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(54) **Title:** METHOD FOR CURING A RESIN SYSTEM

(57) **Abstract:** Method for curing a resin system comprising (i) an epoxy resin and (ii) an unsaturated polyester resin or a vinyl ester resin, the method comprising the addition to said resin system of a formulation obtained by mixing an organic hydroperoxide and an amine. Mixtures of amines and organic hydroperoxides are stable and can be used in a two-component system.



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METHOD FOR CURING A RESIN SYSTEM

The present invention relates to a method for curing a resin system comprising (i) an epoxy resin and (ii) an unsaturated polyester resin or a vinyl ester resin.

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Thermosetting polyester resins and thermosetting epoxy resins are each well-known compositions having utility in reinforced and unreinforced plastics as well as in coatings. The polyester resins, which are unsaturated polyester-unsaturated monomer mixtures, have a low viscosity in the uncured state and have good flow, wetting, and penetrating properties. When cured, the polyester resins have good chemical (particularly acid) resistance and good weathering properties. However, these resins exhibit high shrinkage upon cure and the cured resins have poor impact resistance and poor adhesion to many substrates, particularly concrete and carbon fibres.

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Thermosetting epoxy resins in general have higher viscosities than thermosetting polyester resins, with correspondingly poorer flow, wetting, and penetrating properties.

Epoxy resins cured at room temperature with conventional aliphatic amines have somewhat poor acid resistance. Furthermore, they are far more expensive than polyester resins. However, epoxy resins exhibit low shrinkage upon cure and the cured compositions have good impact resistance and outstanding adhesion to a variety of substrates, including carbon and aramid fibres.

25 Various attempts have been made to combine thermosetting epoxy resins and thermosetting polyester resins in order to take advantage of the good properties of each.

For instance, US 2,859,199 describes heat curable compositions made from an

epoxy resin, an unsaturated polyester, and a vinyl monomer. These materials are said to co-react at temperatures of 75°C to 300°C to form cross-linked products.

5 A room-temperature curable blend of a thermosetting polyester resin and an epoxy/amine thermosetting resin has been disclosed by US 3,508,951. Methyl ethyl ketone peroxide and cobalt naphthenate were used as the respective peroxide and accelerator for polyester cure and an aromatic amine was said to be required for getting sufficient hardness.

10 Mixtures of amines with peroxides, however, are known to be unstable as they react with each other. Unsaturated polyester (UP) and vinyl ester (VE) resins are reactive towards a peroxides (free radical initiated polymerization) as well as to amines (Michael addition). Epoxy resins are reactive towards amines. Hence, mixing these compounds may only take place when curing is actually intended.

15 Therefore, at least three components are needed to store a curing system comprising these resins, a peroxide, and an amine. One option is to combine the epoxy resin and the peroxide in a first package, the amine in a second, and the UP or VE resin in a third package. Another possibility is to store the epoxy resin and the UP or VE resin in a first package, the amine in a second, and the peroxide in a
20 third package.

However, three-component systems are more difficult to handle than two-component systems, which means that there is a desire for two component curing systems for the resin combination discussed above.

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Such a two-component resin system is disclosed by WO 2011/098561, as it was found that an aliphatic amine and a peroxyester could be safely stored in the same package. The two-component system according to this document contains a first

component comprising an epoxy resin and an unsaturated polyester or vinyl ester resin, and a second component comprising both an aliphatic amine and a peroxyester.

5 Mixtures of amines with other types of peroxides were said to be unstable, which was concluded from DSC measurements 8 hours after mixing the amine and the peroxide. With these DSC measurements the reaction enthalpy of amine with peroxide was measured. If the reaction enthalpy was lower than theoretically expected, it was concluded that the amine and peroxide had already reacted in the 8 hours preceding the measurement.

10 Peroxyester/aliphatic amine mixtures were concluded to be stable, presumably because all the theoretical reaction enthalpy was detected during the DSC measurement. T-butyl hydroperoxide/amine mixtures were labelled unstable because the detected enthalpy was less than theoretically expected.

15 Surprisingly, it has now been found that mixtures of amines and organic hydroperoxides *are* stable and can be used in a two-component system as described above.

