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(54) **Title:** HARDENERS FOR COLD-CURING EPOXY SYSTEMS

(57) **Abstract:** A hardener composition comprising: a) an isolated adduct comprising a reaction product of i) a polymer with a functionality of at least three, wherein said polymer contains at least one epoxy group; and ii) an amine wherein the isolated adduct is present as an aqueous solution; and b) a capping agent. This hardener can be used with a liquid epoxy resin to form a curable composition.

HARDENERS FOR COLD-CURING EPOXY SYSTEMS

BACKGROUND OF THE INVENTION

Introduction

5 Amine-containing hardeners are useful for epoxy resin applications. One type of
amine hardener is a waterborne hardener. Water is an ideal “solvent” as it is non-flammable,
non-VOC, non-toxic, and non-odorous. Waterborne hardeners exhibit easy workability, low
sensitivity to wet substrates, good drying, excellent adhesion to most substrates, very good
intercoat adhesion, and good corrosion protection on steel. Waterborne hardeners can be
10 categorized into: polyaminoamides, amine/epoxy adducts with “free” monomeric amines, and
amine/epoxy adducts without free amines. Waterborne hardeners are often made from polymeric
starting materials. Waterborne hardeners are used where a very low viscous epoxy
resin/hardener combination must be achieved without using solvents or any other volatile organic
compounds (VOCs). In principle, water can be used with both components as an aqueous epoxy
15 resin or an aqueous hardener. The preferred technical solution is to introduce self-emulsifiable
groups via chemical reaction into the hardener. The water will evaporate upon film formation
and curing. In non-aqueous systems, high boiling VOCs such as benzyl alcohol are used in the
formulation. They act as plasticizers and can lower the glass transition temperature (T_g) of a
formulation.

20 The groups introduced into the hardener which provide the self-emulsifiability are
often of polyalkylenoxide type (EO/PO/BuO). They provide a little flexibility but not as much as
using a plasticizer like benzyl alcohol. One drawback to these hardeners is that upon curing, they
form a three dimensional network with epoxy resins that are not flexible. Other hardeners that
are able to reduce the three dimensional density normally have bad chemical resistance.

25 Therefore, a need remains for waterborne, amine-containing hardener compounds
that have flexibility upon curing without having a density too high and also having good
chemical resistance, and that also provide self-emulsifiability and flexibility without use of a
plasticizer.

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SUMMARY OF THE INVENTION

In one broad embodiment of the invention, there is disclosed a hardener composition comprising, consisting of, or consisting essentially of: a) an isolated adduct comprising a reaction product of i) a polymer with a functionality of at least three, wherein said
5 polymer contains at least one epoxy group; and ii) an amine, wherein the isolated adduct is present as an aqueous solution; and b) a capping agent.

DETAILED DESCRIPTION OF THE INVENTION

10 Isolated adduct

In an embodiment, one component of the composition is an isolated adduct comprising a reaction product of a polymer and an amine.

The polymer is the product of a polyfunctional aliphatic or aromatic alcohol reacted with alkyleneoxide (ethyleneoxide, propylene oxide, butylene oxide) to an extent that every OH-group
15 is at least alkoxyated three times. End OH-groups are terminated by glycidyl groups by reaction with epichlorohydrin and subsequent dehydrohalogenation.

Examples of the polymer generally include polymer particles comprising an epoxy compound having at least one epoxy group and an average functionality of at least 1.8. The polymer can have a functionality in the range of from 1.8 to 3.8 in another embodiment, a
20 functionality in the range of from 2.2 to 3.2 in yet another embodiment, and a functionality in the range of from 2.3 to 3.0 in yet another embodiment. Examples of the polymer include, but are not limited to Polypox™ VE 101592, D.E.R.™ 732, and D.E.R.™ 736.

Examples of the amine include but are not limited to aliphatic polyamines, arylaliphatic polyamines, cycloaliphatic polyamines, aromatic polyamines, heterocyclic
25 polyamines, polyalkoxypolyamines, and combinations thereof. The alkoxy group of the polyalkoxypolyamines is an oxyethylene, oxypropylene, oxy-1,2-butylene, oxy-1,4-butylene or a co-polymer thereof.

