

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

#### Improvements in or relating to Polyepoxide Compositions and their use

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new resinous compositions containing a special extending and flexibilizing material, and to their use, particularly in the preparation of coating and sealing compositions.

There is a growing need for a cheap surfacing composition that can be applied to surfaces such as concrete, both cement and asphaltic, and metal surfaces to protect them from being worn away and broken up by constant use and exposure to inclement weather conditions. There is also a need for such a coating for cement and asphaltic roadways and walkways to reduce their tendency to skid when wet. In the case of the asphaltic surfaces, there is a further need for coatings which would improve resistance to solvents. This is particularly urgent in the case of asphalt runways for jet aircraft as the jet fuels readily attack and soften asphalt surfaces.

Various coatings have been suggested for the above applications, but they have not proved very satisfactory. In many cases, the coatings have failed to have the necessary adhesion to the surface, such as cement, asphalt and metal. In other cases, the coatings fail to stand up under constant wear and exposure to weather. In still other cases, the coating tends to be brittle and is easily cracked, particularly when applied in large areas. In still other cases, the coatings fail to have the necessary solvent resistance and

resistance to skidding when wet. Further, in many cases, the coatings require a long time for cure or require special curing conditions. In other cases, the coatings are too expensive for use on large areas as roadways and walkways.

It has now been found that these and other drawbacks may be obviated by the cold curable compositions of the invention comprising a mixture of (1) a polyepoxide having an epoxy equivalency greater than 1.0, and preferably a glycidyl polyether of a polyhydric phenol, suitably one having a molecular weight between 250 and 900, and (2) an alkyl substituted monohydric phenol, and preferably a polyalkyl phenol wherein at least one of the alkyl groups contains at least 7 carbon atoms, most preferably a dinonyl phenol, (3) a bituminous material composed mainly of hydrocarbons, said composition being capable of cold cure with an aliphatic or cycloaliphatic amine, thus leading to compositions having lower viscosities than similar systems without the substituted phenols. It has been found that these compositions when combined with aliphatic or cycloaliphatic amines cure rapidly at low temperatures to form hard and tough insoluble, infusible homogeneous coatings. The coatings have good adhesion to cement, asphalt and metal surfaces. In addition, the coatings have good resistance to wear and resistance to solvents and jet fuels. The coatings are particularly attractive in that they can be prepared at a low cost, can be easily applied to large areas without the use of solvents and cure very rapidly at low temperatures.

When small inert particles or aggregates are added to the compositions before or during cure, the cured coatings also display excellent resistance to skidding. The coatings are particularly attractive for use on

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highways and runways, they can be easily applied to large areas and set up quickly without the use of any special curing conditions.

- 5 The new compositions have been found to be useful as binders for aggregate in the formation of top coatings or as roadways, runways and walkways.

- 10 The fact that the compositions when containing large amounts of the bituminous materials, still cure rapidly to hard tough coatings, was quite unexpected in view of the fact that epoxy resin-bituminous mixtures heretofore gave soft heterogeneous products.
- 15 The alkyl phenols appear, as part of their function in the composition, to act as an unexpected compatibilizing agent permitting the composition to retain large amounts of the bituminous material without affecting the
- 20 cure and homogeneity of the resulting product.

- Further, it was unexpected to find that the coatings had good flexibility and heat resistance as it is known that bituminous materials generally form brittle coatings which soften on heating. The polyepoxides also form relatively brittle coatings in comparison with those of the compositions described.

- 30 The polyepoxides to be used in preparing the compositions of the invention comprise those materials possessing more than one vicinal epoxy group, i.e., more than one

- 35  $\text{—C—C—}$  group. These compounds may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with substituents, such as chlorine, hydroxyl groups, ether radicals and the like. They may be monomeric or polymeric.

- The polyepoxides used in the present process are those having an epoxy equivalency greater than 1.0, i.e. having an average number of vicinal epoxy groups in the average molecule which is greater than 1.0.

- Various examples of polyepoxides that may be used in the process of the invention are given in U.S. 2,633,458 and it is to be understood that the disclosure of that patent relative to examples of polyepoxides is incorporated by reference into this specification.

- Other examples include the epoxidized esters of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut and dehydrated castor oil, methyl linoleate, butyl linoleate, ethyl, 9-12-octadecadienoate, butyl 9,12,15-octadecatrienoate, butyl eleostearate, monoglycerides of tung oil fatty acids, and monoglycerides of fatty acids of soybean, sunflower, rapeseed, hempseed, sardine and cotton-seed oil.

