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3,033,088

COMPOSITION COMPRISING A COAL PRODUCT, A POLYEPOXIDE AND ABRASIVE PARTICLES AND PROCESS FOR TREATING SURFACES THEREWITH

Clifford V. Wittenwyler, Union, N.J., assignor to Shell Oil Company, a corporation of Delaware
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This invention relates to new surfacing compositions. More particularly, the invention relates to new surfacing compositions containing products derived from coal which are particularly useful as non-skid coatings for concrete, asphalt, wood and steel.

Specifically, the invention provides new and particularly useful surface coating compositions comprising a product derived from coal of the group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and a solubility in carbon disulfide of at least 50%, a polyepoxide possessing more than one vic-epoxy group, and at least 50% by weight of the combined mixture of small inert particles. The invention further provides a process for using these compositions in the treatment of concrete, asphalt, wood and steel surfaces.

There is a growing need for a cheap surface coating composition that can be applied to concrete and asphalt road surfaces and exposed metal in bridges, etc. to reduce their tendency to skid when wet. In the case of asphalt surfaces, there is also a need for coatings which would have improved resistance to solvents and other chemicals. This is particularly urgent in the case of asphalt runways for jet aircraft as the jet fuels now available readily attack asphalt surfaces. In view of the increased cost of resurfacing and rebuilding roads and runways, it would also be desirable to have a coating which would help reduce the destruction of the road and runway due to wear, rain, deicing salts and cold weather.

Various coatings have been suggested for the above purposes, but heretofore they have not proved very satisfactory. In many cases, the coatings failed to have the necessary adhesion to the grit, concrete, asphalt and metal surfaces, particularly if they were oily or dirty. In other cases, the coatings failed to stand up under inclement weather conditions. In still other cases, the coatings failed to have the necessary resistance to solvents and chemicals and failed to have the desired wear and non-skid properties. In other cases, the coatings were too difficult or expensive to apply.

It is an object of the invention, therefore, to provide a new class of surfacing compositions. It is a further object to provide new non-skid surfacing compositions which form coatings having excellent adhesion to concrete, asphalt, wood and metal surfaces. It is a further object to provide new surfacing compositions which form coatings having excellent skid-resistance and are resistant to wear, rain and cold weather. It is still a further object to provide a coating which has good resistance to solvents, deicing salts and acids. It is a further object to provide new road coatings which are relatively inexpensive and can be easily applied to new or old road surfaces. Other objects and advantages of the invention will be apparent from the following detailed description thereof.

It has now been discovered that these and other objects may be accomplished by the surfacing compositions of the invention comprising a mixture of a product derived from coal of the group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and a solubility in carbon disulfide of at least 50%, a polyepoxide possessing more than one

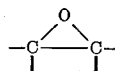
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vic-epoxy group and at least 50% by weight of the combined mixture of small inert particles. It has been found that these compositions can be easily applied to all types of surfaces, and particularly to concrete, asphalt, wood or metal surfaces, and can be cured thereon to form hard tough coatings. The coatings have been found to have excellent adhesion to these surfaces, and stand up well after long periods even if surfaces were oily or dirty before application. The coatings also show excellent resistance to hot and cold weather conditions. In addition, these new coatings display excellent resistance to solvents, deicing salts, acids and various types of jet fuels. The coatings are particularly attractive in that they may be applied to old or new road beds or runways and set up very quickly without the use of any special curing conditions. As noted hereinafter, these compositions have been found to be useful not only for the treating of highway road surfaces, but are equally valuable for coating of dock areas, warehouse floors, sidewalks, tennis courts, ship decks and the like where the non-skid weather resistance properties are desirable.

The products derived from coal which are used in preparing the compositions of the invention comprise the coal tars, refined coal tars and coal tar pitches which have a softening point below 190° F. and a solubility in carbon disulfide of at least 50%. The expression "tar" as used herein refers to products obtained in connection with the destructive distillation of coal. When part of the volatile material is removed, the residue is called "refined coal tar." When additional volatile material is removed, the residue is termed "coal tar pitch." Residuals having a fusing point below 70° F. are referred to herein as refined coal tars while those having fusing points 70° F. or above are coal tar pitches. As used herein, "softening point" or "fusing point" refer to values obtained by the cube method as described in vol. II, Abraham, "Asphalts and Allied Substances," 5th edition. The coal products should possess at least 50% and preferably 75% solubility in carbon disulfide. The coal tar, refined coal tar and cold tar pitch may be acidic, basic or neutral, depending on whether the acid and/or bases have been removed. These coal products may be obtained from various types of bituminous coals, such as, for example, cannel, bog-heat, tarbonite, and the like, and may be derived from various processes, such as from gas works, coke ovens, blast furnaces, gas producers and various low temperature processes. Description of examples of various coal tars, refined coal tars and coal tar pitches may be found on pages 384 to 405 of Abraham, "Asphalts and Allied Substances," 5th edition, vol. I, Van Nostrand Co., Inc.