Examples of aliphatic polyamines include, but are not limited to ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), trimethyl hexane diamine
30 (TMDA), hexamethylenediamine (HMDA), N-(2-aminoethyl)-1,3-propanediamine (N3-Amine), N,N'-1,2-ethanediybis-1,3-propanediamine (N4-amine), and dipropylenetriamine. Examples of

arylaliphatic polyamines include, but are not limited to m-xylylenediamine (mXDA), and p-xylylenediamine. Examples of cycloaliphatic polyamines include, but are not limited to 1,3-bisaminocyclohexylamine (1,3-BAC), isophorone diamine (IPDA), and 4,4'-methylenebiscyclohexylamine. Examples of aromatic polyamines include, but are not limited to

5 m-phenylenediamine, diaminodiphenylmethane (DDM), and diaminodiphenylsulfone (DDS). Examples of heterocyclic polyamines include, but are not limited to N-aminoethylpiperazine (NAEP), and 3,9-bis(3-aminopropyl) 2,4,8,10-tetraoxaspiro(5,5)undecane. Examples of polyalkoxypolyamines where the alkoxy group is an oxyethylene, oxypropylene, oxy-1,2-butylene, oxy-1,4-butylene or a co-polymer thereof include, but are not limited to 4,7-

10 dioxadecane-1,10-diamine, 1-propanamine,2,1-ethanediyl)bis(diaminopropylated diethylene glycol) (ANCAMINE[®] 1922A); poly(oxy(methyl-1,2-ethanediyl)), alpha-(2-aminomethylethyl)omega-(2-aminomethylethoxy) (JEFFAMINE[®] D-230, D-400); triethyleneglycoldiamine and oligomers (JEFFAMINE[®] XTJ-504, JEFFAMINE[®] XTJ-512), poly(oxy(methyl-1,2-ethanediyl)),alpha,alpha'-(oxydi-2,1-ethanediyl)bis(omega-

15 (aminomethylethoxy)) (JEFFAMINE[®] XTJ-511); bis(3-aminopropyl)polytetrahydrofuran 350; bis(3-aminopropyl)polytetrahydrofuran 750; poly(oxy(methyl-1,2-ethanediyl)), a-hydro-w-(2-aminomethylethoxy) ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (JEFFAMINE[®] T-403), and diaminopropyl dipropylene glycol.

In an embodiment, the hardener is present as an aqueous solution. The epoxy

20 component can react with amines, wherein every epoxy group in the molecule will react with 1 molecule of amine. To avoid polymerization, a molar excess of amine is used during the reaction, e.g. 1 epoxy group with 1.3 to 3 moles of amine. The excess of 0.3 to 2 moles must be removed as they will affect the properties of the hardener adversely. Removal is generally done by distillation. The residue is an isolated polymeric amine adduct.

25 In an embodiment, the isolated adduct is present in the composition in the range of from 5 weight percent to 95 weight percent, based on the total weight of the composition. The isolated adduct is present in the range of from 10 weight percent to 80 weight percent in another embodiment, and is present in an amount in the range of from 20 weight percent to 70 weight percent in yet another embodiment.

30

Capping Agent

In an embodiment, the composition can contain a capping agent.

5 Examples of the capping agent include but are not limited to ethylene oxide, propylene oxide, butylene oxide, phenyl glycidyl ether, cresyl glycidyl ether, p.t – butylphenyl glycidyl ether, C12/C14 fatty alcohol glycidyl ether, and formaldehyde.

The capping agent is generally present in an amount in the range of 0.1 weight percent to 10 weight percent, based on the total weight of the hardener composition. In an embodiment, the capping agent can be present in a range of from 0.2 weight percent to 8 weight percent, based on the total weight of the hardener composition, and from 0.5 weight percent to 5 weight percent, based on the total weight of the hardener composition in yet another embodiment.

Modifier

15 The hardener composition may also include a modifier. The modifier is useful for dilution and may accelerate the curing speed in combination with epoxy resins. The modifier can also enhance surface appearance. Acids can be used as modifiers to adjust water solubility.

