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(54) Title: SOLUBLE POLYMERS WITH HIGH CONVERSION OF ACID FROM AROMATIC EPOXY RESINS AND DIACIDS AND CROSSLINKED COATINGS PREPARED THEREFROM

(57) Abstract: An uncrosslinked, soluble, epoxy terminated high molecular weight epoxy ester resin having an acid number of less than about 5 comprising the reaction product of a low molecular weight epoxy resin and a dicarboxylic acid; and a coating produced from the uncrosslinked, soluble, epoxy terminated high molecular weight epoxy ester resin.

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SOLUBLE POLYMERS WITH HIGH CONVERSION OF ACID FROM AROMATIC EPOXY  
RESINS AND DIACIDS AND CROSSLINKED COATINGS PREPARED THEREFROM

Cross-Reference to Related Applications

5           This application claims priority to U.S. Provisional Application Serial No. 60/850,475, filed October 10, 2006, the contents of which are incorporated by reference in their entirety.

Field of Invention

10           The present invention relates to uncrosslinked, soluble, high molecular weight epoxy ester resins prepared from low molecular weight aromatic epoxy resins and dicarboxylic acids. Such uncrosslinked, soluble, high molecular weight epoxy ester resins are advantageously used for preparing crosslinked coatings therefrom.

Background of the Invention

15           Protective coatings for metals is one of the premier applications for epoxy resins, and their use as internal coatings for metal food and beverage containers is one of their largest markets. Typically, internal protective coatings for metal food and beverage containers are made from high molecular weight epoxy resins. And, typically, such high molecular weight epoxy resins are made by reacting a low molecular weight epoxy resin such as diglycidyl ether of bisphenol A with a hydroxyl-containing monomer such as bisphenol A. A cyclic reaction product of  
20           bisphenol A and bisphenol A diglycidyl ether, the so-called cyclic dimer, often precipitates from coating formulation solutions causing fouling of process equipment and concomitant loss of productivity and waste generation. The food and beverage can industry has been seeking technologies which can reduce or eliminate this problem from processes for producing epoxy thermoset interior container coatings.

25           Dicarboxylic acids represent a broad class of potentially effective materials for use in the reaction with low molecular weight epoxy resins to prepare higher molecular weight epoxy ester resins. However, using dicarboxylic acids in accordance with known processes for preparing high molecular weight epoxy resins leads to the formation of crosslinked, insoluble polymers. What is needed in the industry is a process for reacting a dicarboxylic acid as a comonomer with  
30           an epoxy resin monomer which will lead to an uncrosslinked, soluble epoxy functional polymer.

          There are several known processes which teach the use of dicarboxylic acids with epoxy resins such as U.S. Patent No. 4,722,981; U.S. Patent Publication No. 20020128428A1; and European Patent Publication No. 0501575A2. However, U.S. Patent No. 4,722,981 and U.S.

Patent Publication No. 20020128428A1 do not teach the use of dicarboxylic acids as comonomers; and the process disclosed in EP 0501575A2 uses dicarboxylic acids only as catalysts, not as comonomers. Accordingly, the processes taught in the above prior art do not produce an uncrosslinked soluble, high molecular weight epoxy ester resin which is epoxy-terminated.

Several other known processes teach the use of diepoxides and dicarboxylic acids such as the processes disclosed in U.S. Patent Nos. 5,962,621; 5,852,163; and 5,780,582. However, these references do not disclose epoxy-terminated hydroxyl functional polyesters.

Other references such as Suzuki, Akira; Kameyama, Atsushi; Nishikubo, Tadatomi, *Kobunshi Ronbunshu* (1996), 53(9), 522-529; Alvey, Francis B., *Journal of Polymer Science, Polymer Chemistry Edition* (1969), 7(8), 2117-24; and Dusek, K; Matejka, L; *Advances in Chemistry Series* 1984, 208, 15, teach the synthesis of high molecular weight polyesters from an epoxy resin and a dicarboxylic acid. However, the processes disclosed in these references use equimolar amounts of epoxy and dicarboxylic acid, and thus, the resin products obtained by these known processes (1) are not epoxy functional, (2) contain significant amounts of unreacted dicarboxylic acid, or (3) undergo gelation.

U.S. Patent Nos. 4,829,141 and 4,302,574; and Canadian Patent No. 1091690 disclose reactions using epoxy resins and carboxylic acids; but these references do not teach an uncrosslinked, soluble, high molecular weight epoxy ester resin which is epoxy-terminated.

Other references may disclose the use of carboxylic acids but do not teach a process for preparing an epoxy-terminated uncrosslinked, soluble, high molecular weight epoxy ester resin using a dicarboxylic acid as a comonomer with an aromatic diepoxide. For example, U.S. Patent Nos. 3,864,316 and 4,474,935 discloses processes for preparing hydrogenated, i.e. non-aromatic epoxy resins; U.S. Patent No. 5,171,820 discloses a process for preparing hydroxyl-functional polyesters containing methylol groups; and WO 0001779A1 discloses coating compositions comprising epoxy-polyester block copolymers and crosslinker wherein the epoxy-polyester block copolymers are all acid functional.

It is desirable to provide an uncrosslinked, soluble, epoxy-terminated high molecular weight epoxy ester resin by reacting a low molecular weight, aromatic epoxy resin and a dicarboxylic acid, wherein such uncrosslinked, soluble, epoxy-terminated high molecular weight epoxy ester resin can be subsequently reacted with a crosslinking agent to form a coating.

#### Summary of the Invention

One aspect of the present invention is directed to novel uncrosslinked, soluble, epoxy terminated high molecular weight epoxy ester resins having epoxy termination and high conversion of carboxylic acid groups.

In one embodiment, the novel uncrosslinked, soluble, epoxy terminated high molecular weight epoxy ester resins of the present invention are made by reacting low molecular weight aromatic epoxy resins with dicarboxylic acids. By virtue of the epoxy ester resin's epoxy functionality, the resins can be used as precursors to epoxy thermosets, including coatings by crosslinking with crosslinking agents such as phenolic resoles.

