Title: COMPOSITION AND METHOD OF MAKING WATER BORNE EPOXY HARDENER FOR USE IN TWO-COMPONENT EPOXY SELF LEVELLING COMPOUNDS WITH LONG POT LIFE, FAST CURE AND LOW SHRINKAGE CHARACTERISTICS

Abstract: The present invention is directed at water-reducible curing agents for epoxy resins, obtainable by reacting at least one diprimary amine, at least one monoprimar y amine and at least one polyepoxy compound, wherein the molar ratio of the primary amine groups to the epoxy groups in the reaction is in the range of about 1.7:1 to 1:1, the ratio of the primary amines in the diprimary amine to secondary amines optionally present in the diprimary amine is more than 1:1, and the molecular weight (Mw) of the diprimary amine is 500 Daltons or less. These water-reducible curing agents show excellent utility in combination with epoxy resins for self-leveling applications and provide excellent finished properties such as high compressive strength, low shrinkage, high impact resistance and high wear resistance in comparison to the commercially available products.
COMPOSITION AND METHOD OF MAKING WATER BORNE EPOXY HARDENER FOR USE IN TWO-COMPONENT EPOXY SELF LEVELLING COMPOUNDS WITH LONG POT LIFE, FAST CURE AND LOW SHRINKAGE CHARACTERISTICS

Description

The present invention is directed to a water-reducible curing agent for epoxy resins, obtainable by reacting at least one diprimary amine, at least one monoprymary amine and at least one polyepoxy compound, wherein the molar ratio of the primary amino groups to the epoxy groups in the reaction is in the range of about 1.7:1 to 1:1, the ratio of the primary amines in the diprimary amine to secondary amines optionally present in the diprimary amine is more than 1:1, and the molecular weight (Mw) of the diprimary amine is 500 Daltons or less.

The present invention is further directed to the use of a water-dispersible curing agent as described above as a curing agent for epoxy resins, in particular for water-based self-levelling epoxy resin formulations, to a process for coating a substrate utilizing said curing agent and surfaces with an epoxy resin coating obtainable by such a process.

State of the Art

In the state of the art, numerous approaches have been described to provide water-dispersible curing agents for epoxy resins. For example, in EP 1 454 935 A1, Mannich-based adducts in the form of the reaction products of 2,4,6-tris(dimethylaminomethyl)-phenols and diprimary amines such as 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (IPDA) or polyalkoxyalkylenediamines from the JEFFAMINE series had been prepared and were successfully used as curing agents for epoxy resins in concrete applications. Polyether amines such as those of the JEFFAMINE series have also been described as such for the curing of epoxy resins e.g. in EP 0 567 831 A1.
In yet another approach, hardeners comprising pyrrol residues were used as curing agents for epoxy resins and had been demonstrated to have particular utility in epoxy cement concrete (ECC) compositions (cf. EP 2 133 381 A1).

US 5,246,984 describes polyepoxide coating systems cured with polyamine epoxy adduct curatives employing diprimary amines such as triethylenetetraamine, tetraethylenepentaamine and higher molecular weight homologues thereof wherein a monoepoxide is added in a proportion to react with at least part of the primary amine groups. Subsequently, polyepoxides are added to react with up to 65% of the remaining primary amine groups. In the Examples of this document, it was demonstrated that the inventive compositions provided suitable pot life times in the range of hours, and a tack-free time of within 90 to 120 minutes.

EP 0 387 418 describes curing agents for epoxy resins wherein polyalkylene polyether monoamines and/or diamines are reacted with di- or polyepoxy compounds to provide an intermediate product having a ratio of hydrogens bound to nitrogen and capable of reacting with epoxy groups to epoxy groups of 1:1.4 to 6. The intermediate product is then reacted with a primary or secondary amine in a ratio of epoxy groups to hydrogen atoms bound to nitrogen of 1:2 to 1:10. An example of EP 0 387 418 describes the reaction product of Jeffamine 600, bisphenol A diglycidyl ether and isophorone diamine, wherein the molar ratio of the amino groups to the epoxy groups is about 4:1.

US 5,489,630 describes a self-emulsifying epoxy curing agent, which is the reaction product of a poly(alkylene oxide) monoamine or diamine with a di- or polyepoxide, wherein the ratio of epoxide groups to active amine hydrogens is 1.1:1 to 6:1. This intermediate product is then reacted with a di-or polyamine at a ratio of active amine hydrogens to epoxide groups of greater that about 25:1. The two latter documents thus employ relatively high amine to epoxy ratios.

Self-leveling floors are an important application of epoxide coatings in that they provide thin coatings of high hardness and wear resistance. In this type of
applications, polyethylene diamines and polypropylene/polyethylene oxide-based diamines have been described as curing agents. However, these components lead to a high tension network after reacting with epoxies and cause shrinking as a consequence. The available self-levelling epoxy based coatings thus require further improvement.

Despite of recent advancements in technology, there remains a need for epoxy hardening systems and water-dispersible curing agents for epoxy resins which are easy to mix, have a suitable pot life in the range of about up to 1 h, and provide a high hardness in the cured epoxy materials. In addition, the final coatings should exhibit low shrinkage, and preferably low odour and colour or non-transparent appearance so that they can be used for transparent coatings without changing the base colour of the material to which they are applied.

The curing agents should preferably further exhibit a low viscosity, excellent workability and display a suitable pot life. Moreover the curing agents should provide fast cure and excellent final properties in two component epoxy/concrete systems. Finally, they should preferably provide good adhesion on concrete, good impact resistance, good water vapour transmission and excellent compressive strength.

The present application addresses these needs.

Description of the Invention

The present application pertains to a water-reducible curing agent for epoxy resins, obtainable by reacting at least one diprimary amine, at least one mono-primary amine and at least one polyepoxy compound, wherein the molar ratio of the primary amino groups to the epoxy groups in the reaction is in the range of about 1.7:1 to 1.1, the ratio of the primary amines in the diprimary amine to secondary amines optionally present in the diprimary amine is more than 1:1 and the molecular weight (Mw) of the diprimary amine is 500 Daltons or less.
A diprimary amine as this term is used in the context of the present invention means an amine having two primary amine moieties (NH₂). Similarly, a monoprimary amine means an amine having a single primary amine moiety.