Particularly preferred coal derivatives to be used in preparing the compositions of the present invention include the residuals resulting from distillation of coal tar, and preferably refined coal tars having a fusing point of below 70° F. and a solubility in carbon disulfide of at least 75% with a specific gravity of 1.10 to 1.50, and low melting coal tar pitches having a fusing point below 120° F. and a solubility in carbon disulfide of at least 75%.

The polyepoxide materials to be added to the compositions of the invention comprise those organic materials having more than one vicinal epoxy group, i.e. more than one



group, which may be in a terminal or internal position. The polyepoxides may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted if desired with substituents, such as chlorine

atoms, hydroxyl groups, ether radicals, and the like. They may also be monomeric or polymeric.

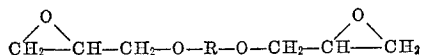
For clarity, many of the polyepoxides and particularly those of the polymeric type will be described throughout the specification and claims in terms of epoxy equivalent value. The meaning of this expression is described in U.S. 2,633,458.

If the polyepoxide material consists of a single compound and all of the epoxy groups are intact, the epoxy equivalency will be integers, such as 2, 3, 4 and the like. However, in the case of the polymeric type polyepoxides many of the materials may contain some of the monomeric monoepoxides or have some of their epoxy groups hydrated or otherwise reacted and/or contain macromolecules of somewhat different molecular weight so the epoxy equivalent values may be quite low and contain fractional values. The polymeric material may, for example, have epoxy equivalent values, such as 1.5, 1.8, 2.5 and the like.

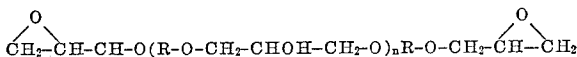
Examples of the polyepoxides include, among others, epoxidized triglycerides as epoxidized glycerol trioleate and epoxidized glycerol trilinoleate, the monoacetate of epoxidized glycerol dioleate, 1,4-bis(2,3-epoxypropoxy)-benzene, 1,3-bis(2,3-epoxypropoxy)benzene, 4,4'-bis(2,3-epoxypropoxy)diphenyl ether, 1,8-bis(2,3-epoxypropoxy)-octane, 1,4-bis(2,3-epoxypropoxy)cyclohexane, 4,4'-bis(2-hydroxy-3,4'-epoxybutoxy)diphenyl dimethylmethane, 1,3-bis(4,5-epoxypentoxo)-5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, 1,3-bis(2-hydroxy-3,4-epoxybutoxy)benzene, 1,4-bis and (2-hydroxy-4,5-epoxypentoxo)benzene.

Other examples include the epoxy polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with a halogen-containing epoxide or dihalohydrin in the presence of an alkaline medium. Polyhydric phenols that can be used for this purpose include among others resorcinol, catechol, hydroquinone, methyl resorcinol, or polynuclear phenols, such as 2,2-bis(4-hydroxyphenyl)propane (Bisphenol-A), 2,2-bis(4-hydroxyphenyl)butane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)pentane, and 1,5-dihydroxynaphthalene. The halogen-containing epoxides may be further exemplified by 3-chloro-1,2-epoxybutane, 3-bromo-1,2-epoxyhexane, 3-chloro-1,2-epoxyoctane, and the like.

The monomer products produced by this method from dihydric phenols and epichlorohydrin may be represented by the general formula



wherein R represents a divalent hydrocarbon radical of the dihydric phenol. The polymeric products will generally not be a single simple molecule but will be a complex mixture of glycidyl polyethers of the general formula



wherein R is a divalent hydrocarbon radical of the dihydric phenol and n is an integer of the series 0, 1, 2, 3, etc. While for any single molecule of the polyether n is an integer, the fact that the obtained polyether is a mixture of compounds causes the determined value for n to be an average which is not necessarily zero or a whole number. The polyethers may in some cases contain a very small amount of material with one or both of the terminal glycidyl radicals in hydrated form.

The aforescribed preferred glycidyl polyethers of the dihydric phenols may be prepared by reacting the required proportions of the dihydric phenol and the epichlorohydrin in an alkaline medium. The desired alkalinity is obtained by adding basic substances, such as sodium or potassium hydroxide, preferably in stoichiometric excess to the epichlorohydrin. The reaction is

preferably accomplished at temperatures within the range of from 50° C. to 150° C. The heating is continued for several hours to effect the reaction and the product is then washed free of salt and base.