Another aspect of the present invention is directed to novel epoxy ester coatings having an excellent balance of properties formed by reacting the above soluble high molecular weight epoxy ester resins with assorted curing agents. One primary purpose of the novel epoxy ester coatings is for the interior of food or beverage cans and/or can ends.

#### Detailed Description of the Preferred Embodiments

The present invention includes novel compositions comprising products having epoxy termination and high conversion of carboxylic acid groups or low acid number. The novel composition of the present invention includes an uncrosslinked, soluble, epoxy terminated high molecular weight epoxy ester resins made by reaction of low molecular weight epoxy resins with dicarboxylic acids which by virtue of their epoxy functionality can be used as precursors to epoxy thermosets, including coatings by crosslinking with phenolic resoles. The uncrosslinked, soluble, epoxy terminated high molecular weight epoxy resins compositions of the present invention are herein termed "solid epoxy ester resins" or "SEERs" to distinguish the epoxy resin of the present invention from the well-known "solid epoxy resins" or "SERs" derived from low molecular weight epoxy resins and bisphenol A.

By "uncrosslinked" it is meant the composition has a finite viscosity and is free of observable gelatinous reaction products.

By "soluble" it is meant the composition dissolves in suitable organic solvents.

By "high molecular weight" it is meant the composition has a molecular weight of at least about 2 times that of the starting epoxy resin, preferably at least about 3 times.

By "acid number" it is meant the amount in milligram (mg) of KOH required to neutralize 1 gram (g). of sample in accordance with the procedure described in ASTM D 1639-83.

By "high conversion of carboxylic acid groups" it is meant the substantially complete reaction of carboxylic acid moieties of the dicarboxylic acid and intermediates as measured by the acid number of the composition such that the acid number is less than about 5.

The epoxy resins of the present invention may be prepared by various processes including for example the process described in U.S. Patent Application filed of even date herewith, Attorney Docket No. 65280, incorporated herein by reference.

For example, the process described in U.S. Patent Application, Attorney Docket No. 65280, comprises reacting a low molecular weight epoxy resin and a dicarboxylic acid, optionally in the presence of another difunctional monomer such as bisphenol A, conducted in solution in the presence of a catalyst at a reaction temperature of up to about 220°C to form the uncrosslinked, soluble, high molecular weight epoxy ester resin of the present invention.

Preferably, the reaction of the dicarboxylic acid and epoxy resin components is conducted in solution and in the presence of an inert reaction diluent. The reaction diluent is preferably a solvent for or miscible with the epoxy resin. Any inert organic solvent which can dissolve the monomers to the appropriate degree and can be heated to the appropriate reaction temperature either at atmospheric, subatmospheric or superatmospheric pressure, and does not interfere with the reaction of a carboxylic acid moiety with an epoxide moiety, can be used. The solvent is desirably substantially free of impurities which will decrease the activity of the catalyst, such as hydrogen peroxide or uncomplexed transition metal ions.

Examples of suitable solvents include, pyridine, triethylamine or mixtures thereof; N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate; cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone; and ethers or hydroxy ethers such as dioxane, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether acetate, propylene glycol methyl ether and tripropylene glycol methyl ether; toluene, mesitylene, xylene, benzene, dipropylene glycol monomethyl ether acetate, halogenated solvents such as dichlorobenzene; propylene carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide, esters such as ethyl acetate or butyl acetate and mixtures thereof. Other suitable diluents are those organic compounds which are inert to the reactants at the reaction temperature, for example, various glycol ethers such as ethylene glycol ethyl ether, ethylene or propylene glycol monomethylether and esters thereof such as ethylene glycol monoethylether acetate; ketones such as methylisobutylketone, methylethylketone (MEK) and acetone; and aromatic hydrocarbons such

as toluene, xylene, cyclohexane or mixtures thereof. The preferred solvents are cyclohexanone and propylene glycol methyl ether acetate. The solvent is generally employed in an amount from about 5 to about 300 percent based on the total weight of all the reactants. If the resulting resin product is to be used for coating purposes, the solvent is typically retained in the reaction mixture. Otherwise, the solvent is removed by any suitable method such as by distillation or the like.

The concentrations at which the monomers are most advantageously employed in the organic liquid reaction medium are dependent on a variety of factors including the specific monomers, the solvent employed, and the polymer being prepared. In general, the monomers are employed in carboxylic acid to epoxy stoichiometric ratio of 0.60:1.0 to 0.95:1.0.

The low molecular weight epoxy resin employed in the present invention include polyepoxides which are compounds possessing more than one vicinyl epoxy group per molecule, i.e. more than one 1,2-epoxy group per molecule. These polyepoxides are saturated or unsaturated, aromatic polyepoxides; and are substituted, if desired, with non-interfering substituents, such as halogen atoms, hydroxy groups, ether radicals, and the like.

By "low molecular weight" epoxy resin it is meant an aromatic epoxy resin precursor that has a number average molecular weight ( $M_n$ ) of less than about 10,000, preferably less than about 8,000, and more preferably less than about 4,000. Generally, the "low molecular weight" epoxy resin precursors useful in the present invention have a number average molecular weight of from about 200 to about 10,000, preferably from about 200 to about 8,000, and more preferably from about 250 to about 4,000.

Preferred low molecular weight epoxy resins are liquid polyepoxides that include, for example, the liquid glycidyl polyethers of polyhydric phenols. More preferred are the glycidyl polyethers of 2,2-bis(4-hydroxyphenyl)propane having an average molecular weight between about 340 and about 900 and an epoxide equivalent weight of between about 170 and about 500. Especially preferred are the glycidyl polyethers of 2,2-bis(4-hydroxyphenyl)propane having an average molecular weight of between about 340 and about 900, an epoxide equivalent weight of between about 170 and about 500, and containing from about 0.01% to about 1.0% weight or higher of saponifiable chlorine. As used herein the terms "epoxide equivalent weight" and "weight per epoxide" refer to the average molecular weight of the polyepoxide molecule divided by the average number of oxirane groups present in the molecule.