Water-reducible in the context of the present invention means, that the material can be diluted with water or a water/co-solvent mixture to provide a homogeneous mixture.

This water reducible curing agent is in particular suitable for non-cementious and cementious self levelling floors and tile grout.

It had been observed, that high molecular weights of the diprimary amine lead to a higher amount of shrinkage. Thus, the molecular weight (Mw) of the diprimary amines in the practice of the present application should be 500 Dalton or less. It is preferred, that the molecular weight (Mw) of the diprimary amine is 400 or less, more preferably 300 or less and most preferably 200 or less. The Mw as used above applies to compounds which have two primary amine functionalities attached to a backbone comprising repeating units. It is noted however, that repeating units in the backbone are not required in the diprimary amine of the present invention. The molecular weight of the diprimary amines of the present invention is determined by conventional techniques, such as electrospray mass spectrometry.

It is preferred, that the molar ratio of the primary amino groups to the epoxy groups in the reaction providing the water-reducible curing agent is about 1.5:1 or less and more preferably about 1.4:1 or less. In addition, it is preferred that the molar ratio of the primary amino groups to the epoxy groups employed in the reaction is more than or equal to about 1.05:1, or preferably more than or equal to about 1.1:1 and most preferably more than or equal to about 1.2:1.

Except for the above mentioned parameters and conditions, the diprimary amine for use as a component for the preparation of the water-reducible curing agent is not subject to any relevant restrictions. In particular suitable are
however aliphatic, cycloaliphatic or arylaliphatic diamines, in particular ethylene diamine, 1,2-propanediamine, 1,3-propanediamine, 2-methyl-1,2-propanediamine, 2,2-dimethyl-1,3-propanediamine, 1,3-butandiamine, 1,4-butandiamine, 1,3-pentandiamine (DAMP), 1,5-pentandiamine, 1,5-diamo-2-methylpentan (MPMB), 2-butyl-2-ethyl-1,5-pentandiamine (C11-neodiamine), 1,6-hexandiamine, 2,5-dimethyl-1,6-hexandiamine, 2,2,4, und 2,4,4-trimethylhexamethylenendiamine (TMD), 1,7-heptandiamine, 1,8-octandiamine, 1,9-nonandiamine, 1,10-decandiamine, 1,11-undecandiamine, 1,12-dodecandiamine, 1,2-, 1,3- and 1,4-diaminocyclohexane, bis-(4-
aminocyclohexyl)-methane (H12-MDA), bis-(4-amino-3-methylcyclohexyl)-methan, bis-(4-amino-3-ethylcyclohexyl)-methane, bis-(4-amino-3,5-dimethylcyclohexyl)-methane, bis-(4-amino-3-ethyl-5-methylcyclohexyl)-methane (M-MECA), 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (= isophorondiamine or IPDA), 2- and 4-methyl-1,3-diaminocyclohexane and mixtures thereof, 1,3- und 1,4-bis-(aminomethyl)-cyclohexane, 2,5(2,6)-bis-(aminomethyl)-bicyclo[2.2.1]heptane (NBDA), 3(4,8)(9)-bis-(aminomethyl)-tricyclo[5.2.1.0^2,0^6]decane, 1,4-diamino-2,2,6-trimethylcyclohexane (TMCPDA), 1,8-menthendiamine, 3,9-Bis-(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5.5]undecane as well as 1,3- and 1,4-xylidendiamine; ether group containing aliphatic diamines, in particular bis-(2-aminoethyl)ether, 3,6-dioxaoctane-1,8-diamine, 4,7-dioxadecane-1-10-diamine, 4,7-dioxadecane-2,9-diamine, 4,9-dioxadecane-1,12-diamine, 5,8-dioxadecane-3,10-diamine, polyamines having secondary amino groups, especially those which are known as polyalkylenamines, such as diethylenetriamine (DETA), dipropylenetriamine, bishexamethylenetriamine (BHMT), 3-(2-
aminoethyl)aminopropylamine (N-3-amine).

Particularly preferred diprimary amines are those having a molecular weight of less than 200, in particular ethylene diamine, diethylene triamine, diethylene glycol diamine, 1,2-propylene diamine, 1,3-propylene glycol diamine, dipropylene diamine, 1,2-methyl-1,2-propanediamine, 2,2-dimethyl-1,3-propane diamine, 1,3-butane diamine, 1,4-butanediamine, 1,3-pentane diamine
and 1,5-pentane diamine. The most preferred primary amine for use in the practice of the present invention is ethylene diamine.

It is further preferred, that the mass ratio of the primary amine moieties (NH₂) in the diprimary amine, to the total mass of the diprimary amine is at least 20%, preferably at least 25%, even more preferably at least 30% and most preferably at least 40%. The mass ratio, as this term is used here, is the ratio of the mass of the primary amine moieties (NH₂) to the total weight of the diprimary amine. E.g. ethylene diamine contains two NH₂-groups = 32 g/mol and has a total weight of 60 g/mol, so that the mass ratio of diprimary amine, with regard to the total mass of the diprimary amines is about 53 %.

In addition it is preferred that the diprimary amine comprises 2 to 12 atoms between the two amino functionalities, wherein not more than one of these atoms is nitrogen in form of a secondary NH.

For diprimary amines it is generally preferred that the ratio of active amine groups (NH₂+NH) to the number of atoms between the NH₂ end groups is not greater than 1/5. This ensures that shrinkage in the final network after two component application is substantially prevented.

The amount of the diprimary amine in the water reducible curing agent is preferably in the range of 2 to 40 % by weight, based on the total weight of the reaction product of diprimary amine(s), mono-primary amine(s) and polyepoxy compounds. Even more preferably, the amount of diprimary amine(s) is in the range of 5 to 35 wt.-%, in particular in the range of 10 to 30 wt.-% and most preferably 14 to 26 wt.-%.