- 65 Another group of the epoxy-containing

materials used in the process of the invention include the epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acids, such, as for example di(2,3-epoxybutyl)adipate, di(2,3-epoxybutyl)oxalate, di(2,3-epoxyhexyl succinate, di(3,4-epoxybutyl)-maleate, di(2,3-epoxyoctyl)pimelate di(2,3-epoxybutyl)phthalate, di(2,3-epoxyoctyl)tetrahydrophthalate, di(4,5-epoxydecyl)maleate, di(2,3-epoxybutyl)terephthalate, di(2,3-epoxypentyl)thiodipropionate, di(5,6-epoxytetradecyl)diphenyl - 4,4' - dicarboxylate, di(3,4-epoxyheptyl)sulfonyldibutyrate, tri(2,3-epoxybutyl)1,2,4-butanetricarboxylate, di(5,6-epoxypentadecyl)tartrate, di(4,5-epoxytetradecyl)maleate, di(2,3-epoxybutyl)azelate, di(3,4-epoxybutyl- $\alpha,\gamma$ -citrate, di(5,6-epoxyoctyl)cyclohexane-1,3-dicarboxylate, and di(4,5-epoxyoctadecyl)malonate.

Another group of the epoxy-containing materials include those epoxidized esters of unsaturated alcohols and unsaturated carboxylic acids, such as 2,3-epoxybutyl 3,4-epoxypentanoate, 3,4-epoxyhexyl 3,4-epoxycyclohexanoate, 3,4-epoxycyclohexyl, 4,5-epoxyoctanoate, and 2,3-epoxycyclohexylmethyl-2,3-epoxycyclohexane carboxylate.

Still another group of the epoxy-containing materials included epoxidized derivatives of polyethylenically unsaturated polycarboxylic acids, such as, for example, dimethyl 8,9,12,13 - diepoxyeicosanedioate, dibutyl, 7,8,11,12 - diepoxyoctadecanedioate, dioctyl 10,11 - diethyl-8,9,12,13 - diepoxy-eicosanedioate, dihexyl 6,7,10,11-diepoxyhexadecanedioate, didecyl 9-epoxy-ethyl-10,11-epoxyoctadecanedioate, dibutyl 3-butyl-3,4,5,6-diepoxyoctadecanedioate, dicyclohexyl 3,4,5,6-diepoxyoctadecanedioate, dibenzyl 1,2,4,5-diepoxyoctadecanedioate, and diethyl 5,6,10,11-diepoxyoctadecyl succinate.

Still another group comprises the epoxidized polyesters obtained by epoxidizing the polyesters obtained by reacting an ethylenically unsaturated polyhydric alcohol and/or ethylenically unsaturated polycarboxylic acid or anhydride groups, with or without other polyester-forming ingredients as appropriate, such as, for example, the polyester obtained by reacting 8,9,12,13-eicosadienedioic acid with ethylene glycol. the polyester obtained by reacting diethylene glycol with 2-cyclohexene-1,4-dicarboxylic acid, and mixtures thereof.

Still another group comprises the epoxidized polyethylenically unsaturated hydrocarbons, such as epoxidized 2,2-bis(2-cyclohexenyl) propane, epoxidized vinyl cyclohexenes and epoxidized dimer of cyclopentadiene.

Another group comprises the epoxidized polymers and copolymers of diolefins, such as butadiene. Examples of this include, among others, butadiene-acrylonitrile copoly-

120 *pentadiene*

mers, and butadiene-styrene copolymers.

The polyepoxides that are particularly useful for the compositions of the invention are the glycidyl ethers and especially the polyglycidyl ethers of polyhydric phenols and polyhydric alcohols. The glycidyl ethers polyhydric phenols are obtained by reacting epichlorohydrin with the desired polyhydric phenols in the presence of alkali. Polyether A and Polyether B described in the above-noted U.S.2,633,458 are good examples of polyepoxides of this type. Other examples include the polyglycidyl ether of 1,1,2,2-tetrakis(4-hydroxyphenyl)-ethane (epoxy value of 0.45 eq/100g and melting point 85°C) and the glycidyl ethers of novolac resins obtained by reacting phenols with formaldehyde.

The second component to be used in the compositions of the invention comprises the alkyl substituted monohydric phenols. These phenols have at least one and preferably two or more alkyl side chains wherein at least one of the alkyl groups contains at least 7 carbon atoms. The position of the side chain or chains on the aromatic ring is not important, but can be in the meta and para positions relative to the OH group. Examples of the alkyl phenols include, among others, dinonyl phenols, dioctyl phenols, didodecyl phenols, ditetradecyl phenols, dioctadecyl phenols, trinonyl phenols, nonyl phenols, octyl phenols, nonyl cresols, heptyl phenols, diheptyl phenols, pentadecyl phenols, heptyl dodecyl phenols, heptyl ditetradecyl phenols, eicosanyl phenols, and tritetradecyl phenols.