20 Examples of modifiers include, but are not limited to, benzyl alcohol, acids such as aceticpropionic or lactic acid, and also medium chain organic diacids, such as sebacic or azelaic acid, or amidosulphonic acid, citric acid, high boiling solvents, such as alkylenglycol ethers, or esters.

The modifier is generally present in a range of from 0.05 weight percent to 5 weight percent, based on the total weight of the composition.

External emulsifiers

25 The composition can also contain external emulsifiers. These can include, but are not limited to alkoxyated fatty alcohols or phenols. The external emulsifier is generally present in the hardener composition in the range of from 0.05 weight percent to 5 weight percent.

Process for Producing the Hardener

The hardener is generally prepared by the following process: epoxy is added to a molar excess of amine at a temperature of from 60°C to 140°C. The excess is then distilled, at which point a capping agent is added at a temperature of from 60° to 140°C. Water is then
5 added at a temperature of less than 100°C, after which an modifier and/or external emulsifier can be added.

In some embodiments (e.g. for self leveling flooring), the hardener formulation can be produced by mixing defoamers, pigments, fillers and thixotropic agents with a dissolver.

Curable Composition Product

In an embodiment, a curable composition comprises, consists of, or consists essentially of: I) the above-described hardener and II) an epoxy resin.

In an embodiment, the epoxy resin is a liquid epoxy resin. Examples of liquid epoxy resins that can be used include, but are not limited to bisphenol-A diglycidyl ethers
15 (BADGE), bisphenol-F diglycidyl ethers (BFDGE), and epoxy novolacs. In another embodiment, the epoxy resin can be a solid bisphenol A epoxy resin.

The curable composition is produced by mixing the above hardener formulation with water and liquid epoxy resin to form an emulsion.

The curable composition can be optionally diluted with reactive diluents such as,
20 for example, cresyl glycidyl ether (CGE), p.tert butyl-phenyl glycidyl ether (ptBPGE), C12/C14 glycidyl ether, butanediol diglycidyl ether (BDDGE), hexanediol- diglycidyl ether (HDDGE), and versatic acid glycidyl ester.

In an embodiment, the hardener component and the epoxy resin are mixed according to the hardener equivalent weight (HEW) and epoxide equivalent weight (EEW). The
25 equivalents can generally be varied between 0.8 and 1.2 equivalents of epoxy to 1 equivalent amine hydrogen. In an embodiment, 1 equivalent of epoxy reacts with 1 equivalent amine hydrogen. The composition is then cured at ambient temperature.

These compositions are generally used as coatings, concrete primers, floorings, flexible mortars, repair systems for concrete, and also for other ambient or post cured curing
30 applications.

EXAMPLES

Example 1 – Preparation of hardener

5 A four-necked glass flask with a mechanical stirrer and a thermometer was charged with 158 g (1 mol) TETA. With a dropping funnel 228.1 grams (0.5 equiv.) of Polypox™ VE 101592 was added at 70°C.

After the addition, vacuum was adjusted to 20 mbar and the batch was heated to 225°C to distill the excess of TETA. The final pressure was 10 mbar. A 82.27 gram quantity (0.52 mol) of TETA was distilled. After cooling at a temperature below 100°C, 130.2 grams of water was added in one portion. A 27.2 gram quantity (0.1184 mol) of Polypox™ R7 was then added drop wise at 60°C. After 1 hour of stirring, 4.14 grams (0.1380 mol) of a formaldehyde solution (19 wt %) was added drop wise at 60°C. A flocculate precipitate was formed and then dissolved. The theoretical solid content of 70% was adjusted with 4 grams of water. A 469.41 gram quantity of a moderately viscous, yellow, clear amine hardener was discharged.

15 Analytical results:

Viscosity (25°C): 4300 mPa*s

Amine number: 227 mg KOH/g

Solids: 70.2%

HEW: 211 g/equiv. HEW is calculated as the sum of all amine equivalents in the hardener divided by the total mass of ingredients of the hardener.