With regard to the at least one mono-primary amine the present application is likewise not subject to any relevant restrictions. Suitable for use as mono-primary amines in the practice of the present application are the following amines:
- aliphatic, cycloaliphatic, acylaliphatic mono-primary amines, especially methylamine, ethylamine, 1-propylamine, 2-propylamine, 1-butylamine, 2-butylamine, tert-butylamine, 3-methyl-1-butylamine, 3-methyl-2-butylamine, cyclopentylamine, hexylamine, cyclohexylamine, octylamine, 2-ethyl-1-hexylamine, benzylamine, 1- or 2-phenylethylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, docosylamine, and fatty amines derived from natural fatty acid mixtures, for example cocoalkylamine, C_{16-22}-alkylamine, soyaalkylamine, oleylamine and tallowalkylamine, obtainable, for example, as Armeen® (from Akzo Nobel) or Rofamin® (from Ecogreen Oleochemicals) trade names. Especially suitable fatty amines are Armeen® 12D, Armeen® 18D, Armeen® CD, Armeen® HT, Armeen® M, Armeen® OD, Armeen® OVD and Armeen® TD, and Rofamin® KD, Rofamin® LD, Rofamin® STD, Rofamin® TD, Rofamin® TD, Rofamin® TD40, Rofamin® OD80, Rofamin® OD85 and Rofamin® OD90;

- aliphatic and cycloaliphatic or arylaliphatic mono-primary amines containing ether groups, especially 2-methoxy-ethylamine, 2-ethoxyethylamine, 3-methoxypropylamine, 3-ethoxypropylamine, 3-(2-ethyl-hexyloxy)propylamine, 3-(2-methoxyethoxy)propylamine, 2(4) methoxyphenyl-ethylamine;

- aliphatic, cycloaliphatic or arylaliphatic amines having one primary and at least one secondary amino group, especially N-methyl-1,2-ethanediamine, N-ethyl-1,2-ethanediamine, N-buty1-1,2-ethanediamine, N-hexyl-1,2-ethanediame, N-buty1-1,6-hexanediamine, N-cyclohexyl-1,2-ethanediame, 4-aminomethyl-piperidine, 3-(4-aminobutyl)piperidine, N-(2-amino-ethyl)piperazine (N-AEP), N-(2-amino-propyl)-piperazine, diamines from the cyanoethylation or cyanobutylation and subsequent hydrogenation of primary monoamines, for example N-methyl-1,3-propanediamine, N-ethyl-1,3-propanediamine, N-buty1-1,3-propanediamine, N-hexyl-1,3-propanediamine, N-(2-ethylhexyl)-1,3-propanediamine, N-dodecyl-1,3-propanediamine, N-cyclohexyl-1,3-
propanediamine, 3-methylamino-1-pentylamine, 3-ethylamino-1-pentylamine, 3-butylamino-1-pentylamine, 3-hexylamino-1-pentylamine, 3-(2-ethylhexyl)amino-1-pentylamine, 3-dodecylamino-1-pentylamine, 3-cyclohexylamino-1-pentylamine, and additionally diamines obtainable by cyanoethylation and subsequent reduction of fatty amines, such as N-cocoalkyl-1,3-propanediamine, N-oleyl-1,3-propanediamine, N-soyaalkyl-1,3-propane-diamine, N-tallowalkyl-1,3-propanediamine or N-(C_{16:22}-alkyl)1,3-propanediamine, obtainable, for example, as Duomeen® CD, Duomeen® M, Duomeen® O, Duomeen® OV and Duomeen® T (Akzo Nobel), and additionally triamines derived from fatty amines, such as cocoalkyldipropyleneetriamine, oleyldipropyleneetriamine, and tallowalkydipropylenetriamine, obtainable, for example, as Triameen® C, Triameen® OV, and Triameen® T (Akzo Nobel); mono-primary amines which in addition have secondary amino functionalities lead to a longer pot life without slowing down the cure of epoxy by the secondary amine groups on the curing agent.

- aliphatic, cycloaliphatic or arylaliphatic amines having one primary and at least one tertiary amino group, especially N,N-diethyl-1,2-ethanediamine, N,N-dimethyl-1,3-propanediamine, N,N-diethyl-1,3-propanediamine and N,N-diethyl-1,4-pentanediamine.

Preferred amines contain at least 2 carbon atoms, especially 3 to 15 carbon atoms, and optionally have either primary or secondary amino groups. In the practice of the present application, it is preferred, that the mono primary amine in addition to the primary amine contains one or more secondary amines.

Preferred amines thus preferably contain 0 to 5 secondary amine functionalities, more preferably 1 to 4 secondary amine functionalities, and 0 to 1 hydroxy functionalities.

Particular preferred amines are aminoethyl ethanol amine, ethanol amine, N-ethyl ethylene diamine and N-ethanol-diethylene triamine. In the practice of the
present application, aminoethylethanolamine is most preferably used as mono-
primary amine.

The amount of the mono-primary amine in the water reducible curing agent is
preferably in the range of 1 to 20 % by weight, based on the total weight of the
reaction product of diprimary amine(s), mono-primary amine(s) and polyepoxy
compounds. Even more preferably, the amount of diprimary amine(s) is in the
range of 2 to 8 wt.-%, and most preferably 3 to 6 wt.-%.

For the water-reducible curing agent it is further preferred that the molar ratio of
the at least one diprimary amine to the at least one mono-primary amine is at
least 1:1, preferably at least 2:1 and most preferably at least 4:1. If more than
one diprimary amines and/or more than one mono-primary amines are present
in the composition, the mentioned molar ratios apply to the combined molar
amounts of all diprimary amines and all mono-primary amines in the
composition, respectively.

Generally, it is preferred in the present invention, that amines having a high
number of functional amino groups, e.g. four or more amino groups, such as
triethylene tetraamine and higher homologues thereof, are not included into the
water-reducible curing agent for epoxy resins in substantial amounts. This
means that that they should preferably be used as an ingredient for the
preparation of the same in not more than 5% by weight, based on the total
weight of the reaction product of diprimary amine(s), mono-primary amine(s)
and polyepoxy compounds, preferably in not more than 2% by weight, and
more preferably in not more than 1% by weight. It is particularly preferred, if
such compounds are not present in the water-reducible curing agents in
detectable amounts.