The DSC method used in WO 2011/098561 to determine the stability of mixtures of t-butyl hydroperoxide (Trigonox® A-W70) with amines appears to be unsuitable for
20 the purpose. It is theorized that the hydroperoxide and the amine form a salt at room temperature, which salt only decomposes at elevated temperatures, i.e. above the temperature reached with the DSC measurement.

The present invention therefore relates to a method for curing a resin system
25 comprising (i) an epoxy resin and (ii) an unsaturated polyester resin or a vinyl ester resin, said method comprising the addition to said resin system of a formulation obtained by mixing an organic hydroperoxide and an amine.

In other words, the method according to the present invention comprises the steps of:

- 1) providing a mixture of an organic hydroperoxide and an amine,
- 2) adding the mixture of step 1) to a resin system comprising (i) an epoxy resin and
- 5 (ii) an unsaturated polyester resin or a vinyl ester resin, and
- 3) curing said resin system.

In a preferred embodiment, the method involves the mixing of two components that are part of a two component system, i.e. a system comprising two spatially

10 separated components – a first component and a second component – in order to prevent premature polymerization of the compounds prior to the mixing of the components.

According to this embodiment, the resin system containing both resins will be present in the first component and the formulation obtained by mixing an organic

15 hydroperoxide and an amine will be present in the second component.

The method according to the present invention allows for the formation of a polyester or vinyl ester-based resin system that is compatible with a wide variety of reinforcing fibres, including carbon fibres, and has sufficient hardness after room

20 temperature cure. At the same time, it allows for the room temperature cure of an epoxy resin. Without being bound to theory, it is thought that the heat released during polyester/vinyl ester cure promotes epoxy cure.

All this by requiring only two components to be mixed by the end user.

25 The term “organic hydroperoxide” refers to any organic compound with at least one hydroperoxide functions. It thus includes monohydroperoxides, dihydroperoxides, and poly-hydroperoxides. Preferred organic hydroperoxides include cumyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, tert-butyl hydroperoxide,

isopropylcumyl hydroperoxide, tert-amyl hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, pinane hydroperoxide, pinene hydroperoxide, and combinations thereof.

The peroxide is preferably added to the resin system in an amount of 0.1-10 wt%,
5 relative to the weight of unsaturated polyester and vinyl ester resin, more preferably 0.5-5 wt%, and most preferably 0.5-2 wt%.

Suitable amines to be mixed with the organic hydroperoxide in accordance with the present invention include primary amines (including aliphatic, aromatic, and
10 modified amines), polyamines, tertiary, and secondary amines.

Preferred amines are polyamines. More preferred are di-amines.

Examples of suitable di-amines are isopropyl diamine, diaminomethane, 1,2-diamino ethane, 1,3-diamino propane, 1,2-diamino butane, 1,2-diamino propane, 1,4-diamino butane, 1,5-diamino pentane, 1,3-diamino pentane, 2,2-dimethyl-1,3-diaminopropane, 1,5-diamino(2-methyl)pentane, 1,6-diamino hexane, 1,7-diamino
15 heptane, 1,8-diamino octane, 1,9-diamino nonane, 1,10-diamino decane, 1,12-diamino dodecane, 1,6-diamino-(2,2,3-trimethyl)hexane, 1,6-diamino-(2,2,4-trimethyl)hexane, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane, 1,3-bis(aminomethyl)cyclohexane, isophorone diamine, tricyclododecane diamine,
20 dianiline methane, dianiline ether, dianiline sulphone, 2,2',6,6'-tetraethyl dianiline methane, 1,8-diamino-3,6-dioxaoctane, 1,5-diamino-3-oxapentane, alpha, omega-polytetrahydrofuryl diamines, alpha, omega-polyglycol diamines (JeffamineTM), alpha, omega-polypropoxy diamines (JeffaminesTM), alpha, omega-polyethoxypropoxy diamines, 3,5-diamino benzoic acid, 3,4-diamino benzophenone, 1,2-diamino cyclohexane, diamino naphthalene, diamino toluene, m-xylylene diamine,
25 (ortho-, meta-, and para) diamino benzene, and 2-methyl-pentamethylenediamine (Dytec A).

Examples of other suitable polyamines are diethylene triamine, triethylene tetramine, tetraethylene pentamine, polyamide-amine, and adducts of any of these amines.