Preferred alkyl phenols to be employed include those possessing at least 7 carbon atoms in the side chain or in at least one of the side chains, and especially the di-tri- and tetraalkyl substituted monohydric phenols and dihydric phenols wherein at least two of the alkyl side chains contain from 7 to 24 carbon atoms.

Most preferred phenols to be employed include the polyalkyl phenols having from 2 to 3 alkyl groups all of which contain from 7 to 20 carbon atoms each, such as, for example, dinonyl phenols, trinonyl phenols, dioctyl phenols, trioctyl phenols, dieicosanyl phenols, trieicosanyl phenols, dioctadecyl phenols and trioctadecyl phenols.

Coming under special consideration, particularly because of their low cost and superior properties obtained therewith are the crudes obtained by the alkylation of phenols with long chain hydrocarbons to obtain derivatives for detergent purposes. Such crudes normally contain large amounts of the dialkyl phenol along with portions of the monoalkyl and possibly trialkyl or higher alkyl substituted products. Crude dinonyl phenol which has been found to be particularly useful, for example, contains large

amounts of dinonyl phenols along with monononyl phenols.

Also according to the present invention, bituminous materials are present in the compositions; these bituminous materials include substances containing bitumens or pyrobitumens, pyrogenous distillates and tar, pyrogenous waxes and pyrogenous residues (pitches and pyrogenous asphalts). They are composed mainly of hydrocarbons although they may contain amounts of sulfur, nitrogen and oxygen-containing materials. They are also preferably fusible and largely soluble in carbon disulfide. Examples of such bituminous materials may be found in Abraham's Asphalts and Allied Substances, Vol. I, page 57, 5th Edition.

An especially preferred group of bituminous materials to be used in the compositions of the invention include the asphalts. These asphalts may be naturally occurring asphaltic material (such as Gilsonite) or petroleum derived materials, such as straight run, blown, cracked and catalytically or non-catalytically polymerized asphalts. All such asphalts are useful regardless of their original penetrations or softening points.

Especially preferred are the straight run asphalts used for paving, such as those having penetrations between 40 and 300 and softening points within the range from about 65°C to about 35°C. Blown asphalts are normally produced in the presence or absence of catalysts by blowing asphalts or flexes at elevated temperatures with an oxygen-containing gas such as air. Typical blown asphalts may have a softening point range of between about 150°C and about 50°C and a penetration within the range from about 100 to about 0.

Aromatic asphalts, such as those comprising the bottoms products from the distillation of catalytically cracked gas oil, are also preferred.

Other preferred materials include high boiling extracts of petroleum, such as those obtained by extracting petroleum with solvents having preferential selectivity for aromatic. To obtain such extracts various non-reactive, highly polar, aromatically preferential solvents are used such as liquid SO<sub>2</sub>, phenol, cresylic acid, furfural, beta, beta'-dichloroethyl ether, nitrobenzene and the like. The use of the so-called double solvent process employing mutually immiscible solvents like cresylic acid and propane also gives suitable extracts. Especially preferred are the Edeleanu and furfural extracts of petroleum distillates, i.e., extracts obtained by use of liquid SO<sub>2</sub> or liquid SO<sub>2</sub> in combination with benzene, etc. The extracts are high-boiling materials which range in general from viscous liquids to tar-like materials at ordinary temperatures. Extracts boiling above 300° at 760 mm Hg are preferred.

Another preferred group of bituminous materials include residual fuel oils, such as residual fuel oils having a viscosity between 10 cs at 38°C to about 1500 cs at 38°C.

- 5 Also preferred are the products derived from coal such as coal tars, refined coal tars and coal tar pitches, and preferably those having a softening point below 90°C and a solubility in carbon disulfide of at least 50%.
- 10 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
- 15 volatile material is removed, the residue is termed coal tar pitch. Residuals having a fusing point below about 32°C are referred to herein as refined coal tars while those having fusing points of 32°C or above are
- 20 coal tar pitches. As used herein, in reference to coal tar products, "softening point" or "fusing point" refers to values obtained by the cube method as described in Vol. II, Abraham, *Asphalts and Allied Substances*,
- 25 5th Edition. The coal products should possess at least 50% and preferably 75% solubility in carbon disulfide. The coal tar refined coal tar and coal tar pitch may be
- 30 acidic, basic or neutral, depending on whether the acid and/or basic constituents have been removed. These coal products may be obtained from various types of bituminous coals, such as, for example,
- 35 cannel, bog-peat, carbonite, 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
- 40 of various coal tars, refined coal tars and coal tar pitches may be found on pages 384-405 of Abraham, *"Asphalts and Allied Substances"*.

- Particularly preferred coal derivatives to be used in preparing the compositions of the
- 45 present invention include the residuals resulting from distillation of coal tar, and preferably refined coal tars having a fusing point of below 21°C and a solubility in carbon disulfide of at least 75% with a
- 50 specific gravity of 1.10 and 1.50, and low melting coal tar pitches having a fusing point below 50°C and a solubility in carbon disulfide of at least 75%.