Further, it is preferred, that also polyoxyalkylenediamines with a molecular
weight in excess of 500 are not present in the water-reducible curing agents in
substantial amounts, which means, that preferably these compounds should
not be present in the water-reducible curing agent in contents of more than 5%
by weight, based on the total weight of the reaction product of diprimary
amine(s), mono-primary amine(s) and polyepoxy compounds, preferably not
more than 2% by weight, even more preferably not more than 1% by weight
and most preferably they should not be present in the water-reducible curing
agent in detectable quantities. More preferably, the water-reducible curing
agent does not contain substantial amounts of polyoxyalkylenediamines with a
molecular weight in excess of 200, wherein substantial amounts has the
meaning as defined above.

The polyepoxide used as the third component for the preparation of the water-
reducible curing agent for epoxy resins, preferably has an epoxy equivalent
weight (EEW) of 65 to 500 g/eq. Polyepoxides can be prepared in a known
manner, for example by oxidation of the corresponding olefines or by reacting
epichlorhydrin with corresponding polyols, polyphenols or amines.

Especially suitable as polyepoxides are what are known as polyepoxide liquid
resins, referred to hereinafter as "liquid resin". These materials have a glass
transition temperature which is typically below 25°C. In contrast solid
polyepoxide resins can be comminuted to powders, which are pourable at
25°C and have a glass transition temperature above 25°C. Polyepoxides which
are known to the person skilled in the art as "reactive diluents" are also
referred to in the present document as liquid resins.

In one embodiment, the polyepoxide is an aromatic polyepoxide. Suitable
examples are liquid resins of the formula (I)

![Formula Image]

where R' and R" are each independently a hydrogen atom or a methyl group,
and s has an average value of 0 to 1. Preference is given to those liquid resins
of the formula (I) in which the index s has an average value of less than 0.2.

The liquid resins of the formula (I) are diglycidyl ethers of bisphenol A, bisphenol F and bisphenol A/F, where A represents acetone and F formaldehyde, which serve as reactants for preparation of these bisphenols. A bisphenol A liquid resin accordingly has methyl groups, a bisphenol F liquid resin hydrogen atoms, and a bisphenol A/F liquid resin both methyl groups and hydrogen atoms, as R' and R" in formula (I). In the case of bisphenol F, it is also possible for positional isomers to be present, especially derived from 2,4'- and 2,2'-hydroxyphenylmethane.


Further suitable aromatic polyeoxides are the glycidylization products of dihydroxybenzene derivatives such as resorcinol, hydroquinone and catechol; further bisphenols or polyphenols such as bis(4-hydroxy-3-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane (bisphenol C), bis(3,5-dimethyl-4-hydroxyphenyl)methane, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxy-phenyl)propane, 2,2-bis(4-hydroxy-3-tert-butyl-phenyl)propane, 2,2-bis(4-hydroxyphenyl)butane (bisphenol B), 3,3-bis(4-hydroxyphenyl)pentane, 3,4-bis(4-hydroxyphenyl)hexane, 4,4-bis(4-hydroxyphenyl)-heptane, 2,4-bis(4-hydroxyphenyl)-2-methylbutane, 2,4-bis(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis(4-hydroxyphenyl)cyclohexane (bisphenol Z), 1,1-bis(4-
hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC), 1,1-bis(4-
hydroxyphenyl)-1-phenyl-ethane, 1,4-bis[2-(4-hydroxyphenyl)-2-
propyl]benzene (bisphenol P), 1,3-bis[2-(4-hydroxyphenyl)-2-propyl]benzene) 
(bisphenol M), 4,4'-dihydroxydiphenyl (DOD), 4,4'-dihydroxybenzophenone, 
5 bis(2-hydroxynaphth-1-yl)methane, bis(4-hydroxynaphth-1-yl)methane, 1,5-
dihydroxynaphthalene, tris(4-hydroxyphenyl)methane, 1,1,2,2-tetrakis(4-
hydroxyphenyl)ethane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl) 
sulfone; condensation products of phenols with formaldehyde, which are 
obtained under acidic conditions, such as phenol novolacs or cresol novolacs; 
aromatic amines, such as aniline, toluidine, 4-aminophenol, 4,4'-
methylenediphenyldiamine (MDA), 4,4'-methylenediphenyldi(N-methyl)amine, 
4,4'-[1,4-phenylenebis(1-methylethylidene)]bisaniline (bisaniline P), 4,4'-[1,3-
phenylenebis(1-methylethylidene)]bisaniline (bisaniline M).

15 Commercially available epoxy novolacs are, for example, Araldite® EPN 1179, 
Araldite® GY 289, Araldite® PY 307-1 (from Huntsman), D.E.N.® 425 and 
D.E.N.® 431 (from Dow), Epalloy® 8240 and Erisys® RF50 (from CVC); a 
commercially available N,N-diglycidylaniline is, for example, Epikote® Resin 
493 (from Hexion); a commercially available resorcinol diglycidyl ether is, for 
example, Erisys® RDGE (from CVC).

In a further embodiment, the polyepoxide is an aliphatic or cycloaliphatic 
polyepoxide, for example diglycidyl ether; a glycidyl ether of a saturated or 
unsaturated, branched or unbranched, cyclic or open-chain C₂ to C₃₀ diol, for 
example ethylene glycol, propylene glycol, butylene glycol, hexanediol, 
25 octanediol, a polypropylene glycol, dimethylcyclohexane, neopentyl glycol; a 
glycidyl ether of a tri- or tetrafunctional, saturated or unsaturated, branched 
or unbranched, cyclic or open-chain polyol such as castor oil, trimethylolpropane, 
trimethylolmethane, penta-erythritol, sorbitol or glycerol, and alkoxylated glycerol 
or alkoxylated trimethylolpropane; a hydrogenated bisphenol A, F or A/F liquid 
resin, or the glycidylation products of hydrogenated bisphenol A, F or A/F; an 
N-glycidyl derivative of amides or heterocyclic nitrogen bases, such as
triglycidyl cyanurate and triglycidyl isocyanurate, and reaction products of epichlorohydrin and hydantoin.