- 5 Most preferred amines are isophorone diamine, 1,5-diamino pentane, 2-methyl-pentamethylenediamine (Dytec A), diethylenetriamine, and 1,6 diamine-(2,2,3-trimethylcyclohexane),

The amine curing agent is preferably added to the resin system in such an amount
10 that the molar ratio of amine functionality to epoxy functionality is in the range 1:5 to 5:1, more preferably 1:2 to 2:1, and most preferably around 1:1.

The formulation comprising the amine and the organic hydroperoxide can be prepared by slowly adding the organic hydroperoxide to the amine. During said
15 addition, the formulation may be cooled.

Upon mixing, the organic peroxide can be added as a formulation in a phlegmatizer. Examples of suitable phlegmatizers are aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, and solvents that carry an aldehyde, ketone, ether, ester,
20 alcohol, phosphate, or carboxylic acid group. Examples of suitable solvents are aliphatic hydrocarbon solvents such as white spirit and odourless mineral spirit (OMS), aromatic hydrocarbon solvents such naphthenes and mixtures of naphthenes and paraffins, isobutanol; pentanol; 1,2-dioximes, N-methyl pyrrolidinone, N-ethyl pyrrolidinone; dimethyl formamide (DMF); dimethylsulfoxide
25 (DMSO); 2,2,4-trimethylpentanediol diisobutyrate (TxIB); esters such as dibutyl maleate, dibutyl succinate, ethyl acetate, butyl acetate, mono- and diesters of ketoglutaric acid, pyruvates, and esters of ascorbic acid such as ascorbic palmitate;

aldehydes; mono- and diesters, more in particular diethyl malonate and succinates; 1,2-diketones, in particular diacetyl and glyoxal; benzyl alcohol; and fatty alcohols. The most preferred phlegmatizers are TxIB and dimethyl phthalate.

- 5 The resulting mixture will preferably contain 0.1-5 wt%, more preferably 0.5-4 wt%, and most preferably 1-2 wt% of organic hydroperoxide, 95-99.9 wt%, more preferably 96-99.5 wt%, and most preferably 98-99 wt% amine, all based on the combined weight of hydroperoxide and amine.

In addition, the mixture may contain, based on the total weight of the mixture, 0-20
10 wt%, more preferably 0-5 wt%, and most preferably 0-2 wt% of a phlegmatizer.

Preferred hydroperoxide/amine combinations include:

- cumyl hydroperoxide/ diethylenetriamine,
1,1,3,3-tetramethyl hydroperoxide/1,5-diamino pentane,
15 tert.-amylhydroperoxide/2-methylpentamethylenediamine,
pinane hydroperoxide/ diethylenetriamine,
tert.-butyl hydroperoxide/1,6 diamine-(2,2,3-trimethylcyclohexane),
tert-butyl hydroperoxide/isopherone diamine, and
pinane hydroperoxide/isopherone diamine.

20

The epoxy resin present in the resin system can be any epoxy resin. It can be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, monomeric or polymeric in nature. Preferred, however, are phenol-based epoxy resins. Examples of suitable phenol-based epoxy resins are the diglycidyl ethers of
25 bisphenol A, bisphenol F, bisphenol S, resorcinol, hydroquinone, 4,4'-dihydroxydiphenylethane, 4,4'-dihydroxybenzophenone, 1,5-dihydroxynaphthalene, and 4,4'-dihydroxybiphenyl, condensed or extended glycidyl ethers of a bisphenol, and glycidyl ethers of polyhydric phenols, for example an epoxy novolac resin.

Other glycidyl ethers of polyhydric phenols are polymers prepared by reacting 1.1 up to about 2 mols of epichlorohydrin with 1 mol of dihydric phenol or by reacting di-epoxides with added dihydric phenol. Additional epoxides are glycidyl ethers of polyhydric alcohols made by reacting a polyhydric alcohol and epichlorohydrin with
5 an acidic catalyst such as boron trifluoride and subsequently treating the resulting product with an alkaline dehydrohalogenating agent. Included among the polyhydric alcohols that can be used in the preparation of these epoxides are glycerine, ethylene glycol, propylene glycol, diethylene glycol, hexanetriol, pentaerythritol, trimethylol ethane and trimethylol propane, as well as hydroxy-
10 containing esters, such as castor oil.