The preparation of some of the glycidyl polyethers of dihydric phenols will be illustrated below. Unless otherwise specified, parts indicated are parts by weight.

PREPARATION OF GLYCIDYL POLYETHERS OF DIHYDRIC PHENOLS

Polyether A.—About 2 moles of 2,2-bis(4-hydroxyphenyl)propane was dissolved in 10 moles of epichlorohydrin and 1% to 2% water added to the resulting mixture. The mixture was then brought to 80° C. and 4 moles of solid sodium hydroxide added in small portions over a period of about 1 hour. During the addition, the temperature of the mixture was held at about 90° C. to 110° C. After the sodium hydroxide had been added, the water formed in the reaction and most of the epichlorohydrin was distilled off. The residue that remained was combined with an approximately equal quantity by weight of benzene and the mixture filtered to remove the salt. The benzene was then removed to yield a viscous liquid having a viscosity of about 150 poises at 25° C. and a molecular weight of about 350 (measured ebullioscopically in ethylene dichloride). The product had an epoxy value eq./100 g. of 0.50 so the epoxy equivalency was 1.75. For convenience, this product will be referred to hereinafter as polyether A. A low viscosity portion of polyether A is generally preferred for the application of the present invention.

Polyether B.—A solution consisting of 11.7 parts of water, 1.22 parts of sodium hydroxide, and 13.38 parts of 2,2-bis(4-hydroxyphenyl)propane was prepared by heating the mixture of ingredients to 70° C. and then cooling to 46° C. at which temperature 14.06 parts of epichlorohydrin was added while agitating the mixture. After 25 minutes had elapsed, there was added during an additional 15 minutes' time a solution consisting of 5.62 parts of sodium hydroxide in 11.7 parts of water. This caused the temperature to rise to 63° C. Washing with water at a temperature of 20° C. to 30° C. was started 30 minutes later and continued for 4½ hours. The product was dried by heating to a final temperature of 140° C. in 80 minutes, and cooled rapidly. At room temperature, the product was an extremely viscous semi-solid having a melting point of 27° C. by Durrant's Mercury Method and a molecular weight of 483. The product had an epoxy value eq./100 g. of 0.40. For convenience, this product will be referred to as polyether B.

Preferred members of the above-described group of polyepoxides are the glycidyl polyethers of the dihydric phenols, and especially 2,2-bis(4-hydroxyphenyl)propane, having an epoxy equivalency between 1.0 and 2.0 and a molecular weight between 300 and 900. Particularly preferred are those having a Durrant's Mercury Method softening point no greater than 60° C.

The glycidyl polyethers of polyhydric phenols obtained by condensing the polyhydric phenols with epichlorohydrin as described above are also referred to as "ethoxylene" resins. See Chemical Week, vol. 69, page 27, for September 8, 1951.

Another group of polyepoxides that may be used in preparing the emulsions comprises the glycidyl ethers of novalac resins which resins are obtained by condensing an aldehyde with a polyhydric phenol. A typical member of this class is the epoxy resin from formaldehyde 2,2-bis(4-hydroxyphenyl)propane novalac resin.

A further group of polyepoxides comprises the polyepoxy polyethers obtained by reacting, preferably in the presence of an acid-acting compound, such as hydrofluoric acid, one of the afore-described halogen-containing epoxides with a polyhydric alcohol, and subsequently treating the resulting product with an alkaline component. As used herein and in the claims, the expression "polyhydric alcohol" is meant to include those com-

pounds having at least two free alcoholic OH groups and includes the polyhydric alcohols and their ethers and esters, hydroxy-aldehydes, hydroxy-ketones, halogenated polyhydric alcohols, and the like. Polyhydric alcohols that may be used for this purpose may be exemplified by glycerol, propylene glycol, ethylene glycol, diethylene glycol, butylene glycol, hexanetriol, sorbitol, mannitol, pentaerythritol, polyallyl alcohol, polyvinyl alcohol, inositol, trimethylolpropane, bis(4-hydroxycyclohexyl) dimethylmethane, 1,4-dimethylolbenzene, 4,4'-dimethyloldiphenyl, dimethyltoluenes, and the like.