Aliphatic or cycloaliphatic liquid resins are, for example, commercially available as Araldite® DY-C, Araldite® DY-F, Araldite® DY-H, Araldite® DY-T, Araldite® DY 0397, Araldite® DY 3601 (from Huntsman), D.E.R.® 732, D.E.R.® 736 (from Dow); Heloxy® BD, Heloxy® HD, Heloxy® TP, Epikote® 877 (from Hexion), Beckopox® EP 075 (from Cytec).

Mixture of aliphatic or cycloaliphatic polyepoxides and aromatic epoxides of the formula (I) can also be used, such as in particular mixtures of diglycidyl ethers of bisphenol A, bisphenol F and bisphenol A/F and diglycidylethers of α,ω-alkandiols, wherein the α,ω-alkandiols preferably comprise 2 to 10 carbon atoms. Such mixtures are commercially available for example from Dow as D.E.R. 358.

In a further embodiment, the polyepoxide is a polyepoxide which has been prepared from the oxidation of olefins, for example from the oxidation of vinylcyclohexene, dicyclopentadiene, cyclohexadiene, cyclododecadiene, cyclododecatriene, isoprene, 1,5-hexadiene, butadiene, polybutadiene or divinylbenzene.

The polyepoxide is preferably a diepoxide A1.

The diepoxide A1 is more preferably selected from the group consisting of a bisphenol A, bisphenol F and bisphenol A/F diglycidyl ether having an epoxy equivalent weight of 156 to 250 g/eq, especially Araldite® GY 250, Araldite® PY 304, Araldite® GY 282 (from Huntsman); D.E.R.® 331, D.E.R.® 330 (from Dow); Epikote® 828, Epikote® 862 (from Hexion), N,N-diglycidylaniline and a polyglycol diglycidyl ether having an epoxy equivalent weight of 170 to 340 g/eq, especially D.E.R.® 732 and D.E.R.® 736 (from Dow). Further preferred is D.E.R.® 358 from Dow Chemical.
A particularly preferred diepoxide is 1,4-butane diglycidylether sold for example as Epiol DE-200 from HAJIN CHEMTECH and Grilonit RV 1806 from EMS-GrilTech.

In addition, polyalkyleneglycol based di- or triepoxides may be used in admixture with the above-mentioned epoxides. Preferred polyalkyleneglycol include polyalkyleneglycol di- and triepoxides, which can be based on polyethyleneglycol, polypropyleneglycol or polyethylene/polypropylene mixed glycols. In a particularly preferred embodiment the polyalkyleneglycol epoxides are polyalkyleneglycol glycidyl ethers. A suitable polyalkyleneglycol diepoxide is e.g. Erisys GE-24.

The polyalkyleneglycols based epoxides are preferably included into the composition in 0 to 20 wt-% based on the total weight of the combined polyepoxy compounds. In a yet preferred embodiment, the polyalkyleneglycol based epoxides are present in 5 wt-% or less, preferably 2 wt-% or less and even more preferably 1 wt-% or less based on the total weight of the combined polyepoxy compound. Most preferably, polyalkyleneglycol based epoxides are absent from the polyepoxy compound (i.e. they are present in about 0 wt-%).

The above mentioned diepoxides may contain up to 50 wt.-%, based on the respective weight of the diepoxide, of a monoepoxide, wherein only one of the two hydroxyl groups of the diepoxide precursor has been functionalized with epoxy. Preferably, the content of monoepoxide should be 30 wt.-% or less, more preferably 20 wt.-% or less, based on the weight of the diepoxide.

In the practice of the present application, it is particularly preferred if the polyepoxy compound comprises a mixture of at least one aromatic diepoxide and at least one aliphatic diepoxide. It is further preferred, if the aromatic diepoxide is derived from Bisphenol A, Bisphenol F or mixtures thereof, which are functionalized with glycidyl groups. As concerns the aliphatic diepoxide, it is preferred that this compound comprises one or more diglycidylethers of \( \alpha,\omega \)-alkandiols, preferably with 2 to 10 carbon atoms and more preferably 2 to 6 carbon atoms.
The amount of polyepoxide compound in the water reducible curing agent of
the present application is not particularly limited. The combined polyepoxides
should account however preferably for 30 to 90 wt.-%, more preferably for 40
to 85 wt.-% and most preferably for 50 to 80 wt.-%, based on the total weight of
the reaction product of diprimary amine(s), mono-primary amine(s) and
polyepoxy compounds.

A particularly preferred polyepoxide mixture comprises:

20-80 wt.-% Bisphenol A diglycidylether
0-50 wt.-% Bisphenol F diglycidylether,
0-20 wt.-% octandioldiglycidylether,
0-50 wt.-% hexandioldiglycidylether,
10-50 wt.-% butandioldiglycidylether and
0-20 wt.-% butandiolmonoglycidylether,

based on the total weight of the reaction product of diprimary amine(s), mono-
primary amine(s) and polyepoxy compounds, respectively.

In the practice of the present application, it is conventional, that the curing
agent is at least water-reducible which means that a homogeneous dispersion
which does not separate upon storage into the different phases is formed in
water, whereas the material does not dissolve.