- The compositions of the invention may be
- 55 prepared by any suitable method. The compositions may be prepared, for example, by simply mixing the components together with or without the application of heat. With liquid polyepoxides, the mixtures may
- 60 have low viscosities and it is not necessary to employ solvents or diluents. However, if desired, various solvents or diluents which will evaporate before or during cure may be added to assist in the preparation of the
- 65 mixtures. Suitable solvents include, among

others, hydrocarbons, such as xylene and benzene. It is also convenient to sometimes use liquid polyepoxides, such as normally liquid glycidyl polyethers of polyhydric alcohols, or to utilize monoglycidyl derivatives such as butylglycidyl ether and phenyl glycidyl ether.

The ratio of the components to be utilized in the above compositions may vary within certain limits. The polyepoxide should preferably make up at least 10% by weight of the total mixture and more preferably from 10% to 70% by weight of the mixture. The alkyl substituted phenol should preferably make up at least 3% by weight of the total mixture and preferably not more than 85% by weight of the total mixture. Particularly superior results are obtained when the polyepoxide makes up at least 10%, and preferably not more than 60%, of the combined mixture, and the phenol makes up at least 5%, and preferably not more than 50% of the total mixture. With these proportions it is particularly suitable that the bituminous material should be present in an amount of from 30% to 65% by weight of the total mixture.

As noted above, the compositions of the invention may also be used as binders for grit layers for the coating of already prepared concrete and metal surfaces and as binders for aggregate in the preparation of new roadways and walkways. In the case of the grit layers, the compositions are combined with a relatively large proportion of hard abrasive inert particles which are preferably finely divided and have a mesh size varying from about 4 to 500 (U.S. Standard Sieve size). Preferred materials include sand, crushed rock, finely divided shells, crushed quartz, aluminium oxide and finely divided resinous particles. Preferred materials to be employed are the minerals and especially the siliceous materials, such as, for example, sand and ground rock. Mixtures of various types of particles may also be employed.

When being used as a binder for aggregate for the preparation of new roadways, the above compositions are mixed with various types of aggregate, such as ground rock and the like which have a larger size than the afore-described grit particles. These materials preferably have a mesh size varying from about 0 to 50.

The amount of the inert particles and aggregate employed preferably comprises at least 50% by weight of the above compositions and still more preferably, makes up from 75% to 100% by weight of the above compositions. When used with aggregate for the construction of roads, the compositions are preferably laid down in layers of about 2.5 cm to 15 cm thickness.

In making the grit layers and the roadway compositions, the particles and aggregate

may be added at any time during the preparation of or after the preparation of the above-described compositions. It is also possible, preferably in the case of the grit layers, to apply the compositions without the inert particles as a coating and then sprinkle the inert particles on the top of the coating and then compact by means of rollers and the like.

- 10 When used as coatings, the compositions of the invention may be applied to any surface, but are particularly suitable for use as surfacing compositions for cement, asphalt, wood and steel. The cement surfaces may be any of the usual types such as may be prepared from hydraulic cements, such as Portland cement and other types of aluminous cement. 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. The applications to the surface can be accomplished in any suitable manner. If the material is thick or contains large amounts of inert particles, the material may best be applied by use of a screed, trowel, shovel or broom. If it is of a more fluid nature, it may be applied by brushing or spraying. The coating will generally vary in thickness from about 1.5 mm to about 12 mm.

The compositions of the invention may be utilized for a great variety of other applications. They may be used, for example, in the preparation of roofing materials, potting, castings and encapsulations, sealing and impregnating compositions, as coatings for pipes, off-shore drilling rigs, outdoor wood and metal equipment, and in the lamination field.

- As cold-hardening agents for the resin-forming ingredients of the composition are used aliphatic or cycloaliphatic amino compounds such as triethylamine, ethylene diamine, diethylamine, diethylene triamine, triethylene tetramine, 1,4-diaminocyclohexane, N,N'-diethyl-1,3-propane-diamine, dicyandiamide, melamine and fatty acid salts of amines. The curing agent is added and mixed in with the composition after its preparation as noted above. The amounts vary considerably depending upon the particular agent employed. The amino compounds are preferably used in amounts of about 3 to 15% by weight of polyepoxide.

The following examples illustrate the present invention. Unless otherwise specified, parts disclosed in the examples are parts by weight.

- 60 The concrete used in the examples was prepared from hydraulic cement (Portland cement), aggregate, sand and water.