Still other epoxides are glycidyl esters of polycarboxylic acids, such acids being azelaic acid, adipic acid, isophthalic acid, terephthalic acid, dimerized and trimerized unsaturated fatty acids, etc. Useful epoxides also include epoxidized hydrocarbons, such as vinyl cyclohexene dioxide, butadiene dioxide,
15 dicyclopentadiene dioxide, epoxidized polybutadiene, and limonene dioxide. Other epoxides are epoxidized esters, for example, epoxidized soybean oil, epoxidized glycerol trilinoleate, and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate. Still other epoxides are polymers and copolymers of vinyl polymerizable monoepoxides, such monoepoxides being allyl glycidyl ether,
20 glycidyl acrylate, and glycidyl methacrylate.

Examples of suitable unsaturated polyester or vinyl ester resins to be present in the resin system are:

- Ortho-resins: these are based on phthalic anhydride, maleic anhydride, or fumaric
25 acid and glycols, such as 1,2-propylene glycol, ethylene glycol, diethylene glycol, methylene glycol, 1,3-propylene glycol, dipropylene glycol, tripropylene glycol, neopentyl glycol or hydrogenated bisphenol-A. Commonly the ones derived from

1,2-propylene glycol are used in combination with a reactive diluent such as styrene.

- Iso-resins: these are prepared from isophthalic acid, maleic anhydride or fumaric acid, and glycols. These resins may contain higher proportions of reactive diluent than the ortho resins. (3) Bisphenol-A-fumarates: these are based on ethoxylated bisphenol-A and fumaric acid.

- Chlorendics: these are prepared from chlorine/bromine containing anhydrides or phenols in the preparation of the UP resins.

- Vinyl ester resins: these are resins which are mostly used because of their hydrolytic resistance and excellent mechanical properties, as well as for their low styrene emission and having unsaturated sites only in the terminal position; they are introduced by reaction of epoxy resins (e.g. diglycidyl ether of bisphenol-A, epoxies of the phenol-novolac type, or epoxies based on tetrabromobisphenol-A) or urethane resins with (meth)acrylic acid or (meth)acrylamide.

- Dicyclopentadiene (DCPD) resins: these are resins obtained either by modification of any of the above resin types by Diels-Alder reaction with cyclopentadiene, or by first reacting maleic acid with dicyclopentadiene, followed by the resin manufacture as shown above for the other types of resins.

All of these resins may be modified according to methods known to the skilled man, e.g. for achieving a lower acid number, hydroxyl number or anhydride number, or for becoming more flexible due to the insertion of flexible units into the backbone, etc.

The weight ratio of epoxy resin to unsaturated polyester and vinyl ester resin in the resin system is preferably in the range 10:90 – 90:10, more preferably 40:60 to 60:40.

The unsaturated polyester or vinyl ester resin preferably also contains a reactive diluent. Examples of suitable reactive diluents are ethylenically unsaturated monomeric compounds such as styrene and styrene derivatives like α -methyl styrene, vinyl toluene, indene, divinyl benzene, vinyl pyrrolidone, vinyl siloxane, vinyl caprolactam, stilbene, but also diallyl phthalate, dibenzylidene acetone, allyl benzene, methyl methacrylate, methylacrylate, (meth)acrylic acid, diacrylates, dimethacrylates, acrylamides; vinyl acetate, triallyl cyanurate, triallyl isocyanurate, allyl compounds which are used for optical application (such as (di)ethylene glycol diallyl carbonate), chlorostyrene, tert-butyl styrene, tert-butylacrylate, butanediol dimethacrylate, and mixtures thereof. Suitable examples of (meth)acrylate reactive diluents are PEG200 di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 2,3-butanedioldi(meth)acrylate, 1,6-hexanediol di(meth)acrylate and its isomers, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, glycerol di(meth)acrylate, trimethylol propane di(meth)acrylate, neopentyl glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, PPG250 di(meth)acrylate, tricyclodecane dimethylol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, glycidyl (meth)acrylate, bismaleimides, biscitraconimides, bisitaconimides, itacon-citraconimides, and mixtures thereof.

The amount of reactive diluent present in the resin system is preferably at least 0.1 wt%, based on the weight of the unsaturated polyester and vinyl ester resin, more preferably at least 1 wt%, and most preferably at least 5 wt%. The amount of reactive diluent is preferably not more than 50 wt%, more preferably not more than 40 wt%, and most preferably not more than 35 wt%.