The water-reducible curing agent according to the present invention may be
formulated with further ingredients to provide a curing agent for epoxy
formulations. Such additives include

- nonreactive diluents, solvents or film-forming assistants, such as toluene,
xylene, methyl ethyl ketone, 2-ethoxyethanol, 2-ethoxyethyl acetate or
benzyl alcohol, ethylene glycol, diethylene glycol butyl ether, dipropylene
glycol butyl ether, ethylene glycol butyl ether, ethylene glycol phenyl ether,
N-methylpyrrolidone, propylene glycol butyl ether, propylene glycol phenyl
ether, bisphenols and phenol resins, diphenylmethane,
diisopropynaphthalene, mineral oil fractions, for example Solvesso® products (from Exxon), aromatic hydrocarbon resins, sebacates, phthalates, organic phosphoric and sulfonic esters and sulfonamides;

- reactive diluents and extenders, for example reactive diluents containing epoxy groups as already mentioned above, epoxidized soybean oil, butyrolactone, triphenyl phosphite, and additionally polyamides, polymers having carboxyl groups, isocyanates, silicones having reactive groups, polysulfides, butadiene-acrylonitrile copolymers and polyurethanes;

- polymers, for example polyamides, polysulfides, polyvinyl formal (PVF), polyvinyl butyral (PVB), polyurethanes (PUR), styrene-butadiene copolymers, homo- or copolymers of unsaturated monomers, especially from the group comprising ethylene, propylene, butylene, isobutylene, isoprene, vinyl acetate and alkyl(meth)acrylates, especially chlorosulfonated polyethylenes and fluorinated polymers, sulfonamide-modified melamines;

- thermoplastic polymers such as polyether sulfone, polyether imide and bitumen;

- inorganic and organic fillers, for example ground or precipitated calcium carbonates, which have optionally been coated with fatty acids, especially stearates, baryte (heavy spar), talcs, quartz flours, quartz sand, dolomites, wollastonites, kaolins, mica (potassium aluminum silicate), molecular sieves, aluminum oxides, aluminum hydroxides, silicas, cements, gypsiums, fly ashes, carbon black, graphite, metal powders such as aluminum, copper, iron, silver or steel, PVC powders or hollow spheres;

- fibers, for example of polymer or glass;

- pigments, for example titanium dioxide or iron oxides;
- accelerators which accelerate the reaction between amino groups and epoxy groups, for example acids or compounds hydrolyzable to acids, for example organic carboxylic acids such as acetic acid, benzoic acid, salicylic acid, 2-nitrobenzoic acid, lactic acid, organic sulfonic acids such as methanesulfonic acid, p-toluenesulfonic acid or 4-dodecylbenzenesulfonic acid, sulfonic esters, other organic or inorganic acids, for example phosphoric acid, or mixtures of the aforementioned acids and acid esters; and also tertiary amines such as 1,4-diazabicyclo[2.2.2]octane, benzyldimethylamine, α-methylbenzyldimethylamine, 2-(dimethylaminomethyl)-phenol or 2,4,6-tris(dimethylaminomethyl)phenol, triethanolamine, dimethylaminopropylamine, salts of such tertiary amines, and quaternary ammonium salts, for example benzyltrimethylammonium chloride;

- rheology modifiers, such as especially thickeners, for example sheet silicates such as bentonites, derivatives of castor oil, hydrogenated castor oil, polyamides, polyurethanes, urea compounds, fumed silicas, cellulose ethers and hydrophobically modified polyoxyethylene;

- adhesion improvers, for example organoalkoxysilanes such as 3-glycidoxypropyltrimethoxysilane, 3-amino-propyltrimethoxysilane, N-(2-aminoethyl)-3-amino-propyltrimethoxysilane, N-(2-aminoethyl)-N'-[3-(trimethoxysilyl)propyl]ethylenediamine, 3-ureido-propyltrimethoxysilane, 3-chloropropyltrimethoxysilane, vinyltrimethoxysilane, or the corresponding organoalkoxysilanes with ethoxy instead of the methoxy groups;

- heat, light or UV stabilizers;

- flame-retardant substances;

- surface-active substances, for example wetting agents, levelling agents, deaerating agents or defoamers;
- biocides, for example algaeicides, fungicides or fungal growth inhibitors,
- thixotropic agents and defoamers.

A suitable defoamer for use in the practice of the present application is e.g. BYK® 1615 or BYK® 024 from BYK.

The above mentioned additives can be added to the curing agent, but may also be added to the composition to be cured by the curing agent prior to mixing with the curing agent. Preferably, the further additives are directly added to the curing agent.

The amount of further additives is not particularly limited, except that the curing agent still has to be present in an amount sufficient to provide curing. In particular, the further additives can be present in amounts of up to 90 wt.-%, based on the total weight of a curing agent comprising the water reducible curing agent, the further additives and water. More preferably the further additives are present in amounts of 10 to 85 wt.-% and most preferably in amounts of 30 to 80 wt.-%. In such compositions the water reducible curing agent preferably accounts for 2 to 50 wt.-%, more preferably 5 to 35 wt.-% and most preferably 8 to 20 wt.-%. Water preferably accounts for 5 to 70 wt.-%, more preferably 10 to 50 wt.-% of such compositions. All these wt.-%ages are based on the total weight of a curing agent comprising the water reducible curing agent, the further additives and water, but exclusive of the epoxy resin to be cured.

A particularly preferred mixture of the above mentioned additives comprises a thixotropic agent, one or more filler, a pigment and a defoamer.

A further aspect of the present application is directed to the use of a water-reducible curing agent as described above for the curing of epoxy resins, preferably as a curing agent for water-based epoxy resins and more preferably as a curing agent for self-levelling water-based epoxy resins.
Suitable epoxy resins are epoxy resins customary in epoxy chemistry such as for example:
- the polyepoxides described above,
- a Bisphenol A, F or A/F solid resin which is of similar composition as that of the formula (I) specified for the polyepoxide, but wherein the index s is in the range of 2 to 12 and which has a glass transition temperature above 25°C,
- one of the epoxy resins mentioned which has been modified hydrophilically by the reactions at least one polyoxyalkylene polyl.

Preferred epoxy resins are based on Bisphenol A, F or A/F solid or liquid resins, as available commercially for example from Dow, Huntsman and Hexion.

The epoxy resin may comprise what is known as a reactive diluent. Suitable reactive diluents are mono- and polyepoxides, for example the glycidyl ethers of mono- or polyhydric phenols and aliphatic or cycloaliphatic alcohols, especially the polyglycidyl ethers of di- or polyols already mentioned as aliphatic or cycloaliphatic polyepoxides, and additionally especially phenyl glycidyl ether, cresyl glycidyl ether, p-n-butylphenyl glycidyl ether, p-tert-butylphenyl glycidyl ether, nonylphenyl glycidyl ether, allyl glycidyl ether, butyl glycidyl ether, hexyl glycidyl ether, 2-ethylhexyl glycidyl ether, and glycidyl ethers of natural alcohols, for example C₈ to C₉₀-alkyl glycidyl ethers or C₁₂ to C₁₄-alkyl glycidyl ethers, commercially available as Erysis® GE-7 and Erysis® GE-8 (from CVC). The addition of a reactive diluent to the epoxy resin causes a reduction in the viscosity and - in the hardened state of the epoxy resin composition - a reduction in the glass transition temperature and in the mechanical values.