The preparation of some of these polyepoxy polyethers may be illustrated by the following:

PREPARATION OF GLYCIDYL POLYETHERS OF POLYHYDRIC ALCOHOLS

Polyether C.—About 276 parts (3 moles) of glycerol was mixed with 832 parts (9 moles) of epichlorohydrin. To this reaction mixture was added 10 parts of diethyl ether solution containing about 4.5% boron trifluoride. The temperature of this mixture was between 50° C. and 75° C. for about 3 hours. About 370 parts of the resulting glycerol-epichlorohydrin condensate was dissolved in 900 parts of dioxane containing about 300 parts of sodium aluminate. While agitating, the reaction mixture was heated and refluxed at 93° C. for 9 hours. After cooling to atmospheric temperature, the insoluble material was filtered from the reaction mixture and low boiling substances removed by distillation to a temperature of about 150° C. at 20 mm. pressure. The polyglycidyl ether, in amount of 261 parts, was a pale yellow viscous liquid. It had an epoxide value of 0.671 eq./100 g. and the molecular weight was 324 as measured ebullioscopically in the dioxane solution. The epoxy equivalency of this product was 2.13. For convenience, this product will be referred to hereinafter as polyether C.

Particularly preferred members of this group comprise the glycidyl polyethers of aliphatic polyhydric alcohols containing from 2 to 10 carbon atoms and having from 2 to 6 hydroxyl groups and, more preferably, the alkane polyols containing from 2 to 8 carbon atoms and having from 2 to 6 hydroxyl groups. Such products preferably have an epoxy equivalency greater than 1.0, and still more preferably between 1.1 and 4 and a molecular weight between 300 and 1000.

Another group of polyepoxides includes the epoxy esters of polybasic acids, such as diglycidyl phthalate and diglycidyl adipate, diglycidyl tetrahydrophthalate, diglycidyl maleate, epoxidized dimethylaliphthalate and epoxidized dicrotyl phthalate.

Other polyepoxide compounds include the polymers and copolymers of the epoxy-containing monomers possessing at least one polymerizable ethylenic linkage, such as, for example, allyl glycidyl ether. When this type of monomer is polymerized in the substantial absence of alkaline or acidic catalysts, such as in the presence of heat, oxygen, peroxy compound, actinic light, and the like, it undergoes additional polymerization at the multiple bond leaving the epoxy group unaffected. These monomers may be polymerized with themselves or with other ethylenically unsaturated monomer, such as styrene, vinyl acetate, methacrylonitrile, acrylonitrile, vinyl chloride, vinylidene chloride, methyl acrylate, methyl methacrylate, diallyl phthalate, vinyl allyl phthalate, divinyl adipate, chlorallyl acetate, and vinyl methallyl pimelate. Illustrative examples of these polymers include poly(allyl 2,3-epoxypropyl ether), poly(2,3-epoxypropyl crotonate), allyl 2,3-epoxypropyl ether-styrene copolymer, methallyl 3,4-epoxybutyl ether-allyl benzoate copolymer, poly(vinyl 2,3-epoxypropyl ether), allyl glycidyl ether-vinyl acetate copolymer and poly(4-glycidylstyrene).

These polymers are preferably prepared by heating the monomer of monomers in bulk or in the presence of an inert solvent, such as benzene, in the presence of air or a peroxy catalyst, such as ditertiary-butyl peroxide, at temperatures ranging from 75° C. to 200° C.

The preparation of polymers of this type may be illustrated by the following example showing the preparation of poly(allyl glycidyl ether).

PREPARATION OF POLYMERS OF UNSATURATED GLYCIDYL ETHERS

Polyether D.—About 100 parts of allyl glycidyl ether was heated at 155° C. in a glass flask and ditertiary-butyl peroxide added incrementally for 15 hours until 3% had been added. Excess monomer was removed, leaving 36 g. of polymer. The poly(allyl glycidyl ether) obtained as the resulting product had a molecular weight of about 481-542 and an epoxy value of 0.50 eq./100 g. and a viscosity of 15 poises. For convenience, this product will be referred to hereinafter as polyether D.

Particularly preferred members of the above-described group comprise the polymers and copolymers of the 2-alkenyl glycidyl ethers having a molecular weight between 300 and 1000 and an epoxy equivalency greater than 1.0 and preferably between 1.2 and 6.0.

Other examples include those polyepoxides having one or more internal epoxy groups, such as vinyl cyclohexene dioxide, epoxidized unsaturated esters as epoxidized tetrahydrobenzyl tetrahydrobenzoate, epoxidized dicrotyl phthalate, epoxidized 2,2-bis(cyclohexenyl)propane, epoxidized ethylene glycol dicyclohexenecarboxylate and the like.

The small particles present in the compositions of the invention may be particles of any inert solid material. The particles should be rather finely divided and preferably have a mesh size varying from 20 to 300. Preferred materials include sand, finely divided rocks, finely divided shells, crushed quartz, aluminum oxide, finely divided resinous particles, and the like. Particularly preferred are the mineral, and especially the siliceous materials, such as, for example, sand and ground rock. Mixtures of various types of particles may also be used.