Diepoxides which can be employed in the practice of the present invention include the diglycidyl ethers of dihydric phenols, such as those described in U.S. Patent Nos. 5,246,751; 5,115,075; 5,089,588; 4,480, 082 and 4, 438,254, all of which are incorporated herein by reference, or the diglycidyl esters of aromatic dicarboxylic acids such as those described in U. S. Patent No. 5,171, 820 incorporated herein by reference. Other suitable diepoxides include  $\alpha\omega$ -diglycidylisopropylidene-bisphenol-based epoxy resins, commercially known as D.E.R.® 300 and 600 series epoxy resins, and commercially available from The Dow Chemical Company. Preferred diepoxides are the epoxy resins having an epoxy equivalent weight of from about 100 to about 4000. Most preferred diepoxides are the diglycidyl ethers of bisphenol A; 4,4'-sulfonyldiphenol; 4,4'-oxydiphenol; 4,4'-dihydroxybenzophenone; resorcinol; hydroquinone; 9,9'-bis(4-hydroxyphenyl)fluorene; 4,4'-dihydroxybiphenyl or 4, 4'-dihydroxy- $\alpha$ -methylstilbene and the diglycidyl esters of the dicarboxylic acids mentioned previously. Such aromatic diepoxides are much more reactive than non-aromatic diepoxides towards dicarboxylic acids and are thereby much more prone to crosslink or gel. Surprisingly, in the present invention, an uncrosslinked, soluble resin product is prepared using such aromatic diepoxides.

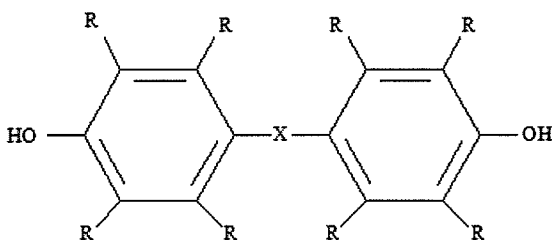
The amount of epoxy resins used depends on the targeted molecular weight and epoxy functionality. In general, the epoxy resin is used in an amount of from about 30 wt.% to about 85 wt.%, more preferably, from about 40 wt.% to about 75 wt.% and, most preferably, from about 45 wt.% to about 70 wt.%, based on the weight of reactants.

The carboxylic acids used in the present invention may be, for example, saturated, unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic. Examples of such acids include, among others, succinic acid, glutaric acid, adipic acid (AA), pimelic acid, suberic acid, azelaic acid, sebacic acid, oxalic acid, abietic acid, maleic acid, aconitic acid, chlorendic acid, phthalic acid (PA), terephthalic acid (TPA), isophthalic acid (IPA), 2,6-naphthalenedicarboxylic acid, 3,4'-biphenyldicarboxylic acid, 4,4'-biphenyldicarboxylic acid, malonic acid, 1,4-cyclohexanedicarboxylic acid, 1,10-decanedicarboxylic acid, 1,12-dodecanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid (1,3-CHDA), 1,4-cyclohexanedicarboxylic acid (1,4-CHDA), tartaric acid, citramalic acid and hydroxyglutaric acid. The more preferred carboxylic acids include terephthalic acid, isophthalic acid, adipic acid and mixtures thereof.

The amount of carboxylic acid used in the present invention may vary over a wide range. In general, the amount of carboxylic acid used in the present invention is from about 1 wt.% to about 50 wt.%, more preferably, from about 5 wt.% to about 45 wt.% and, most preferably, from about 10 wt.% to about 40 wt.%, based on the weight of reactants.

The low molecular weight epoxide and carboxylic acid reaction mixture may optionally be carried out in the presence of a difunctional monomer such as a hydroxyl or thiol group-containing compound such as a phenol or thiophenol. The preferred optional hydroxyl group-containing compounds are phenols having at least one hydroxyl group attached to an aromatic nucleus. The phenols can be monohydric or polyhydric and can be substituted or unsubstituted. Polymeric polyhydric phenols can be obtained by condensing monohydric or polyhydric phenols with formaldehyde.

Preferred optional phenols are the polyhydric phenols containing from 2 to 6 OH groups and up to 30 carbon atoms, including those represented by the formula:



wherein X is a polyvalent element or radical and each R is independently selected from hydrogen, halogen and hydrocarbon radicals. The preferred radicals represented by X are oxygen, sulfur, --SO--, --SO<sub>2</sub>--, divalent hydrocarbon radicals containing up to 10 carbon atoms and oxygen, silicon, sulfur or nitrogen containing hydrocarbon radicals. The preferred phenol is 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A), in which each R is H and X is isopropylidene.

Preferred dihydric phenols which can be employed in the practice of the present invention for preparing the resin of the present invention include 4,4'-isopropylidene bisphenol (bisphenol A), 4,4'-dihydroxydiphenylethylmethane, 3,3'-dihydroxy-diphenyldiethylmethane, 3,4'-dihydroxydiphenyl-methylpropylmethane, bisphenol, 4,4'-dihydroxy-diphenyloxide, 4,4'-dihydroxydiphenylcyanomethane, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl sulfone, 2,6-dihydroxynaphthalene, 1,4'-dihydroxy-naphthalene, phenol, resorcinol, o-cresol, m-cresol, p-cresol, chlorophenol, nitrophenol, hydroquinone, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)pentane, catechol, halogenated bisphenol such as tetrabromobisphenol A and other dihydric phenols listed in U.S. Patent Nos. 3,395, 118; 4,438,254 and 4,480,082 which are hereby incorporated by reference. In addition, mixtures of different dihydric phenols can be employed. Of these dihydric phenols, bisphenol A, hydroquinone and mixtures thereof are most preferred.

The amount of phenol used in the present invention depends on the molecular weight of the phenol, the molecular weight of the epoxy, as well as the target equivalent weight of the SEER and level of branching. In general, the phenol is used in an amount of from about 1 wt. % to about 60 wt. %, more preferably, from about 5 wt. % to about 50 wt. % and, most preferably, from about 20 wt. % to about 45 wt. %, based on the weight of reactants.

In general, the reaction of the low molecular weight epoxy resin with a dicarboxylic acid requires a catalyst or any material capable of catalyzing the reaction. In preparing the epoxy resins of the present invention, the dicarboxylic acid and the epoxy resin components are contacted in the presence of a catalyst for the reaction between the carboxylic groups of the dicarboxylic acid and the epoxy groups of the epoxy resin and at conditions sufficient to form the desired resin.