A further aspect of the present invention is a process for the preparation of a water-reducible curing agent comprising
- providing at least one diprimary amine and at least one mono-primary amine, wherein the molar ratio of the primary amines in the diprimary amine to secondary amines optional present in the diprimary amine is more than 1:1 and wherein the Molecular weight (Mw) of the diprimary amine is 500 or less.;

- adding at least one polyoxy compound to the amines, wherein the molar ratio of the primary amino groups to the epoxy groups employed in the reaction is in the range of about 1.7:1 to 1:1, and

- reacting the amine groups with the epoxy groups.

The reaction of the at least one diprimary amine, the at least one mono-primary amine and the at least one polyeoxy compound is preferably carried out at temperatures of about 20 to 150°C. For this purpose, the epoxy compounds should be added into the amine/water solution at a temperature of preferably between 40-70°C, during which water is added progressively. The benefit of such process is that better reaction selectivity is obtained at relatively low temperature for the reaction of primary amines over secondary amines, resulting in the formation of a linear adduct with minimal primary amine groups left. This is preferable over branched adducts having primary amine group. A product, which generates less secondary amine groups and more primary amine groups in the system could results in inferior pot life and leads to high shrinkage in two component epoxy formulations. Another advantage of the process is that no heating is required as the reaction enthalpy can maintain the batch temperature and allow for autocatalytic reaction to occur. Thus, energy is saved and production is made safer.

Yet another aspect of the present application is a process for coating a substrate, characterized in that a water-reducible curing agent as described above is mixed with an epoxy resin, applied to a surface of the substrate and cured.
Yet another aspect of the present application is a surface with an epoxy resin coating obtainable by the afore-mentioned process. The epoxy resin coating preferably is a non-cementious or cementious self-levelling floor or tile grout.

5 In the following, the present application invention is demonstrated by way of Examples, which however should not be considered as limiting to the present application.

Example 1

10 41.38 kg of ethylene diamine and 10.34 kg of aminoethyl ethanolamine are charged into a reaction vessel pre-charged with 17 kg of water with agitation. At 50°C, 68.97 kg of D.E.R. 358 (from Dow Chemical) was charged over 90 minutes whilst the temperature is maintained between 55 and 65°C by controlling the rate of addition and cooling. Subsequently, 88.28 kg of Epiol DE-200 (from HAJIN CHEMTECH) is charged over 2 h whilst the temperature is maintained between 55 and 65°C, by controlling the rate of addition and cooling. Over the course of polyepoxide addition, a total of 137.03 kg of water is added to the reaction mixture. The batch is stirred for further 60 minutes before isolating of the pale clear liquid with a viscosity, as determined according to DIN 16945 (1989), of 4000 cp at 20°C.

The obtained material (10% by weight) was compounded with a defoamer (0.8 wt.-%), a pigment TiO₂ (3.8 wt.-%), Fillers (baryte and quartz; 13 wt.-% and 62 wt.-%, respectively), a thixotropic agent (0.4 wt.-%) and water (10 wt.-%). The material was cured by adding 9 wt.-% of an epoxy resin (D.E.R. 358). The properties of the resulting coating were determined and compared with a similar cured composition, which instead of the water-reducible curing agent described above contained a curing agent based on the reaction product of ethylene oxide with ammonia and an N-benzyl derivative thereof.

The results of these investigations are presented below.
Table 1: 2k test results

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<th>Comparative Example</th>
<th>Inventive Example</th>
<th>Remarks</th>
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<tr>
<td>Ease of mixing</td>
<td>Good</td>
<td>Easier</td>
<td>Better</td>
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<tr>
<td>Flow property</td>
<td>Good</td>
<td>Very good</td>
<td>Better</td>
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<tr>
<td>Pot life [min]</td>
<td>25-35</td>
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<tr>
<td>1-Day Shore D hardness</td>
<td>45</td>
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<td>2-Day Shore D hardness</td>
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<td>Match</td>
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<td>7-Day Shore D hardness</td>
<td>70</td>
<td>70</td>
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<tr>
<td>Shrinkage (%)</td>
<td>0.9</td>
<td>0.8</td>
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<tr>
<td>Odour</td>
<td>Ammoniacal</td>
<td>None</td>
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<tr>
<td>VOC and plasticizer</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Appearance</td>
<td>Beige</td>
<td>lighter</td>
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The flow property was assessed by an empirical method by observing the self-levelling property and the recovery of levelling after the coating has been disturbed.

The pot life was determined in the same manner until the levelling of the paste could no longer be recovered after being disturbed.

The hardness was measured using a shore D durometer. The results were in shore D scale with no unit.

The shrinkage was obtained by measuring the length of a sample bar made in a W/D/H: 436/20/5 mm mould after 7 days.

Neither solvents nor plasticizers were used in the Inventive sample so that the VOC is zero. This was confirmed by a micro-chamber emission test according to AgBB/DIBt standard with a 2-K application formulation.

Further properties of the materials are described in the following Table 2.