The ratio of the coal products and the polyepoxide in the composition may vary depending upon the properties desired in the resulting product. Compositions having the above-described unexpected properties, such as excellent adhesion and improved weather resistance and solvent resistance, are obtained when the coal products and polyepoxides are combined in a ratio varying from about 15:1 to 1:15. Particularly good results are obtained when the coal products and polyepoxides are combined in weight ratios varying from about 5:1 to 1:5. Especially preferred ratios vary from 6:4 to 4:6.

The amount of the inert particles present in the composition should be at least 50% by weight of the total mixture of coal product and polyepoxide and should preferably be between 70% and 500% by weight of the total mixture.

The compositions may be prepared by any suitable method. The coal products and the polyepoxides are preferably both liquids and in that case the compositions may be prepared by simply mixing the two components together with or without the application of heat. If one or more of the components are thick liquids or solids, it is generally preferred to heat them before or during the mixing. Various solvents or diluents which will evaporate before or during cure may be added to assist in the preparation of the mixture, but the addition of these materials is not generally desirable as it usually lengthens the time of cure of the finished product. Suitable solvents include alcohols, such as isopropyl, butyl and amyl alcohol; ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, isophorone; esters, such as ethyl acetate, butyl acetate, Cellosolve acetate (ethylene glycol monoacetate); hydrocarbons, such as xylene, benzene, and the like; cyano-substituted hydrocarbons, such as propionitrile, adiponitrile, acetonitrile, acrylonitrile, and the like, and mixtures thereof. It is also convenient in some cases where employing solid polyepoxides to em-

ploy liquid polyepoxides, such as normally liquid glycidyl polyethers of polyhydric alcohols, as the diluent.

The inert particles may be added to the composition before it is applied to the desired surface, or the coal product-polyepoxide mixture may be first applied to the surface and then the inert particles placed in the coating so that they become imbedded in the mixture. Thus, in coating highway surfaces, the coal product-polyepoxide mixture may be applied directly to the road surface and then the inert particles, such as sand, may then be sprinkled onto the coating before it is cured.

The composition of the invention is cured by the action of a curing agent. For this purpose, epoxy curing agents, which may be acidic, neutral or alkaline, are added. Examples of the curing agents include, among others, alkalies like sodium or potassium hydroxides; alkali phenoxides like sodium phenoxide; carboxylic acids or anhydrides, such as formic acid, oxalic acid or phthalic anhydride; dimer or trimer acids derived from unsaturated fatty acids, 1,20-eicosanedioic acid, and the like. Friedel-Crafts metal halides like aluminum chloride, zinc chloride, ferric chloride; salts, such as zinc fluoborate, magnesium perchlorate and zinc fluosilicate; phosphoric acid and partial esters thereof including n-butyl ortho-phosphate, diethyl ortho-phosphate and hexaethyltetraphosphate; amino compounds, such as, for example, diethylene triamine, triethylene tetramine, dicyandiamide, melamine, pyridine, cyclohexylamine, benzyldimethylamine, benzylamine, diethylaniline, triethanolamine, piperidine, tetramethylpiperazine, N,N-dibutyl-1,3-propane diamine, N,N-diethyl-1,3-propane diamine, 1,2-diamino-2-methylpropane, 2,3-diamino-2-methylbutane, 2,4-diamino-2-methylpentane, 2,4-diamino-2,6-dimethyloctane, dibutylamine, diethylamine, dinonylamine, distearylamine, diallylamine, dicyclohexylamine, methylethylamine, ethylcyclohexylamine, o-tolyl-naphthylamine, pyrrolidine, 2-methylpyrrolidine, tetrahydropyridine, 2-methylpiperidine, 2,6-dimethylpiperidine, diaminopyridine, tetramethylpentane, meta-phenylene diamine, and the like, and soluble adducts of amines and polyepoxides and their salts, such as described in U.S. 2,651,589 and U.S. 2,640,037.

Preferred curing agents are the polycarboxylic acid anhydrides, the primary and secondary aliphatic, cycloaliphatic and aromatic amines and adducts of the amines and polyepoxides.

The amount of the curing agent employed will vary depending upon the type of agent selected. In general, the amount of the curing agent will vary from about 0.5% to 200% by weight of the polyepoxide. The tertiary amines and BF_3 complexes are preferably employed in amounts varying from about 0.5% to 20% and the metal salts are preferably employed in amounts varying from about 1% to 15%. The secondary and primary amines, acids and anhydrides are preferably employed in at least stoichiometric amounts, i.e., sufficient amount to furnish one amine hydrogen or one carboxyl group or anhydride group for every epoxy group, and more preferably stoichiometric ratios varying from 1:1 to 1:1.5.

