emulsifying agent described in claim 2 is employed in an amount of from about 0.5 to about 3.5 weight percent.

5. A method for making an asphalt emulsion comprising contacting asphalt, an aqueous dispersing liquid, and an effective emulsifying amount of an emulsifier formed from an alkali metal base with a partially hydrogenated complex polynuclear, aromatic, polycarboxylic acids prepared by reacting extracts produced in extracting mineral lubricating oils with a solvent selective for aromatic compounds, with at least one alkali metal to form alkali metal adducts, carboxylating the adducts to form alkali metal salts of said acid and acidizing the resulting salts to form the complex polynuclear, aromatic, polycarboxylic acids, mixing said contacted materials to form an emulsion, and recovering said emulsion.

6. The method of claim 5 wherein the dispersing liquid is water, the alkali metal base is sodium hydroxide and the alkali metal is sodium.

7. An asphalt emulsion consisting essentially of asphalt, an aqueous dispersing liquid, and an effective emulsifying amount of an emulsifying agent comprising a partially hydrogenated alkali metal salt of complex polynuclear, aromatic, polycarboxylic acids prepared by reacting an aromatic hydrocarbon extract produced in the solvent refining of heavy cycle oils produced from cracking fractions of crude mineral oils with a solvent selective for aromatic compounds, with at least one alkali metal to produce alkali metal adducts and carboxylating said adducts.

8. The asphalt emulsion of claim 7 wherein the amount of emulsifying agent present is from about 0.5 to about 3.5 weight percent.

9. The asphalt emulsion according to claim 7 wherein said aqueos dispersing liquid is water and said emulsifying agent is prepared by extracting a heavy cycle oil having the characteristics of 400 to 1000° F. boiling range, 3 to 40° API gravity, —20 to 100° F. pour point, 1.460 to 1.630 refractive index, 0 to 2 weight percent sulfur, 20 to 100 Bureau of Mines Correlation Index (BMCI), and 130 to 400 molecular weight with a solvent selective for aromatic compounds to form an extract having the characteristics of —5 to 20° API gravity, 130 to 300 molecular weight, 400° F. initial boiling point, 0 to 4 weight percent sulfur, 0 to 5 weight percent sulfur compound, 70 to 100 aromatics and thio compounds, 0 to 30 volume percent thio compounds, 1.3 to 3.5 average number of rings/mean aromatic mol, 1.5/1 to 1/0.8 aromatic portion H/C atom ratio, 70 to 120 Bureau of Mines Correlation Index (BMCI), reacting the aromatic hydrocarbon extract thus formed with an alkali metal to form alkali metal adducts and carboxylating the adducts.

10. The asphalt emulsion according to claim 7 wherein said aqueous dispersing liquid is water, and said emulsifying agent is prepared by reacting extracts produced in extracting mineral lubricating oils with a solvent selective for aromatic compounds with at least one alkali metal to form alkali metal adducts, carboxylating the adducts to form alkali metal salts of said acids and acidizing the resulting salts to form a complex polynuclear, aromatic, polycarboxylic acid.

11. The asphalt emulsion according to claim 10 wherein the alkali metal base is sodium hydroxide and the alkali metal is sodium.

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