In the Examples, various standard analytical equipment and test methods are used including the following: viscosity is measured by ISO 3219-B; amine number is measured by ISO 9702; color is measure by ASTM D1544; refractive Index is measured by ASTM D1804; Shore D/A hardness is measured by ASTM D2240; pot life is measured by the gel time of a 100 g mixture according to DIN 16945; and surface appearance is measured by visual and/or haptic inspection. “Solids” are calculated as the total mass of hardener minus the mass of volatiles (i.e. water).

30

Table 1. Comparison of Comparative Example A (POLYPOX W 804) vs. Example 1

	POLYPOX W 804 (Comparative Example A)	Example 1 (inventive)
solid content [%]	70 ± 1	70 ± 1
HEW [g/equiv.]	175	217
viscosity [mPas]	8000 ± 3000	app. 4300

The pure binder systems (meaning the hardener of Comparative Example A or Example 1) with POLYPOX E 411 were also tested to show the difference between the common water based hardener and the flexible water based hardener. The formulations are shown in Tables 2 and 3, below. The binder system performance is shown in Table 4.

Table 2. Formulation with Example 1 Hardener

Component A		supplier		pbw
1.	Example 1 hardener			138 g
2.	Water			57 g
3.	EFKA 2526	EFKA	Defoamer	5 g
4.	Kronos 2063	Kronos	Pigment	29 g
5.	Flammruß 101	Degussa	Pigment	1 g
6.	EWO	Alberti/Sachtleben	Barium sulfate	300 g
7.	ISG 100	Dorfner	Quartz (0,06 – 0,25)	450 g
8.	Water			30 g
9.	Deuteron VT 819 (3% in water)	Deuteron	Thixotropic agent	2 g
			Total Comp. A:	1012 g
Component B				
	POLYPOX E 411	UPPC		125.5 g

Table 3. Formulation with Comparative Example A hardener (POLYPOX W 804)

Component A		supplier		pbw
1.	POLYPOX W 804	UPPC		120 g
2.	Water			63 g
3.	EFKA 2526	EFKA	Defoamer	5 g
4.	Kronos 2063	Kronos	Pigment	29 g
5.	Flammruß 101	Degussa	Pigment	1 g
6.	EWO	Alberti/Sachtleben	Barium sulfate	300 g
7.	ISG 100	Dorfner	Quartz (0,06 – 0,25)	450 g
8.	Water			30 g
9.	Deuteron VT 819 (3% in water)	Deuteron	Thixotropic agent	2 g
			Total Comp. A:	1000 g
Component B				
	POLYPOX E 411	UPPC		140 g

Table 4. Binder System Performance

Formulation 1 with		
	Example 1 Hardener	Comparative Example A (POLYPOX W 804)
resin	POLYPOX E 411	POLYPOX E 411
solid content Comp. A [%]	~ 85	~ 85
defoaming	++	++
surface	++	++
Shrinkage at the beginning [%]	1.6	0.0
Shrinkage after 7d [%]	0.20	0.17
Shore-A at 23°C / 50% rel. hum.		
16h	57	79
18h	63	80
24h	67	89
48h	77	96
7d (Shore-D)	54	80
Shore-A at 13°C / 80% rel. hum.		
16h	n.d.	74
18h	30	76
24h	39	85
48h	73	96
7d	86 (43 D)	100 (74 D)
early water spot resistance 23°C / 50% rel. hum.	++	++
early water spot resistance 13°C / 80% rel. hum.	++	++
leveling	++	++

+=good; -=bad

In the Examples, various standard analytical equipment and test methods are used including the following: viscosity is measured by ISO 3219-B; amine number is measured by ISO 9702; color is measure by ASTM D1544; refractive Index is measured by ASTM D1804; Shore D/A hardness is measured by ASTM D2240; pot life is measured by the gel time of a 100 g mixture according to DIN 16945; and surface appearance is measured by visual and/or haptic inspection. “Solids” are calculated as the total mass of hardener minus the mass of volatiles (i.e. water).

Shrinkage is measured on a 2 mm thick coating on polyethylene foil with a dimension of 5 cm x 100 cm.