The curing agents may be added to the compositions at any time. It is generally preferred to prepare the coal product-polyepoxide compositions and the curing agents as separate packages and then mix the two just before application to the desired surface. The curing agent may also be sprayed or otherwise applied to the coating of the coal product-polyepoxide mixture after it has been applied to the desired surface, but this procedure is less preferred. It is possible also to add the curing agent to the coal tar product before combining with the polyepoxide. In the case of the amine curing agents, it is sometimes preferred to make a precondensate or adduct of the amine and coal tar prior to combination with the polyepoxide.

The compositions of the invention may be applied to any surface but are particularly suitable for use as surfacing compositions for concrete, asphalt, wood and steel.

The concrete may be of any of the usual types such as may be prepared from hydraulic cements, such as Portland cement, and other types as aluminous and oxy salt type cements. The asphalt surfaces may be those prepared from straight run asphalts or further refined or modified asphalts. The compositions may be applied in very thin coatings or in very thick coatings as shown in Example V.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific compounds or conditions recited therein. Unless otherwise specified, parts disclosed in the examples are parts by weight.

Concrete used in the examples was prepared from hydraulic cement (Portland cement) aggregate containing sand, and water.

Example I

This example illustrates the preparation and some of the properties of a non-skid surfacing composition prepared from a coal tar pitch having a melting point of 77° F., a specific gravity of 1.25 (25°/25° C.) and solubility in carbon disulfide of 86.5%, and polyether B described above.

The coal tar pitch described above was heated to 100° F. Polyether B was then added to the coal tar pitch so as to form a composition having the coal tar pitch and polyether B in a weight ratio of 10:9. 1 part per 9 parts of polyether B of diethylene triamine was then added and 80 parts of the mixture combined with 80 parts of crushed quartz.

This mixture was then spread (at a rate of about 2 lbs. per square yard) on concrete panels some of which had been freshly prepared and some of which had been soiled with oil. In a short period at room temperature, the compositions set up to very hard tough solvent-resistant coatings. The coatings adhered well to the fresh concrete as well as the oil stained concrete. The coating on the oily concrete failed at 550 p.s.i. in block shear as compared to a coating prepared from straight polyether B which failed at 48 p.s.i. The coatings had good resistance to change in weather as shown by tests wherein the coated concrete blocks were subjected to wide changes in temperature and placed in contact with water. In most cases the concrete cracked before the coatings. Samples of the above composition have also been placed on portions of well traveled highways in the East. The test samples show excellent non-skid resistance when wet and excellent wear resistance.

Example II

This example illustrates the preparation and some of the properties of a non-skid coating composition prepared from a refined coal tar having a specific gravity at 25° C. of 1.210, a specific viscosity Engler 50/50 of 26.4, and a solubility in carbon disulfide of 90.2% and polyether A.

The refined coal tar described above was mixed with polyether A to form a composition having the refined coal tar and polyether A in a weight ratio of 9:10. 10 parts per 100 parts of polyether A of diethylene triamine was then added and 80 parts of the mixture combined with 80 parts of crushed quartz.

This mixture was then spread on concrete panels some of which had been freshly prepared and some of which had been stained with oil and excess crushed quartz added. In a short period at room temperature, the compositions set up to very hard, tough, solvent-resistant coatings. The coatings adhered well to the fresh concrete as well as the oil stained concrete. The coatings had good resistance to change in weather as shown by tests wherein the coated blocks were subjected to rapid changes in temperature and placed in contact with water. Testing of samples placed on highway strips indicates that the coatings have excellent non-skid properties when wet.

Related results are obtained when the above-described coating is applied to asphalt, steel and wood.

Example III

This example illustrates the preparation and some of the properties of a non-skid coating prepared from a refined coal tar having a fusing point below 40° F., 5–20% tar acids and 80% solubility in carbon disulfide and polyether B.

The coal tar described above and polyether B were combined in a weight ratio of 12:7. 0.9 part of diethylene triamine was then added and 80 parts combined with 80 parts of crushed quartz.

This mixture was spread on concrete panels some of which had been freshly prepared and some of which had been stained with oil. In a short period at room temperature, the compositions set up to very hard, tough, solvent-resistant coatings. The coatings adhered well to the fresh concrete as well as the oil stained concrete. The coatings also had good resistance to change in weather as indicated by tests wherein the coated concrete blocks were subjected to wide changes in temperature and placed in contact with water. Samples of the above composition were placed on strips of highway and after 6 months the coatings still displayed excellent wear resistance and non-skid properties.