The catalysts useful in the present invention include, but are not limited to, phosphines, amines, quaternary ammonium and phosphonium salts, such as tetraethylammonium chloride, tetraethylammonium bromide, tetraethylammonium iodide, tetraethylammonium hydroxide, tetra(n-butyl)ammonium chloride, tetra(n-butyl) ammonium bromide (TBAB), tetra(n-butyl)ammonium iodide, tetra(n-butyl) ammonium hydroxide, tetra (n-octyl) ammonium chloride, tetra(n-octyl) ammonium bromide, tetra(n-octyl)ammonium iodide, tetra(n-octyl)ammonium hydroxide, methyltris(n-octyl)ammonium chloride, bis(tetraphenylphosphoranylidene)ammonium chloride, ethyltri-p-tolylphosphonium acetate/acetic acid complex, ethyltriphenylphosphonium acetate/acetic acid complex, N-methylmorpholine, 2-phenylimidazole, or combinations thereof and the like as described in U.S. Patent Nos. 5,208,317; 5,109,099; and 4,981,926, incorporated herein by reference. Most preferred catalysts include tetrabutylphosphonium bromide (TBPB), tetraethylammonium bromide, tetraethylammonium hydroxide, ethyltritolylphosphonium acetate, ethyltriphenylphosphonium acetate, and N-methylmorpholine, 2-phenylimidazole (2-PhIm).

While any material capable of catalyzing the reaction can be used, the preferred catalysts are the onium catalysts. Preferred onium catalysts include the phosphonium or ammonium salt catalysts. More preferred onium catalysts include tetrabutylammonium bromide, tetrabutylphosphonium bromide (TBPB), ethyltriphenylphosphonium iodide, tetraphenylphosphonium bromide and tetrakis(n-butyl)ammonium bromide and the corresponding chloride, iodide, bromide, acetate, formate, phosphate, borate, trifluoroacetate, oxalate and bicarbonate, with tetrabutylphosphonium bromide (TBPB) being most preferred.

The amount of catalyst used depends on the molecular weight of the catalyst, the activity of the catalyst and the speed at which the polymerization is intended to proceed. The amount of catalyst employed in the process of the present invention can vary over a wide range, so long as a catalytic amount is present. In general, the amount of catalyst used in the present invention will  
5 fall within the range of from about 0.001 percent (%) to about 10 percent, preferably from about 0.001% to about 5% by weight of the total reactants, more preferably from about 0.002% to about 2%, and most preferably from about 0.03% to about 1% by weight of the reactants.

Generally, the epoxy resin compositions of the present invention can be prepared by reacting a low molecular weight aromatic epoxy resin and a dicarboxylic acid in the presence of a  
10 catalyst and in the presence of a solvent under conditions sufficient to form the uncrosslinked, soluble, high molecular weight epoxy ester resin.

By "high molecular weight" epoxy resin it is meant an epoxy resin product that has a number average molecular weight ( $M_n$ ) of less than about 20,000, preferably less than about 10,000, and more preferably less than about 8,000. Generally, the "high molecular weight"  
15 epoxy resins useful in the present invention have a number average molecular weight of from about 1,000 to about 20,000, preferably from about 1,000 to about 10,000, and more preferably from about 1,200 to about 8,000.

The reaction for preparing the SEER of the present invention can be done using a batch process or a continuous process conducted in a reactive extruder, such as that described in  
20 European Patent No. EP 0193809. The process of the present invention can be conducted in an open container or in an extruder or in an injection molding machine.

The conditions at which the polymerization reaction is most advantageously conducted are dependent on a variety of factors, including the specific reactants employed, solvent employed, and catalyst employed. In general, the reaction is conducted under a non-oxidizing atmosphere  
25 such as a blanket of nitrogen or other inert gases. It is desirable to use inert organic solvents for the reactants in order to ensure homogeneous reaction mixtures and to moderate exothermic reactions at such temperatures.

The reaction conditions employed in the process of the present invention may be varied. The time and temperature most advantageously employed will vary depending on the specific  
30 monomers employed, particularly their reactivity, the specific oligomer, and the organic liquid. Generally, however, convenient rates of reaction to form the polyesters are obtained at reaction temperatures in the range of from about 50 °C to about 300 °C, at reaction pressures ranging from

about atmospheric to about 150 psig, and at reaction times of from about 30 minutes to about 24 hours.

The reaction of the epoxy resin and carboxylic acid is advantageously carried out at an elevated temperature. The reaction temperature is preferably from about 60 °C to about 220 °C and, more preferably, from about 100 °C to about 150 °C, and most preferably, from about 120°C to about 140°C.

The reaction time is preferably from about 1 hour to about 24 hours and, most preferably, from about 2 hours to about 8 hours.

The reaction is continued until the desired conversion, as determined by measuring the acid conversion of the resin by acid number (AN) titration and when the target molecular weight or EEW of the resin, is achieved, at which point, the reaction is effectively terminated.

In one embodiment the reaction is generally carried out by combining the polyepoxide and the dicarboxylic acid reactants at a starting temperature of about 100°C to about 120°C and allowing the reaction to exotherm to a temperature of about 160°C to about 200°C, for a time of about 1 hour to about 2 hours.

The relative amount of the reactants depends upon the characteristics, particularly the molecular weight, of the product desired. For the preferred high molecular weight epoxy-terminated polyester resin products having an epoxide equivalent weight of between about 600 and about 4,000, about 0.60 to 0.95 mole dicarboxylic acid will be reacted with each mole of a diglycidyl ether of bisphenol-A having an epoxide equivalent weight of between about 170 and about 500.

The present reaction can be done in one step wherein a liquid aromatic epoxy resin (LER), dicarboxylic acid, and catalyst are reacted and the reaction terminated at a point such that the targeted epoxy reaction product is obtained prior to gelation.

Alternatively, if an optional difunctional monomer is used such as a dihydric phenol, the liquid aromatic epoxy resin and the dihydric phenol may be reacted first and then the dicarboxylic acid may be added to the reaction mixture; or the LER and dicarboxylic acid may be reacted first, and then the dihydric phenol may be added to the reaction mixture; and the reaction terminated at a point when the reaction product contains the target epoxy equivalent weight prior to gelation.