The polyethers A, B and D referred to in the Examples are polyglycidyl ethers of 2,2-bis(4-hydroxyphenyl)propane, such as are

prepared from bisphenol-A and epichlorohydrin under the action of sodium hydroxide, having the following properties.

|                                               | Poly-<br>ether<br>A. | Poly-<br>ether-<br>B. | Poly-<br>ether<br>D. |    |
|-----------------------------------------------|----------------------|-----------------------|----------------------|----|
| Viscosity                                     | 150 poises<br>(25°C) | —                     | —                    |    |
| Melting point<br>(Durran's Mercury<br>Method) | —                    | 27°C                  | 70°C                 | 75 |
| Molecular weight                              | 350                  | 483                   | 900                  |    |
| Epoxy value eq./100                           | 0.50                 | 0.40                  | 0.20                 |    |
| Epoxy equivalency                             | 1.75                 | 1.9                   | 1.8                  |    |

#### EXAMPLE I

This example illustrates the preparation and some of the properties of a composition containing Polyether A, dinonyl phenols and paving grade asphalt.

20% By weight of Polyether A, 40% by weight of dinonyl phenols and 40% straight run asphalt were combined with stirring. 13 Parts per 100 parts of Polyether A of diethylene triamine was then added to the mixture. This mixture was stirred and spread between two glass plates and allowed to cure at room temperature over night. The self-supporting film that was removed was strong, tough, flexible and had good resistance to jet fuels. The product had a tensile strength of about 55kg/cm<sup>2</sup> and an elongation of 50%.

A composition was prepared as above and spread out as a thin film on cement concrete surfaces and the film allowed to cure at room temperature. The resulting coating showed good adhesion to the cement and had excellent hardness and resistance to jet fuels.

A further composition was prepared as above and spread out as thin film on cement concrete surfaces, 100% By weight of sand was sprinkled on the composition and compacted by rolling. This combination was then allowed to set at atmospheric temperature. The resulting coating was a very hard tough skid resistant coating. The coating also demonstrated good resistance to jet fuels.

#### EXAMPLE II

Example I was repeated with the exception that the rates of components were changed as follows:

| Polyether A | Asphalt | Dinonyl Phenols |     |
|-------------|---------|-----------------|-----|
| 50%         | 16.7%   | 33.3%           |     |
| 50%         | 25%     | 25%             | 120 |
| 50%         | 33.3%   | 16.7%           |     |
| 50%         | 10%     | 40%             |     |

Similar results are obtained in each case.

#### EXAMPLE III

Example I was repeated with the exception that the ratios of components were changed as follows:—

| <i>Polyether A</i> | <i>Asphalt</i> | <i>Dinonyl Phenols</i> | <i>Polyether A</i> | <i>Dutrex 20</i> | <i>Dinonyl Phenols</i> |
|--------------------|----------------|------------------------|--------------------|------------------|------------------------|
| 20%                | 16%            | 64%                    | 20%                | 26.7%            | 53.3%                  |
| 20%                | 26.7%          | 53.3%                  | 20%                | 40%              | 40%                    |
| 20%                | 53.3%          | 26.7%                  | 20%                | 16%              | 64%                    |

5 Similar results are obtained in each case.

#### EXAMPLE IV

This example illustrates the preparation and some of the properties of a composition containing Polyether A, dinonyl phenols and industrial fuel oil (Bunker C) having a viscosity of approximately 85° Engler at 50°C.

20% By weight of Polyether A, 26.7% dinonyl phenols and 53.3% by weight of fuel oil were combined together with stirring. 13 Parts per 100 parts of Polyether A of diethylene triamine were then added to the mixture. This mixture was stirred and spread between two glass plates and allowed to cure at room temperature. The self-supporting film that was removed was strong, tough and flexible and had good heat resistance to jet fuels. The product possessed a tensile strength of 37 kg/cm<sup>2</sup> and elongation of 25%.

#### EXAMPLE V

Example IV was repeated with the exception that the proportions were as follows:

| <i>Polyether A</i> | <i>Fuel Oil</i> | <i>Dinonyl Phenols</i> |
|--------------------|-----------------|------------------------|
| 20%                | 26.7%           | 53.3%                  |
| 20%                | 40%             | 40%                    |
| 20%                | 16%             | 64%                    |

Related results are obtained.

#### EXAMPLE VI

Example IV was repeated with the exception that the components are combined in a ratio of 30 parts Polyether A, 50 parts Bunker C fuel oil and 20 parts dinonyl phenols. Similar results were obtained.

#### EXAMPLE VII

This example illustrates the preparation and some of the properties of a composition containing Polyether A, an Edeleanu petroleum extract (Dutrex 20—"Dutrex" is a Registered Trade Mark) and dinonyl phenols. Dutrex 20 has the following properties: Gravity, 1.031 gr/cm<sup>3</sup>; Flash point (Cleaveland open cup) 213°C.; viscosity, at 99°C 2070cS; Aniline Point, 27°C; Acid No. 0.05; and Iodine Number 69.