Table 2

<table>
<thead>
<tr>
<th></th>
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</table>

<table>
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<tr>
<th>Property</th>
<th>Example</th>
<th>Example</th>
<th>Result</th>
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<td>Impact resistance [Nm] BS EN ISO 6271: 2011</td>
<td>Failure load 6.9 (IR6)</td>
<td>Failure load 7.4 (IR7)</td>
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<tr>
<td>Wear resistance [mm] BS EN 13892-4: 2002</td>
<td>Wear depth 0.033 (AR0.5)</td>
<td>Wear depth 0.023 (AR0.5)</td>
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</tr>
<tr>
<td>Adhesion on concrete [MPa] BS EN 13892-8: 2002</td>
<td>1.3 with primer 0.9 no primer</td>
<td>1.1 with primer 1.1 no primer</td>
<td>Similar (all substrate failure)</td>
</tr>
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<td>Compressive strength [MPa] BS EN 13892-8: 2002</td>
<td>21.5</td>
<td>26.7</td>
<td>Better</td>
</tr>
<tr>
<td>Compressive modulus [mg.m⁻².h⁻¹] BS 6391-6: 1994</td>
<td>201</td>
<td>194</td>
<td>Similar</td>
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<tr>
<td>Water vapour transmission [mg.m⁻².h⁻¹.Pa⁻¹] BS EN 12086: 1997</td>
<td>0</td>
<td>0,00036</td>
<td>Better</td>
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</table>

As can be taken from the above, the Inventive Example provides improved workability properties, a long pot life, and excellent finished properties such as impact resistance, water vapour transmission and compressive strength.
Claims

1. A water-reducible curing agent for epoxy resins, obtainable by reacting at least one diprimary amine, at least one mono-primary amine and at least one polyepoxy compound, wherein the molar ratio of the primary amino groups to the epoxy groups in the reaction is in the range of about 1.7:1 to 1:1, the ratio of the primary amines in the diprimary amine to secondary amines optionally present in the diprimary amine is more than 1:1, and the molecular weight (Mw) of the diprimary amine is 500 Dalton or less.

2. Water-reducible curing agent according to claim 1, characterized in that the molar ratio of the primary amino groups to the epoxy groups in the reaction is about 1.5:1 or less, preferably about 1.4:1 or less.

3. Water-reducible curing agent according to claim 1 or 2, characterized in that the molar ratio of the at least one diprimary amine to the at least one mono-primary amine is at least 1:1, preferably at least 2:1 and most preferably at least 4:1.

4. Water-reducible curing agent according to anyone of claims 1 to 3, characterized in that the mass ratio of the primary amines in the diprimary amine, with regard to the molar mass of the diprimary amines is at least 20% or more.

5. Water-reducible curing agent according to anyone of the preceding claims, characterized in that the diprimary amine is selected from the group comprising of ethylene diamine, diethylene triamine, diethylene glycol diamine, 1,2-propylene diamine, 1,3-propylene glycol diamine, dipropylene diamine, 1,2-methyl-1,2-propanediamine, 2,2-dimethyl-1,3-propane diamine, 1,3-butane diamine, 1,4-butanediamine, 1,3-pentane diamine and 1,5-pentane diamine.
6. Water-reducible curing agent according to anyone of the preceding claims, characterized in that the mono-primary amine in addition contains one or more secondary amines.

7. Water-reducible curing agent according to anyone of the preceding claims, characterized in that the mono-primary amine is selected from the group comprising aminoethyl ethanol amine, ethanol amine, N-ethyl ethylene diamine and N-ethanol-diethylene triamine.

8. Water-reducible curing agent according to anyone of the preceding claims, characterized in that the polyepoxy compound comprises a mixture of at least one aromatic diepoxide and at least one aliphatic diepoxide.

9. Water-reducible curing agent according to claim 8, characterized in that the aromatic diepoxide is derived from bisphenol A, bisphenol F or mixtures thereof, which are functionalized with glycidyl groups.

10. Water-reducible curing agent according to claim 8 or 9, characterized in that the aliphatic diepoxide comprises one or more diglycidethers of \( \alpha,\omega \)-alkandiols, preferably with 2 to 10 carbon atoms.

11. Use of a water-reducible curing agent according to anyone of claims 1 to 10 as a curing agent for epoxy resins, preferably as a curing agent for water-based epoxy resins and more preferably as a curing agent for self-levelling water-based epoxy resins.

12. Process for the preparation of a water-reducible curing agent comprising - providing at least one diprimary amine and at least one mono-primary amine, wherein the molar ratio of the primary amines in the diprimary amine to secondary amines optionally present in the diprimary amine is
more than 1:1 and wherein and the molecular weight (Mw) of the
diprimary amine is 500 or less;
- adding at least one polyepoxy compound to the amines, wherein the
molar ratio of the primary amino groups to the epoxy groups employed
in the reaction is in the range of about 1.7:1 to 1:1, and
- reacting the amine groups with the epoxy groups.

13. Process for coating a substrate, characterized in that a water-reducible
curing agent according to anyone of claims 1 to 10 is mixed with an
epoxy resin, applied to a surface of the substrate and cured.

14. Substrate with an epoxy resin coating obtainable by a process according
to claim 13.
### INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/18

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>EP 0 387 418 A2 (RUETGERSWERKE AG [DE]) 19 September 1990 (1990-09-19)</td>
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<td>Y</td>
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<td>US 5 489 630 A (WALKER FREDERICK H [US]) 6 February 1996 (1996-02-06)</td>
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<td>EP 1 136 509 A1 (BAKELITE AG [DE]) 26 September 2001 (2001-09-26) paragraph [0024]; examples</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  * "A" document defining the general state of the art which is not considered to be of particular relevance
  * "E" earlier application or patent but published on or after the international filing date
  * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  * "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

"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

"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

"B" document member of the same patent family

Date of the actual completion of the international search: 18 March 2014

Date of mailing of the international search report: 27/03/2014

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 340-3040, Fax: (+31-70) 340-3016

Authorized officer: Ellrich, Klaus
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</tr>
<tr>
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<tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>US 5032629 A</td>
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</tr>
<tr>
<td>US 5489630</td>
<td>06-02-1996</td>
<td>DE 69517772 D1</td>
<td>10-08-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69517772 T2</td>
<td>09-11-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0714924 A2</td>
<td>05-06-1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2836811 B2</td>
<td>14-12-1998</td>
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<td>JP H08208810 A</td>
<td>13-08-1996</td>
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<td>US 5599855 A</td>
<td>04-02-1997</td>
</tr>
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<td>CA 2390776 A1</td>
<td>15-12-2002</td>
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<tr>
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<td>DE 10128889 A1</td>
<td>19-12-2002</td>
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<td>DE 10013735 A1</td>
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</tr>
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<td>DE 50106240 A1</td>
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