During polymer synthesis, the polymers are recovered from the reaction mixture by conventional methods. For example, the reaction mixture containing the polymer as a precipitate can be filtered to remove the solid polymer. The solid monomer can then be rinsed with water, methanol, and ether or other solvents which are non-solvents for the polymer, but good solvents for the impurities. The polymer also can be isolated by pouring the reaction mixture into a non-solvent for the polymer and collecting the precipitated product. Additionally, the product polymer can be isolated by removal of the solvent by vacuum distillation, wiped-film evaporation or devolatilization extrusion.

The epoxy ester resin of the present invention can be cured with a variety of epoxy curing agents such as phenolics, amines, carboxylic acids, phenol formaldehyde resins, and anhydrides, as well as through the hydroxyl group or an epoxy group. The resin of the present invention can be reacted with a hardener such as, for example, an amine-terminated polymer, a carboxy-terminated polymer, a phenol-terminated polymer, a multifunctional amine, carboxylic acid or phenol, or a phenolic resole polymer.

The SEER of the present invention can be used in a variety of industrial applications or other epoxy applications such as coatings, laminates and composites. Industrial coatings are surface protective coatings (paint coatings) applied to substrates and typically cured or crosslinked to form continuous films for decorative purposes as well as to protect the substrate. A protective coating ordinarily comprises an organic polymeric binder, pigments, and various paint additives, where the polymeric binder acts as a fluid vehicle for the pigments and imparts rheological properties to the fluid paint coating. Upon curing or crosslinking, the polymeric binder hardens and functions as a binder for the pigments and provides adhesion of the dried paint film to the substrate. The pigments may be organic or inorganic and functionally contribute to opacity and color in addition to durability and hardness. The manufacture of protective coatings involves the preparation of a polymeric binder, mixing of component materials, grinding of pigments in the polymeric binder, and thinning to commercial standards.

The coating of the present invention using the SEER prepared as described herein is prepared under the conditions described in accordance with ASTM 4147-99.

The polymeric binder can include a wide variety of other additives such as, for example, hardeners, dyes, pigments and flow modifiers, fire-retardants, self extinguishing agents, desiccants and all manner of additives which are used herein for their known purposes. Examples of fire retardants include: monoammonium phosphate, diamonium phosphate and

aluminum trihydrate. These additives can be in the form of liquids or particles so long as the binder remains solid, has the desired particle size and imparts no adverse effects to the binder.

A liquid coating composition can be obtained which comprise the resin of the present invention, and suitable pigments, catalysts and additives. The coatings therefrom have a surprisingly good combination of highly prized properties. Depending on the choice and the amount of polymer, crosslinker, catalyst and other components one can obtain, for example good flow, good chemical resistance, high gloss, high scratch resistance, good mechanical properties, good outdoor durability and good color stability.

Water-dispersed coating compositions containing the resin of the present invention are highly desirable for can and coil coating compositions.

In order to provide a better understanding of the present invention including representative advantages thereof, the following Examples are offered.

Various terms, abbreviations and designations for raw materials used in the following Examples are explained as follows:

“EEW” stands for epoxy equivalent weight.

“AN” stands for acid number.

D.E.R.<sup>TM</sup> 331 (EEW = 188), D.E.R. 383 (EEW = 180), and D.E.R. 354LV (EEW = 170) are liquid aromatic epoxy resins (LERs). D.E.R. 661 (EEW = 534), D.E.R. 667 (EEW = 1850) and D.E.R. 669E (EEW = 3290) are solid epoxy resins (SERs). These products are commercially available from The Dow Chemical Company.

“A1” is a catalyst (70 wt. % *n*-Bu<sub>4</sub>POAc/HOAc in methanol) available from Morton Chemical Company.

TBAB, TBPB, 2-PhIm, TPA, AA, PA, 1,4-CHDA, 1,3-CHDA, diglyme, cyclohexanone, Dowanol<sup>TM</sup> PMA (PMA), Dowanol PM (PM), and di(propylene glycol) methyl ether acetate (DPMA) are chemicals commercially available from Aldrich.

Isophthalic acid (IPA) is an acid commercially available from Aldrich or MB Biomecids, Inc.

Methylon 75108 is a methylolphenyl allyl ether commercially available from Occidental Chemical Co.

Super phosphoric acid (105 %), methyl ethyl ketone (MEK), lactic acid, and 2-butoxyethanol (Dowanol™ EB) are chemicals commercially available from Aldrich Chemical Co.

“HPLC” stands for high pressure liquid chromatography.

5 HPLC grade water, acetonitrile (ACN), and tetrahydrofuran (THF) are chemicals commercially available from EMD.

BYK-310 silicone surfactant is commercially available from Byk Chemie.

The various standard test methods and procedures used in the Examples to measure certain properties are as follows:

10 Epoxide Equivalent Weight (EEW) titrations are done according to a procedure equivalent to ASTM D-1652-97.

Acid number (AN) analysis is done according to a procedure equivalent to ASTM D 1639-83.

15 Cyclic dimer analysis is done by HPLC using a water/ACN gradient elution program with an Agilent 1100 LC system.

Number average molecular weight ( $M_n$ ) analysis is done using a Viscotek GPC analysis system.

20 The following Examples are for illustrative purposes only and are not intended to limit the scope of the present invention. Unless otherwise indicated, all parts and percentages are by weight.

Example 1 - Preparation of Resin Product

Solution resin advancement reactions were done using the following procedure: Preparation of a 7-type D.E.R. 661-AA SEER is described as follows. To a 1 liter (L) resin kettle fitted with a mechanical stirrer, condenser, heating mantle and thermocouple connected to a programmable controller was added 100 grams (g) D.E.R. 661 SER (previously vacuum dried at 100°F for 18 hours), 9.22 g AA, and 110 g diglyme. The reactor was padded with N<sub>2</sub> while heating with gentle mixing to 110°C at which point 0.77 g TBAB in 10 milliliters (mL) diglyme was added. (Complete solids dissolution was observed at about 60°C) The reaction mixture was maintained at about 112°C for a period of 320 minutes during which time samples were occasionally removed for EEW titration.