The resin system preferably also contains accelerators to speed up the cure of the UP or VE resin, especially at low temperatures. Preferred accelerators are

transition metal compounds, more preferably manganese, copper, and/or iron compounds. Suitable compounds are the halides, nitrates, sulphates, sulphonates, phosphates, phosphonates, oxides, carboxylates, and complexes of these metals. Examples of suitable carboxylates are lactate, 2-ethyl hexanoate, acetate, 5 propionate, butyrate, oxalate, laurate, oleate, linoleate, palmitate, stearate, acetyl acetate, octanoate, nonanoate, heptanoate, neodecanoate, and naphthenate. Examples of complexes are metal-ligand complexes. Preferred ligands are pyridine and the tridentate, tetradentate, pentadentate, and hexadentate nitrogen donor ligands disclosed in WO 2011/83309.

- 10 Preferred manganese compounds are manganese chloride, nitrate, sulphate, lactate, 2-ethyl hexanoate, octanoate, nonanoate, heptanoate, neodecanoate, naphthenate, acetate, porphirines, crown ethers, enamines, and the Mn complexes of pyridine and of the tridentate, tetradentate, pentadentate, or hexadentate nitrogen donor ligands disclosed in WO 2011/83309. Any one of Mn(II), Mn(III), 15 Mn(IV), and Mn(VII) compounds can be used.

Preferred copper compounds are copper chloride, nitrate, sulphate, lactate, 2-ethyl hexanoate, octanoate, nonanoate, heptanoate, neodecanoate, naphthenate, acetate, porphirines, crown ethers, and enamines. Both Cu(I) and Cu(II) compounds can be used.

- 20 Preferred iron compounds are iron chloride, nitrate, sulphate, lactate, 2-ethyl hexanoate, octanoate, nonanoate, heptanoate, neodecanoate, naphthenate, acetate, porphirines, crown ethers, enamines, and iron complexes of pyridine or the tridentate, tetradentate, pentadentate, or hexadentate nitrogen donor ligands of WO 2011/83309. Both Fe(II) and Fe(III) can be used. More preferably, it is an 25 iron(II) or iron (III) complex of a tridentate or pentadentate nitrogen donor ligand according to WO 2011/83309.

Preferred nitrogen donor ligands according to WO 2011/83309, for both Mn and Fe, are the bispidon ligands and the TACN-N_x ligands. The preferred bispidon ligand is

dimethyl-2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-Cl). The preferred TACN-Nx ligand is 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃-TACN).

The total amount of transition metal in the resin system is preferably 0.5-75 mmol/kg unsaturated polyester and vinyl ester resin, more preferably 2-50 mmol/kg, even more preferably 2-25 mmol/kg, and most preferably 2-10 mol/kg unsaturated polyester and vinyl ester resin.

The resin system may also contain promoters, flexibilizers, and/or inhibitors.

Examples of flexibilizers are benzyl alcohol and polysulfides.

Examples of promoters are metal carboxylate salts, 1,3-diketones, and phosphorous-containing compounds.

Examples of 1,3-diketones are acetyl acetone, benzoyl acetone, and dibenzoyl methane, and acetoacetates such as diethyl acetoacetamide, dimethyl acetoacetamide, dipropylacetoacetamide, dibutylacetoacetamide, methyl acetoacetate, ethyl acetoacetate, propyl acetoacetate, and butylacetoacetate.

Examples of suitable metal carboxylate salts are the 2-ethyl hexanoates, octanoates, nonanoates, heptanoates, neodecanoates, and naphthenates of ammonium, alkali metals, and alkaline earth metals. A preferred alkali metal is K.

The salts may be added to the resin system as such, or they may be formed in situ. For example, alkali metal 2-ethyl hexanoates can be prepared in situ from an alkali metal hydroxide and 2-ethyl hexanoic acid.

Examples of phosphorous-containing compounds are phosphorous compounds with the formulae P(R)₃ and P(R)₃=O, wherein each R is independently selected from hydrogen, alkyl with 1 to 10 carbon atoms, and alkoxy groups with 1 to 10 carbon atoms. Preferably, at least two R-groups are selected from either alkyl groups or alkoxy groups. Specific examples of suitable phosphorous-containing

compounds are diethyl phosphate, dibutyl phosphate, tributyl phosphate, triethyl phosphate (TEP), dibutyl phosphite, and triethyl phosphate.