Example IV

A mixture of 60% low viscosity polyether A (Epon resin 820) and refined coal tar having a specific viscosity (Engler) of 50 at 40° C. and a solubility of at least 70% in carbon disulfide cut with xylene and catalyzed with 12 parts per hundred parts of resin of triethylene tetramine was sprayed with a spray nozzle at 100 p.s.i. The mixture was applied over smooth concrete at a rate of 1 pound per square yard. Before the hardening was complete, 30 mesh aluminum oxide was strewn over the surface. When curing was complete, the excess aluminum oxide was removed leaving a rough textured, though even, surface on the concrete. This wearing course showed little effect of wear after six weeks on one of the busiest highways in the United States (U.S. Route 22).

Quarter-inch coatings of the above compositions were applied to concrete blocks, sprinkled with aluminum oxide and cured. The coatings on clean concrete had a shear strength of 700 p.s.i. and on oily concrete a shear strength of 500 p.s.i. Similar coatings containing polyether A on oily concrete had a shear strength of only 50 p.s.i. and coatings containing only a polyester resin on clean concrete had a shear strength of 20 p.s.i.

Example V

This example illustrates the formation of a thick road-way facing.

A mixture composed of equal parts by weight of low viscosity polyether A and refined coal tar having a fusing point below 70° F. and a solubility in carbon disulfide of at least 70% was combined with 12 parts per hundred parts of resin of diethylene triamine and this mixture combined with an equal weight of crushed quartz. When the mixing was complete, the composition was applied at a rate of 10 lbs. per square yard on a concrete surface with screeds and/or trowels. After an even layer was applied, additional crushed quartz was sprinkled over the surface and rolled with a lawn roller to gain greater compaction. After hardening was complete, the excess grit was swept off. This material applied to one of New York city's busiest bridges (Triborough) has shown no sign of wear after three months.

Example VI

A series of surfacing compositions was prepared as follows: 100 parts of each of the coal tar products A to I listed below was combined with 100 parts of low viscosity polyether A and 12 parts per hundred of resin of diethylene triamine. 80 parts of each of the mixtures was

combined with 80 parts of crushed quartz. Gel times for the mixtures ranged from 44 minutes to 80 minutes with peak exotherm ranging from 151° F. to 183° F. The mixtures were spread on concrete blocks and excess crushed quartz added. The compositions set up to very hard, tough, solvent-resistant coatings.

COAL TAR PRODUCTS

- A. Refined coal tar having a melting point below 70° F. and a solubility in carbon disulfide of at least 80%.
- B. Refined coal tar product derived by removing acids from the tar defined in A above.
- C. Refined coal tar product derived by removing acids and bases from coal tar defined in A above.
- D. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Engler) of 26 at 40° C.
- E. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Engler) of 20.7 at 40° C.
- F. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Engler) of 21.1 at 50° C.
- G. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Float test) of 53 at 32° C.
- H. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Float test) of 132 at 50° C.
- I. Refined coal tar product having a solubility in carbon disulfide of at least 70% and having a specific viscosity (Float test) of 124 at 50° C.

Example VII

This example illustrates the preparation and some of the properties of a composition prepared from refined coal tar pitch as described in Example I and vinyl cyclohexene dioxide.

The coal tar pitch described in Example I was heated to 120° F. Vinyl cyclohexene dioxide was then added so as to form a mixture having 40% coal tar pitch and 60% vinyl cyclohexene dioxide. A stoichiometric amount of hexahydrophthalic anhydride and 1% benzyldimethylamine were added and the mixture heated to 150° C. and then quickly applied to concrete and steel panels. The coatings set up to form hard tough films which had good adhesion to the concrete and steel, excellent non-skid properties and good resistance to outdoor weather conditions.

Related results are obtained by replacing the vinyl cyclohexene dioxide in the above process with equal amounts of each of the following: epoxidized tetrahydrobenzyl tetrahydrobenzoate, epoxidized 2,2-bis(cyclohexenyl)propane and epoxidized dicrotyl phthalate.

Example VIII

This example illustrates the preparation and some of the properties of a composition containing a refined coal tar having a fusing point below 70° F., a specific gravity at 77° F. of 1.25, 5–20% tar acids and 70% solubility in carbon disulfide, and polyether D.

The refined coal tar described above was heated to 120° F. Polyether D was then added so as to form a mixture having 60% refined coal tar and 40% polyether D. 8 parts of diethylene triamine per 100 parts of polyether D was then added and the mixture applied to concrete and steel. Immediately after application, sand was spread on top of the coating so that the small particles became embedded in the coating. The amount of sand applied amounts to about 60% by weight of the coating. The coating set up in a short time at room temperature to form hard, tough films which had good adhesion to the concrete and steel, good non-skid properties and good resistance to outdoor weather conditions.