20% By weight of Polyether A, 26.7% dinonyl phenols and 53.3% by weight of Dutrex were combined with stirring. 13 Parts per 100 parts of Polyether A of diethylene triamine were then added to the mixture. This mixture was stirred and spread between two glass panels and allowed to cure at room temperature. The self-supporting film that was removed was strong, tough and flexible and had good heat resistance and resistance to jet fuels. The product possessed a tensile strength of about 30 kg/cm<sup>2</sup> and elongation of 35%.

#### EXAMPLE VIII

Examples VII was repeated with the exception that the proportions were as follows:

Similar results are obtained.

#### EXAMPLE IX

This example illustrates the preparation and some of the properties of a composition containing Polyether A, didodecyl phenols and straight run asphalt.

20% By weight of Polyether A, 53.3% didodecyl phenols and 26.7% straight run asphalt were combined with stirring. 13 Parts per 100 parts of Polyether A of diethylene triamine were then added to the mixture. This mixture was stirred and spread between two glass panels and allowed to cure at room temperature. The self-supporting film that was removed was strong, tough and flexible and had good solvent and heat resistance. The product had a tensile strength of about 40 kg/cm<sup>2</sup> and elongation of 45%.

A composition was prepared as above and spread out as a thin film on cement surfaces. The film was allowed to cure at atmospheric temperature. The resulting coating showed good adhesion to the cement and had excellent hardness and resistance to jet fuels.

A further composition was prepared as above and spread out as thin film on cement concrete surfaces. 100% By weight of sand was sprinkled on the composition and compacted by rolling. This combination was then allowed to cure at atmospheric temperature. The resulting coating was a very hard tough skid-resistant coating. The coating also demonstrated good resistance to jet fuels.

#### EXAMPLE X

Example IX was repeated with the exception that the components were combined in the following proportions.

| <i>Polyether A</i> | <i>Asphalt</i> | <i>Didodecyl Phenols</i> |
|--------------------|----------------|--------------------------|
| 20%                | 16%            | 64%                      |
| 20%                | 40%            | 40%                      |
| 20%                | 53.3%          | 26.7%                    |

Similar results are obtained.

#### EXAMPLE XI

This example illustrates the preparation and some of the properties of a composition containing Polyether A, nonyl phenols and straight run asphalt.

20% Polyether A, 26.7% nonyl phenol and 53.3% straight run asphalt were combined with stirring. 13 Parts per 100 parts of Polyether A of diethylene triamine were then added to the mixture. This mixture was stirred and spread between two glass panels and allowed to cure at room temperature. The self-supporting film that was removed had good strength and flexibility and had good resistance to solvent and heat. The product had a tensile strength of about 45 kg/cm<sup>2</sup> and elongation of 30%.

A composition prepared as above was also spread on concrete and cured at atmospheric temperature. The resulting coating was very hard and tough and had good adhesion to the cement.

#### EXAMPLE XII

Example XI was repeated with the exception that the components were used in the following proportions:

|    | Polyether A | Asphalt | Nonyl Phenol |
|----|-------------|---------|--------------|
| 10 | 20%         | 26.7%   | 53.3%        |
|    | 20%         | 40%     | 40%          |

Similar results were obtained.

#### EXAMPLE XIII

15 Examples I, IV, IX and XI were repeated with the exception that 25% of Polyether A was in each case replaced by the same weight of a mixture of equal quantities of diglycidyl ester of dimerized linoleic acid and of triglycidyl ester of trimerized linoleic acid. Similar results were obtained.

#### EXAMPLE XIV

25 Examples I, IV, VIII and X were repeated with the exception that the Polyether A was replaced with Polyether B and a mixture of 10% of Polyether D and 90% of Polyether A. Similar results are obtained.

#### EXAMPLE XV

30 50% by weight of Polyether A, 40% by weight of dioctyl phenol and 10% straight run asphalt were combined with stirring. 13 Parts per 100 parts of Polyether A of diethylene trimaine were then added to the mixture. This mixture was stirred and spread between two glass panels and allowed to cure at room temperature. The resulting film had good strength and flexibility and showed good resistance to jet fuels.

40 A composition was prepared as above and spread out as a thin film on cement concrete surfaces. This combination was then allowed to cure at atmospheric temperature. The resulting coating showed good adhesion to the cement, excellent hardness and solvent resistance.

#### EXAMPLE XVI

This example illustrates the preparation and some of the properties of a composition containing an epoxy-containing adduct of Polyether A and dimerized linoleic acid, dinonyl phenols and industrial fuel oil.