Acetoacetates are particularly preferred promoters. Particularly preferred is diethyl acetoacetamide. Even more preferred is a combination of diethyl acetoacetamide
 5 and potassium 2-ethyl hexanoate. Also preferred is a combination of diethyl acetoacetamide and dibutyl phosphate.

Examples of inhibitors are 2-methoxyphenol, 4-methoxyphenol, 2,6-di-t-butyl- 4-methylphenol, 2,6-di-t-butylphenol, 2,4,6-trimethyl-phenol, 2,4,6-tris-dimethylaminomethyl phenol, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-
 10 isopropylidene diphenol, 2,4-di-t-butylphenol, 6,6'-di-t-butyl-2,2'-methylene di-p-cresol, hydroquinone, 2-methylhydroquinone, 2-t-butylhydroquinone, 2,5- di-t-butylhydroquinone, 2,6-di-t-butylhydroquinone, 2,6-dimethylhydroquinone, 2,3,5-trimethylhydroquinone, catechol, 4-t-butylcatechol, 4,6-di-t-butylcatechol, benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, methylbenzoquinone, 2,6-
 15 dimethylbenzoquinone, naphthoquinone, 1 -oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine-4-ol (a compound also referred to as TEMPOL), 1-oxyl-2,2,6,6-tetramethylpiperidine-4-one (a compound also referred to as TEMPON), 1-oxyl-2,2,6,6-tetramethyl-4-carboxyl-piperidine (a compound also referred to as 4-carboxy-TEMPO), 1-oxyl-2,2,5,5-tetramethylpyrrolidine, 1-oxyl-
 20 2,2,5,5-tetramethyl-3- carboxylpyrrolidine (also called 3-carboxy-PROXYL), aluminium-N-nitrosophenyl hydroxylamine, diethylhydroxylamine, phenothiazine and/or derivatives or combinations of any of these compounds.

The resins are cured when the mixture obtained by mixing the organic
 25 hydroperoxide and the amine is added and mixed into the resin system. The curing process can be carried out at any temperature from -20°C up to 250°C, preferably from -15 to 100 °C, and most preferably from -10 to 60 °C, depending on the initiator system, the accelerator system, the compounds to adapt the curing rate,

and the resin composition to be cured. Preferably, it is carried out at ambient temperatures commonly used in applications such as hand lay-up, spray-up, filament winding, resin transfer moulding, coating (e.g. gelcoat and standard coatings), button production, centrifugal casting, corrugated sheets or flat panels, relining systems, kitchen sinks via pouring compounds, etc. However, it can also be used in SMC, BMC, pultrusion techniques, and the like, for which temperatures up to 180°C, more preferably up to 150°C, most preferably up to 100°C, are used.

In a preferred embodiment, the resin is cured in the presence of a filler and/or a reinforcement fibre. Examples of reinforcement fibres are glass fibres, carbon fibres, aramid fibres (e.g. Twaron®), natural fibres (e.g. jute, kenaf, industrial hemp, flax (linen), ramie, etc.). Examples of fillers are quartz, sand, aluminium trihydroxide, magnesium hydroxide, chalk, calcium hydroxide, clays, and lime.

The cured resin can be subjected to a post-cure treatment to further optimize the hardness. Such post-cure treatment is generally performed at a temperature in the range 40-180°C for 30 min to 15 hours.

The cured resins find use in various applications, including marine applications, automotive parts, boats, chemical anchoring, roofing, construction, containers, relining, pipes and tanks, flooring, windmill blades, laminates, etc.

EXAMPLES

A resin composition was prepared by mixing 100 g of an unsaturated orthophthalic resin (Palatal® P6) with 100 g of a bisphenol A glycidyl ether and 2 g copper naphthenate.

Two amine/organic peroxide formulations were prepared: formulations A and B.

Formulation A contained 30 g 1,5-diamino-2-methylpentane and 4 g t-butylperbenzoate.

Formulation B contained 30 g 1,5-diamino-2-methylpentane and 4 g t-butylhydroperoxide.