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Related results are obtained by replacing the diethylene triamine curing agent with equivalent amounts of each of the following: ethylene diamine, hexamethylene diamine, triethylene tetramine.

Example IX

This example illustrates the preparation and some of the properties of a coal tar pitch composition as defined in Example I, polyether A and trimer acid.

The coal tar pitch was heated to 120° F. 20 parts of polyether A and 30 parts of trimer acid were added to 100 parts of the heated coal tar pitch. This mixture was then applied to concrete and steel. Immediately after application, sand was spread on top of the coating so that the small particles became embedded in the coating. The amount of sand applied amounted to about 80% by weight of the coating. The coating set up to form hard tough films which had good adhesion to the concrete and steel, good non-skid properties and good resistance to outdoor weather conditions.

Trimer acid used above was product of polymerization of unsaturated fatty acids.

I claim as my invention:

1. A road surfacing composition comprising a product derived from coal of the residual group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and having a solubility in carbon disulfide of at least 50%, a polyepoxide having more than one vicinal epoxy group, the coal product and polyepoxide being in a weight ratio of 15:1 to 1:15, and at least 50% by weight of the combined coal product-polyepoxide mixture of small abrasive inert particles.

2. A road surfacing composition comprising a product derived from coal of the residual group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and having a solubility in carbon disulfide of at least 50%, a polyepoxy ether having a 1,2-epoxy equivalency greater than 1.0, the coal product and polyepoxide being in a weight ratio of 5:1 to 1:5, and at least 70% by weight of the total mixture of small abrasive inert particles.

3. A road surface coating composition comprising a refined residual coal tar having a softening point below 70° F. and having a solubility in carbon disulfide of at least 70%, a liquid polyepoxide having more than one vicinal epoxy group, the coal product and polyepoxide being in a weight ratio of 5:1 to 1:5 and at least 70% by weight of the total mixture of sand.

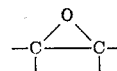
4. A paving composition comprising a residual coal tar pitch having a softening point between 80° F. and 120° F. and having solubility in carbon disulfide of at least 70%, a liquid polyepoxide having more than one vicinal epoxy group, the coal product and polyepoxide being in a weight ratio of 5:1 to 1:5, and at least 70% by weight of the total mixture of sand.

5. A paving composition comprising a residual coal tar having a softening point below 40° F. and a solubility in carbon disulfide of at least 70%, a polyglycidyl ether of a polyhydric phenol having an epoxy equivalency greater than 1.0, the coal product and polyepoxide being in a weight ratio 5:1 to 1:5, and at least 70% by weight of the total mixture of sand.

6. A paving composition comprising a product derived from coal of the residual group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and having a solubility in carbon disulfide of at least 50%, from 20% to 75% by weight

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of the mixture of coal product and polyepoxide of a liquid polyepoxide having at least one internal



group, and from 1 to 6 times the weight of the coal product and polyepoxide of small abrasive inert sharp particles.

7. A composition as in claim 6 wherein the polyepoxide is epoxidized tetrahydrobenzyl tetrahydrobenzoate.

8. A composition as in claim 6 wherein the polyepoxide is epoxidized 2,2-bis(cyclohexenyl)propane.

9. A paving composition comprising a residual coal tar pitch having a softening point of about 77° F. and a solubility in carbon disulfide of at least 80%, 30% to 75% of a polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane and 1 to 6 times the weight of the coal product and polyepoxide of sand grit.

10. A paving composition comprising a residual coal tar pitch having a softening point of 80° F. to 150° F. and having a solubility in carbon disulfide of at least 70%, 30% to 75% of a polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane and 1 to 6 times the weight of the and polyepoxide of sand grit.

11. A process for treating surfaces to render them non-skid which comprises applying to the surface at a temperature between 20° C. and 150° C. a composition comprising a mixture of a product derived from coal of the residual group consisting of coal tars, refined coal tars and coal tar pitches having a softening point below 190° F. and having a solubility in carbon disulfide of at least 50%, a liquid polyepoxide having more than one vicinal epoxy group, the coal product and polyepoxide being present in a weight ratio 15:1 to 1:15, and an epoxy curing agent and then applying to the layer of the composition small abrasive inert sharp particles in an amount of 1 to 6 times the weight of the coal product and polyepoxide, and curing the mixture to hardness.

12. A process as in claim 11 wherein the surface is concrete.

13. A process as in claim 11 wherein the surface is asphalt.

14. A process as in claim 11 wherein the polyepoxide is a polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane.

15. A process as in claim 11 wherein the epoxy curing agent is an amine.

16. A process as in claim 11 wherein the polyepoxide is a liquid product having at least one internal epoxy group.

17. A coating prepared by the process of claim 11.

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