72.8% By weight of an adduct having an epoxy/ greater than 1.0 and obtained by reacting 305 parts of Polyether A with 245 parts of dimerized linoleic acid, were combined with 20% by weight of dinonyl phenols and 7.2% by weight of industrial fuel oil and the mixture stirred. 3.5% by weight (based on the weight of the adduct) of diethylene triamine was then added to the mixture. The mixture was stirred and spread between two glass panels and allowed to cure at room temperature. The self-supporting film that was removed was strong, tough

and flexible and had good resistance to jet fuels.

#### EXAMPLE XVII

A composition was prepared having the following composition:

|       |                                             |    |
|-------|---------------------------------------------|----|
| 13.1% | Polyether A                                 | 70 |
| 25.8% | diglycidyl ester of dimerized linoleic acid |    |
| 12.0% | dinonyl phenols                             | 75 |
| 46.0% | asphalt                                     |    |
| 3.1%  | diethylene triamine                         |    |

This composition was spread out between glass panels and allowed to cure at room temperature. The resulting self-supporting film was very tough and hard and had good resistance to jet fuels. The product had a tensile strength of about 65 kg/cm<sup>2</sup> and an elongation of 47%.

#### EXAMPLE XVIII

85 Examples I, IV, IX, XI and XVI are repeated with the exception that the bituminous material is replaced by each of the following: coal tar pitch, refined coal tar, coal tar and middle oil. (Middle oil is a fraction of coal tar distillates boiling in the range 200°-250°C.) Hard tough films are obtained.

#### EXAMPLE XIX

95 Examples I, IV, IX, XI, XVI and XVIII are repeated with each of the following curing agents in turn: 1,4-diaminocyclohexane and N-aminoethylpiperazine, each in an amount of 12 parts by weight per 100 parts of the polyepoxide component. Similar results are obtained.

#### EXAMPLE XX

A coating composition was prepared using the following formulation:

|                        |             |     |
|------------------------|-------------|-----|
| Asbestin 3X (asbestos) | 245.6 parts |     |
| Cab-O-Sil (Silica)     | 10.1 parts  | 105 |
| Polyether A            | 275.1 parts |     |
| Industrial Fuel Oil    | 229.1 parts |     |
| Dinonyl phenols        | 91.6 parts  |     |
| Xylene                 | 63.7 parts  |     |
| Secondary butanol      | 63.7 parts  | 110 |

To this mixture were added 28.8 parts of diethylene triamine. The resulting composition had a total non-volatile content of 88%.

115 The above composition was sprayed on metal panels at about 4 atm. The resulting coating was allowed to cure at room temperature. The resulting coating had the following properties:

|                              |            |     |
|------------------------------|------------|-----|
| 100°C—Distilled water        | unaffected | 120 |
| 20% sodium chloride          | unaffected |     |
| jet fuel                     | unaffected |     |
| 5% sulfuric acid             | unaffected |     |
| 50% sulfuric acid            | unaffected |     |
| Boiling 20% sodium hydroxide | unaffected | 125 |
| 15% nitric acid              | unaffected |     |
| 10% hydrochloric acid        | unaffected |     |

The composition also showed excellent adhesion to cement and asphalt and formed skid-resistant coatings when combined with

A composition was prepared as above and spread out as a thin film on cement concrete surface. The film was allowed to cure at atmospheric temperature. The resulting coating had good adhesion to the cement and was very hard and had good resistance to jet fuels.

longer than 1 year

dinonyl

sand as noted in the previous examples.

**WHAT WE CLAIM IS:—**

1. A cold curable composition comprising (1) a polyepoxide having anepoxy equivalency greater than 1.0, (2) an alkyl substituted monohydric phenol and (3) a bituminous material composed mainly of hydrocarbons, said composition being capable of cold cure with an aliphatic or cycloaliphatic amine.
2. A composition according to claim 1, characterized in that the polyepoxide is a glycidyl polyether of a polyhydric phenol having a molecular weight between 250 and 900.
3. A composition according to claim 1 or 2 characterized in that the phenol is a polyalkyl phenol wherein at least one of the alkyl groups contains at least 7 carbon atoms.
4. A composition according to claim 3 characterized in that the polyalkyl phenol contains either 2 or 3 alkyl groups each of which contains from 7 to 20 carbon atoms.
5. A composition according to claim 4 characterized in that the polyalkyl phenol is a dinonylphenol.
6. A composition according to claim 4 characterized in that the polyalkyl phenol is a didodecylphenol.
7. A composition according to claim 4 characterized in that the polyalkyl phenol is a dioctylphenol.
8. A composition according to any one of the preceding claims characterized in that the phenol is present in an amount of at least 3% of the total mixture by weight.
9. A composition according to any one of the preceding claims characterized in that the phenol is present in an amount of not more than 85% of the total mixture by weight.
10. A composition according to claim 9 characterized in that the bituminous material is a petroleum derived product.
11. A composition according to claim 10 characterized in that the petroleum derived product is an asphalt.
12. A composition according to claim 10 characterized in that the petroleum derived product is a fuel oil.
13. A composition according to claim 10

characterized in that the petroleum derived product is an Edeleanu extract of petroleum distillates.