The results of this Example 1 are shown in Table I below.

Example 2 - Preparation of Resin Product

Example 2 was carried as described in Example 1 above except that 11.33 g. adipic acid (AA) was used.

Comparative Example A

Comparative Example A was carried as described in Example 1 above using 26.7 g bisphenol A, 32.7 g adipic acid, 150.0 g D.E.R. 331 epoxy resin, and 0.16 g A-1 catalyst and without solvent at the reaction temperature as shown in Table I.

Comparative Example B

Comparative Example B was carried as described in Example 1 above using 24.3 g bisphenol A, 29.8 g adipic acid, 150.0 g D.E.R. 331 epoxy resin, and 0.15 g A-1 catalyst and without solvent at the reaction temperature as shown in Table I.

Comparative Example C

Comparative Example C was carried as described in Example 1 above using 33.3 g. adipic acid, 150.0 g D.E.R. 331 epoxy resin, and 0.14 g A-1 catalyst and without solvent at the reaction temperature as shown in Table I.

Comparative Example D

Comparative Example D, Part 1, was carried as described in Example 1 above using 33.3 g adipic acid, 150.0 g D.E.R. 331 epoxy resin, and 0.14 g A-1 catalyst and without solvent at the reaction temperature as shown in Table I. Part 2 of Comparative Example D was done using the

product from Part 1 and 26.1 g bisphenol A and 0.16 g A-1 catalyst at the reaction temperature as shown in Table I.

Table I. Reactions of liquid epoxy resin (LER) or solid epoxy resin (SER) with AA.

| Example                        | Reactants                           | Catalyst | Conditions             | Target EEW | Actual EEW |
|--------------------------------|-------------------------------------|----------|------------------------|------------|------------|
| Example 1                      | D.E.R. 661 + AA                     | TBAB     | 110°C, 50 % in diglyme | 1800       | 1592       |
| Example 2                      | D.E.R. 661 + AA                     | TBAB     | 110°C, 50 % in diglyme | 3200       | 3115       |
| Comparative Example A          | LER + BA + AA                       | A-1      | 130 – 180°C            | 1800       | gel        |
| Comparative Example B          | LER + BA + AA                       | A-1      | 130 – 180°C            | 1150       | gel        |
| Comparative Example C          | LER + AA                            | A-1      | 160°C                  | 530        | gel        |
| Comparative Example D – Part 1 | LER + AA                            | A-1      | 130°C                  | 530        | 533        |
| Comparative Example D – Part 2 | Comparative Example D – Part 1 + BA | A-1      | 160°C                  | 1800       | gel        |

#### Examples 3-20 - Preparation of Resin Product

5 Two methods were used for SEER resin preparations. In both methods, a heterogeneous system was generated at the beginning of the reaction, and a clear solution was formed when the dicarboxylic acid (DCA) used dissolved completely upon heating. The solution was sampled periodically to follow the EEW and AN changes. When the advancement finished, the SEER solution was allowed to cool to less than 90°C and then was transferred quickly into a glass jar.

10 General Procedure for Method A: LER, DCA, solvent and catalyst were loaded to a 500 mL glass resin kettle fitted with a reflux condenser, a N<sub>2</sub> inlet, a stirring rod connected to an air-driven motor, and a thermocouple and heating mantle connected to a temperature controller. The reaction mixture was heated to the designated temperature in less than 1 hour and was then held isothermally until the target EEW was reached. In this Method A, the reaction time was taken as  
15 the duration between the time at the desired solution temperature and the time after reaching the desired EEW.

General Procedure for Method B: LER, DCA, and partial solvent (about 90 wt. %) were added to a 500 mL glass resin pot fitted as in Method A above. The reaction mixture was heated

to the designated temperature in less than 1 hour. The catalyst and the remaining solvent (about 10 wt. %), or catalyst dissolved in the remaining solvent (~ 10 wt. %), were then added. The solution was held at the designated temperature until the target EEW was reached. The reaction time was from the time of catalyst addition to the time of reaching the target EEW.

- 5 The reaction conditions for the resin preparations are shown in Table II and the results of the analysis of the resin products is shown in Table III.

Table II. Reaction Conditions for Resin Preparations

| Example <sup>a</sup> | LER                 |        | DCA      |       | Solvent       | Catalyst <sup>c</sup> |        | Temperature (°C) |
|----------------------|---------------------|--------|----------|-------|---------------|-----------------------|--------|------------------|
|                      | D.E.R. <sup>d</sup> | (g)    | acid     | (g)   |               | catalyst              | (g)    |                  |
| 3                    | 383                 | 200.03 | IPA      | 79.30 | diglyme       | TBPB                  | 1.9700 | 110              |
| 4                    | 354LV               | 200.00 | IPA      | 84.70 | diglyme       | TBPB                  | 2.0100 | 110              |
| 5                    | 354LV               | 200.08 | IPA      | 90.40 | diglyme       | TBPB                  | 2.0500 | 110              |
| 6                    | 383                 | 199.97 | IPA      | 84.90 | PMA           | TBPB                  | 2.0108 | 110              |
| 7                    | 383                 | 200.00 | IPA      | 84.88 | PMA           | TBPB                  | 2.0100 | 140              |
| 8                    | 383                 | 25.07  | IPA      | 10.61 | diglyme       | TBPB                  | 0.2493 | 160              |
| 9                    | 383                 | 200.06 | TPA      | 84.91 | PMA           | TBPB                  | 2.0100 | 140              |
| 10                   | 383                 | 200.01 | PA       | 84.91 | PMA           | TBPB                  | 2.0111 | 140              |
| 11                   | 383                 | 24.96  | IPA      | 10.58 | PMA           | TBPB                  | 0.1252 | 140              |
| 12                   | 383                 | 60.05  | IPA      | 25.51 | PMA           | TBPB                  | 0.1492 | 140              |
| 13                   | 383                 | 179.98 | IPA      | 76.39 | cyclohexanone | TBPB                  | 1.8074 | 140              |
| 14                   | 383                 | 64.98  | IPA      | 27.59 | DPMA          | TBPB                  | 0.0640 | 180              |
| 15 <sup>b</sup>      | 383                 | 121.87 | 1,4-CHDA | 53.50 | PMA           | TBPB                  | 1.2353 | 140              |

<sup>a</sup> Method A and 50 wt. % solvent were used unless otherwise noted. <sup>b</sup> Solvent: 18 wt. %. <sup>c</sup> Catalyst wt. % was based on amount of LER, DCA, and catalyst. Solution wt. % was based on the amount of whole reaction system, *i.e.* LER, DCA, catalyst, and solvent. <sup>d</sup> D.E.R. epoxy resin type.