5

These mixtures were stored at room temperature (max. 25°C) for three months before they were used in the following experiments.

10 In a comparative experiment, 25 g of the resin composition was mixed with 4.5 g of formulation A.

In an experiment according to the invention, 25 g of the resin composition was mixed with 4.5 g of formulation B.

15 The cure that followed said addition was analysed by the method of the Society of Plastic Institute (SPI method F/77.1; available from Akzo Nobel Polymer Chemicals). This method involves measuring the peak exotherm, the time to peak, and the gel time. The above mixtures were poured into a test tube and a thermocouple was placed through the enclosure at the centre of the tube. The glass tube was then placed in a climate controlled room maintained at 20°C and 50%
20 relative humidity and the time-temperature curve was measured. From the curve the following parameters were calculated:

Gel time (Gt) = time in minutes elapsed between the start of the experiment and 5.6°C above the bath temperature.

25 Time to peak (TTP) = time elapsed between the start of the experiment and the moment that the peak temperature is reached.

Peak exotherm (PE) = the maximum temperature that was reached.

The results are presented in Table 1.

Table 1

	Formulation A	Formulation B
Gt (min)	2.1	0.9
TTP (min)	12.5	12.2
PE (°C)	168	183

Table 1 shows that the use of t-butylhydroperoxide results in a higher reactivity,
5 shorter gel time and higher exotherm – i.e. a more efficient cure – than the use of t-butylperbenzoate. It also shows that the mixture of amine and hydroperoxide was still active after storage for 3 months.

CLAIMS

1. Method for curing a resin system comprising (i) an epoxy resin and (ii) an unsaturated polyester resin or a vinyl ester resin, the method comprising the
5 addition to said resin system of a formulation obtained by mixing an organic hydroperoxide and an amine.
2. Method according to claim 1 comprising the step of mixing the components of a two component system comprising a first and a second component,
10 wherein the first component comprises the resin system comprising the epoxy resin and the unsaturated polyester or vinyl ester resin and the second component comprises the formulation obtained by mixing the organic hydroperoxide and the amine.
- 15 3. Method according to claim 1 or 2 wherein the resin system additionally comprises an iron, copper, or manganese salt or complex.
4. Method according to any one of the preceding claims wherein the resin system comprises an ethylenically unsaturated compound.
- 20 5. Method according to any one of the preceding claims wherein the organic hydroperoxide is selected from the group consisting of cumyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, tert-butyl hydroperoxide, isopropylcumyl hydroperoxide, tert-amyl hydroperoxide, 2,5-dimethylhexyl-
25 2,5-dihydroperoxide, pinane hydroperoxide, pinene hydroperoxide, and combinations thereof.
6. Method according to any one of the preceding claims wherein the amine is selected from the group consisting of isophorone diamine, 1,5-diamino

pentane, 2-methyl-pentamethylenediamine, diethylenetriamine, and 1,6 diamine-(2,2,3-trimethylcyclohexane),

- 5 7. Method according to any one of the preceding claims wherein a reinforcement fibre is added to the resin system.
8. Method according to claim 7 wherein the reinforcement fibre is selected from carbon fibre, glass fibre, aramid fibre, a natural fibre, and combinations thereof.
- 10 9. Method according to any one of the preceding claims wherein a filler is added to the resin system.
- 15 10. Method according to claim 7 wherein the filler is selected from sand, quartz, aluminium trihydroxide, magnesium hydroxide, chalk, calcium hydroxide, clays, and lime.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/078761

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G59/50
ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/079563 A1 (AKZO NOBEL CHEMICALS INT BV [NL]) 6 June 2013 (2013-06-06) claims 11-14 examples 4,7,8; table 1 -----	1,3,5, 7-10
X	WO 2011/098562 A1 (DSM IP ASSETS BV [NL]; BOER DEN ARIE [NL]; JANSEN JOHAN FRANZ GRADUS A) 18 August 2011 (2011-08-18) page 14, lines 20-23 examples 3,4,8,9; table 3 formulation D, E; table 1 page 4, lines 25-30 -----	1,2,5-9
A	US 5 306 773 A (WISEMAN DEAN H [US] ET AL) 26 April 1994 (1994-04-26) the whole document -----	1-10



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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" 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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