14. A composition according to any one of the preceding claims characterized in that the polyepoxide is present in an amount of at least 10% by weight of the total mixture and the phenol is present in an amount of at least 5% by weight of the total mixture.

15. A composition according to claim 14 characterized in that the bituminous material is present in an amount of from 30% to 65% by weight of the total mixture.

16. A composition according to any one of the preceding claims characterized in that the composition also comprises at least 50% by weight of the total mixture of small inert particles.

17. Cold curable compositions substantially as described in any one of the Examples.

18. Process for the cold curing of a composition as claimed in any one of the preceding claims characterized in that an aliphatic or cycloaliphatic amine is used as curing agent.

19. A process according to claim 18, characterized in that the curing agent is diethylene triamine.

20. A process according to claim 18, characterized in that the curing agent is 1,4-diaminocyclohexane.

21. Process according to any one of claims 18 to 20 applied to the coating of surfaces characterized by applying to the surface a coating comprising the cold curable composition and the curing agent and optionally sprinkling hard abrasive particles on top of the coating, compacting the particles and allowing the composition to set hard.

22. Process for preparing flexible products or for coating surfaces substantially as described in any one of the Examples.

23. Shaped articles wholly or partly prepared or coated by a process according to any one of claims 18 to 22.

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Carpmaels and Ransford



sand as noted in the previous examples.

WHAT WE CLAIM IS:—

1. A cold curable composition comprising  
5 (1) a polyepoxide having an epoxy equivalency greater than 1.0, (2) an alkyl substituted monohydric phenol and (3) a bituminous material composed mainly of hydrocarbons, said composition being capable of cold cure with an aliphatic or cycloaliphatic amine.
- 10 2. A composition according to claim 1, characterized in that the polyepoxide is a glycidyl polyether of a polyhydric phenol having a molecular weight between 250 and 900.
- 15 3. A composition according to claim 1 or 2 characterized in that the phenol is a polyalkyl phenol wherein at least one of the alkyl groups contains at least 7 carbon atoms.
- 20 4. A composition according to claim 3 characterized in that the polyalkyl phenol contains either 2 or 3 alkyl groups each of which contains from 7 to 20 carbon atoms.
5. A composition according to claim 4  
25 characterized in that the polyalkyl phenol is a dinonylphenol.
6. A composition according to claim 4 characterized in that the polyalkyl phenol is a didodecylphenol.
- 30 7. A composition according to claim 4 characterized in that the polyalkyl phenol is a dioctylphenol.
8. A composition according to any one of the preceding claims characterized in that  
35 the phenol is present in an amount of at least 3% of the total mixture by weight.
9. A composition according to any one of the preceding claims characterized in that the phenol is present in an amount of not  
40 more than 85% of the total mixture by weight.
10. A composition according to claim 9 characterized in that the bituminous material is a petroleum derived product.
- 45 11. A composition according to claim 10 characterized in that the petroleum derived is an asphalt.
12. A composition according to claim 10 characterized in that the petroleum derived  
50 product is a fuel oil.
13. A composition according to claim 10 characterized in that the petroleum derived product is an Edeleanu extract of petroleum distillates.
14. A composition according to any one 55 of the preceding claims characterized in that the polyepoxide is present in an amount of at least 10% by weight of the total mixture and the phenol is present in an amount of at least 5% by weight of the total mixture. 60
15. A composition according to claim 14 characterized in that the bituminous material is present in an amount of from 30% to 65% by weight of the total mixture.
16. A composition according to any one 65 of the preceding claims characterized in that the composition also comprises at least 50% by weight of the total mixture of small inert particles.
17. Cold curable compositions substan- 70 tially as described in any one of the Examples.
18. Process for the cold curing of a composition as claimed in any one of the preceding claims characterized in that an ali- 75 phatic or cycloaliphatic amine is used as curing agent.
19. A process according to claim 18, characterized in that the curing agent is diethylene triamine. 80
20. A process according to claim 18, characterized in that the curing agent is 1,4-diaminocyclohexane.
21. Process according to any one of claims 18 to 20 applied to the coating of 85 surfaces characterized by applying to the surface a coating comprising the cold curable composition and the curing agent and optionally sprinkling hard abrasive particles on top of the coating, compacting the particles 90 and allowing the composition to set hard.
22. Process for preparing flexible products or for coating surfaces substantially as described in any one of the Examples.
23. Shaped articles wholly or partly pre- 95 pared or coated by a process according to any one of claims 18 to 22.

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