Early water spot resistance is inspected visually by putting a drop of water on the surface of the coating during the curing process.

- 5 Pendulum hardness was measured for the compositions and is shown in Table 5, below.

Table 5. Pure Binder System

	Example 1	Comparative Example A (POLYPOX W 804)
resin	POLYPOX E 411	POLYPOX E 411
solid content	70.1 %	70 %
solid content of the mixture	65 %	65 %
Pendulum hardness [Koenig] at 23°C / 50% rel. hum.		
16h	8	36
18h	8	36
24h	8	51
48h	11	109
7d	21	179
Pendulum hardness [Koenig] at 13°C / 80% rel. hum.		
16h	tack	11
18h	tack	11
24h	8, tack	23
48h	8	41
7d	17	78
early water spot resistance 23°C / 50% rel. hum.	++	+
early water spot resistance 13°C / 80% rel. hum.	++	+
surface	+/-	++

+ = good; - = bad

Both hardeners show clear films. The surface with hardener Example 1 is not as good as the surface with POLPYOX W 804.

The flexibility of coating is measurable and noticeable.

5 Conclusion

The starting formulation with Inventive hardener Example 1 shows more shrinkage and dishing than Comparative Example A, but the flexibility is measurable also in the binder system.

In conclusion, the inventive hardener can be used when flexible properties are required and a waterborne system is desired.

10

THAT WHICH CLAIMED IS:

1. A hardener composition comprising:

a) an isolated adduct comprising a reaction product of

i) a polymer with a functionality of at least three, wherein said polymer contains

5 at least one epoxy group; and

ii) an amine

wherein said isolated adduct is present as an aqueous solution; and

b) a capping agent.

2. A hardener composition in accordance with claim 1 wherein said amine is selected from

10 the group consisting of ethylenediamine, diethylenetriamine, triethylenetriamine, m-xylylenediamine, methylpentamethylenediamine, 1,3 BAC and combinations thereof.

3. A hardener composition in accordance with claim 1 wherein said capping agent is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, phenyl glycidyl ether, cresyl glycidyl ether, p.t – butylphenyl glycidyl ether, C12/C14 fatty alcohol

15 glycidyl ether, and formaldehyde.

4. A hardener composition in accordance with claim 1 wherein said polymer is present in the isolated adduct in an amount in the range of from 30 weight percent to 95 weight percent, and said amine is present in the isolated adduct in an amount in the range of from 5 weight percent to 70 weight percent, based on the total weight of the isolated adduct.

20

5. A hardener composition in accordance with claim 1 wherein said isolated adduct is present in the hardener composition in an amount in the range of from 5 weight percent to 95 weight percent and said capping agent is present in the hardener composition in an amount in the range of from 0.1 weight percent to 10 weight percent, based on the total weight of the hardener composition.
6. A hardener composition in accordance with claim 1 further comprising c) a modifier selected from the group consisting of styrenated phenol, diisopropyl naphthalene, p.-t.-butylphenol, benzyl alcohol, acetic acid, propionic acid, lactic acid, sebacic acid, azelaic acid, amidosulphonic acid, and citric acid.
7. A process comprising:
- a) contacting
 - i) a polymer with a functionality of at least three, wherein said polymer contains at least one epoxy group; and
 - ii) an excess of amine under reaction conditions to form an isolated adduct;
 - b) distilling excess amine to form an aqueous solution of said isolated adduct; and
 - c) admixing
 - i) said aqueous solution of said isolated adduct; and
 - ii) a capping agent
- to form a hardener composition.
8. A process in accordance with claim 7 wherein said reaction conditions in step a) comprise a reaction temperature in the range of from 60°C to 140°C.

9. A curable composition comprising:
- I) the hardener composition of claim 1; and
 - II) an epoxy resin selected from the group consisting of liquid bisphenol-A diglycidyl ethers, liquid bisphenol-F diglycidyl ethers, liquid epoxy novolacs, solid
- 5 bisphenol-A epoxy resins, and combinations thereof.
10. A coating prepared from the composition of claim 9.
11. A primer prepared from the composition of claim 9.