10

Table II (continued). Reaction Conditions for Resin Preparations

| Example <sup>a</sup> | LER                 |        | DCA  |       | Solvent       | Catalyst <sup>c</sup> |        | Temperature (°C) |
|----------------------|---------------------|--------|------|-------|---------------|-----------------------|--------|------------------|
|                      | D.E.R. <sup>d</sup> | (g)    | acid | (g)   |               | catalyst              | (g)    |                  |
| 16                   | 383                 | 200.02 | IPA  | 84.89 | PMA           | TBPB                  | 2.0123 | 140              |
| 17                   | 331                 | 199.97 | IPA  | 81.19 | cyclohexanone | TBPB                  | 1.9805 | 140              |
| 18                   | 383                 | 200.00 | IPA  | 79.40 | cyclohexanone | 2-PhIm                | 0.1975 | 140              |
| 19                   | 383                 | 200.02 | TPA  | 42.45 | PMA           | TBPB                  | 2.0100 | 140              |
| 20                   | 383                 | 180.01 | IPA  | 76.40 | cyclohexanone | TBPB                  | 1.8080 | 140              |

<sup>a</sup> Method A and 50 wt. % solvent were used unless otherwise noted. <sup>b</sup> Solvent: 18 wt. %. <sup>c</sup> Catalyst wt. % was based on amount of LER, DCA, and catalyst. Solution wt. % was based on the amount of whole reaction system, *i.e.* LER, DCA, catalyst, and solvent. <sup>d</sup> D.E.R. epoxy resin type.

Table III. EEW, AN, and M<sub>n</sub> of SEERs

| Example <sup>a</sup> | Time (min) | LER   | Acid     | EEW    |        | AN   | M <sub>n</sub> |
|----------------------|------------|-------|----------|--------|--------|------|----------------|
|                      |            |       |          | target | actual |      |                |
| 3                    | 365        | 383   | IPA      | 1,800  | 1,736  | 0.2  | 2,840          |
| 4                    | 500        | 354LV | IPA      | 1,800  | 1,754  | 0.2  | 3,615          |
| 5                    | 470        | 354LV | IPA      | 3,200  | 2,869  | 0.2  | 7,184          |
| 6                    | 515        | 383   | IPA      | 3,200  | 3,265  | 0.1  | 4,690          |
| 7                    | 85         | 383   | IPA      | 3,200  | 3,612  | 0.1  | 6,671          |
| 8                    | 30         | 383   | IPA      | 3,200  | 3,354  | 0.1  | 5,119          |
| 9                    | 160        | 383   | TPA      | 3,200  | 3,440  | <0.1 | 4,440          |
| 10                   | 67         | 383   | PA       | 3,200  | 3,607  | 0.5  | 7,251          |
| 11                   | 149        | 383   | IPA      | 3,200  | 3,156  | 1.6  | 5,191          |
| 12                   | 285        | 383   | IPA      | 3,200  | 3,234  | 1.2  | 6,194          |
| 13                   | 45         | 383   | IPA      | 3,200  | 3,628  | 0.1  |                |
| 14                   | 83         | 383   | IPA      | 3,200  | 4,110  | 0.1  | 1,778          |
| 15                   | 78         | 383   | 1,4-CHDA | 3,200  | 3,167  | 0.6  | 3,732          |
| 16                   | 45         | 383   | IPA      | 3,200  | 3,570  | 1    |                |

<sup>a</sup> EEW and AN were measured after the bulk resin solution was cooled to room temperature unless otherwise noted. <sup>b</sup> A small amount of the sample (usually < 20 g) was removed from the bulk solution and used for EEW and AN analysis.

Table III (*continued*). EEW, AN, and  $M_n$  of the SEERs

| Example <sup>a</sup> | Time (min)      | LER | Acid | EEW   |                    | AN  | $M_n$ |
|----------------------|-----------------|-----|------|-------|--------------------|-----|-------|
| 17                   | 88 <sup>c</sup> | 331 | IPA  | 3,200 | 3,476              | 0.2 | 3,445 |
| 18                   | 268             | 383 | IPA  | 1800  | 2,758 <sup>b</sup> | 0.9 | 3,317 |
| 19                   | 103             | 383 | TPA  | 3,200 | 3,066              | 0.5 | 7,598 |
| 20                   | 38              | 383 | IPA  | 3,200 | 3,126              | 0.3 | 3,848 |

<sup>a</sup> EEW and AN were measured after the bulk resin solution was cooled to room temperature unless otherwise noted. <sup>b</sup> A small amount of the sample (usually < 20 g) was removed from the bulk solution and used for EEW and AN analysis.

5 The results in Tables I – III show that uncrosslinked, soluble, high molecular weight epoxy ester resins are obtained having desired properties.

#### Examples 21-28 and Comparative Example E - Preparation of Coated Steel Panels

10 Tin free steel (TFS - single reduced electrolytic chromium coated sheet), type L, T4CA, surface 50, commercially available from Weirton Steel Corporation were used as the metal substrate in this Example.

15 Coating formulations were drawn down on TFS panels according to a procedure described in ASTM 4147-99 and cured to give 0.20 +/- 0.02 mil coating thickness. The coated panels were tested for MEK resistance in accordance with ASTM D 5402-93, maximum number of double-rubs (DR) prior to coating failure; and for wedge bend flexibility in accordance with ASTM D 3281-84. Lactic acid pasteurization resistance was done using wedge bend panel samples (~170° bend with coating in tension) immersed in vials containing 2 wt. % lactic acid and heated in an autoclave at 120 °C for 30 minutes. The rating system, described in Table A below, was used to describe the coating performance.

Table A. Rating System for the Lactic Acid Pasteurization Resistance Test.

## Rating Observation

- 5 No blush or blisters on bent or flat sections
- 4 No blush or blisters on flat section
- 3 Blush but no blisters on flat section
- 2 Blush with few small blisters on flat section
- 1 Blush with many large blisters on flat section
- 0 Total coating destruction

All tests were performed in duplicate and the average values of the results are reported

herein.

The properties of some of the coatings prepared in Examples 3-20 were measured and the results of these examples are shown in Table IV below.

Table IV. Properties of Resin Coatings Cured with Phenolic Resole Hardener and H<sub>3</sub>PO<sub>4</sub> Catalyst at 205 °C for 10 Minutes.

| Example               | Resin                     | Hardener<br>(wt. %) | H <sub>3</sub> PO <sub>4</sub><br>(wt. %) | Additive <sup>a</sup><br>(wt. %) | MEK DR<br>(max. pass) | Wedge Bend<br>(% failure) | LAP Test |
|-----------------------|---------------------------|---------------------|-------------------------------------------|----------------------------------|-----------------------|---------------------------|----------|
| Comparative Example E | D.E.R. 669E               | 15                  | 0.75                                      | ---                              | 125                   | 25                        | 3        |
| 21                    | 9T/383/IPA<br>(Example 6) | 15                  | 0.75                                      | ---                              | 175                   | 30                        | 0        |
| 22                    | 9T/383/IPA<br>(Example 6) | 25                  | 0.75                                      | ---                              | 200                   | 41                        | 4        |
| 23                    | 9T/383/IPA<br>(Example 6) | 15                  | 1.50                                      | ---                              | 125                   | 33                        | 4        |
| 24                    | 7T/383/IPA<br>(Example 3) | 15                  | 1.50                                      | 0.1                              | 150                   | 33                        | 2        |
| 25                    | 9T/383/TPA<br>(Example 9) | 15                  | 0.75                                      | 0.1                              | 150                   | 30                        | 2        |

Table IV. Properties of Resin Coatings Cured with Phenolic Resole Hardener  
and H<sub>3</sub>PO<sub>4</sub> Catalyst at 205 °C for 10 Minutes.

| Example | Resin                           | Hardener | H <sub>3</sub> PO <sub>4</sub> | Additive <sup>a</sup> | MEK<br>DR | Wedge<br>Bend | LAP<br>Test |
|---------|---------------------------------|----------|--------------------------------|-----------------------|-----------|---------------|-------------|
| 26      | 9T/383/TPA-AA<br>(Example 19)   | 15       | 0.75                           | 0.1                   | 125       | 31            | 2           |
| 27      | 9T/383/PA<br>(Example 10)       | 10       | 0.75                           | 0.1                   | 150       | 33            | 3           |
| 28      | 9T/383/1,4-CHDA<br>(Example 15) | 5        | 0.75                           | 0.1                   | 100       | 25            | 3           |

<sup>a</sup>Byk-310 silicone surfactant

These results in Table IV show that coatings having desirable properties can be obtained from the uncrosslinked, soluble, high molecular weight epoxy ester resins of the present invention.

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the present invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

## WHAT IS CLAIMED IS:

1. An aromatic group-containing epoxy ester resin composition free of gels comprising an uncrosslinked, soluble, high molecular weight epoxy ester resin having terminal epoxy groups, having an epoxy functionality of greater than 1, having an acid number of less than 5, and having an epoxy equivalent weight (EEW) of about 600 or greater; said uncrosslinked, soluble, high molecular weight epoxy ester resin derived directly from the reaction of (a) a low molecular weight aromatic epoxy resin and (b) a dicarboxylic acid.
2. The epoxy ester resin of Claim 1 wherein the low molecular weight aromatic epoxy resin comprises a diglycidyl ether of a dihydric phenol.
3. The epoxy ester resin of Claim 2 wherein the dihydric phenol comprises 4, 4'-isopropylidene bisphenol, 4,4'-dihydroxydiphenylethylmethane, 3,3'-dihydroxydiphenyldiethylmethane, 3,4'-dihydroxydiphenyl-methylpropylmethane, bisphenol, 4,4'-dihydroxydiphenyl-oxide, 4,4'-dihydroxydiphenylcyanomethane, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl sulfone, 2,6-dihydroxynaphthalene, 1,4'-dihydroxy-naphthalene, catechol, resorcinol, hydroquinone, or tetrabromobisphenol A.
4. The epoxy ester resin of Claim 2 wherein the diglycidyl ether comprises a diglycidyl ether of bisphenol-A, a diglycidyl ether of hydroquinone or a diglycidyl ether of resorcinol.
5. The epoxy ester resin of Claim 1 wherein the dicarboxylic acid comprises adipic acid, isophthalic acid, terephthalic acid, or mixtures thereof.
6. A binder composition comprising the epoxy ester resin of Claim 1.
7. A binder composition comprising the epoxy ester resin of Claim 1 and a hardener.
8. The binder composition of Claim 7 wherein the hardener comprises an amine-terminated oligomers or polymer, a carboxy-terminated oligomers or polymer, a phenol-terminated oligomers or polymer, a phenolic resole oligomers or polymer, a multifunctional amine, carboxylic acid or phenol.
9. The binder composition of Claim 8 further comprising pigments, fillers, flow modifiers, surfactants, lubricants, or solvents.
10. A liquid coating comprising the binder composition of Claim 7.
11. A composite material comprising the composition of Claim 7 and a substrate.

12. The composite material of Claim 11 wherein the substrate is metallic.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2007/080827

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C08G59/18 C08G59/42

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                  | Relevant to claim No. |
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| X         | US 4 778 861 A (DERVAN ANDREW H [US] ET<br>AL) 18 October 1988 (1988-10-18)<br>examples 1,2<br>-----                | 1-12                  |
| X         | US 4 816 528 A (DERVAN ANDREW H [US] ET<br>AL) 28 March 1989 (1989-03-28)<br>examples 1-5<br>-----                  | 1-12                  |
| X         | WO 98/29468 A (SHELL INT RESEARCH [NL])<br>9 July 1998 (1998-07-09)<br>examples 5,6<br>-----                        | 1-12                  |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents :

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*G\* document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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