US 20040116647A1

(19) United States
(12) Patent Application Publication
Swedo
(10) Pub. No.: US 2004/0116647 A1
(43) Pub. Date: Jun. 17, 2004

(54) NOVEL PHENOLIC RESINS

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(21) Appl. No.: **10/383,272**

(22) Filed: **Mar. 7, 2003**

Related U.S. Application Data

(60) Provisional application No. 60/431,142, filed on Dec. 4, 2002.

Publication Classification

(51) **Int. Cl.^{7}** **C08G 8/04**
(52) **U.S. Cl.** **528/145**

(57) **ABSTRACT**

The invention herein disclosed comprises the use of oxazolidines, nitroalcohols, nitroamines, aminonitroalcohols, imines, hexahydropyrimidines, nitrones, hydroxylamines, nitro-olefins and nitroacetals to serve as hardeners and/or as catalysts for curing phenolic resins. The hardeners and catalysts described in the invention can be applied in any application where phenolic resins are used, including but not limited to adhesives, molding, coatings, pultrusion, prepregs, electronics, composites, fire resistant, and flame-retardant end uses.

NOVEL PHENOLIC RESINS

BACKGROUND OF INVENTION

[0001] 1. Field of the Invention

[0002] The invention is directed toward compositions which are useful as hardeners and/or catalysts for novolac and resole phenolic resins.

[0003] 2. Description of the Prior Art

[0004] Phenolic resins can be broadly divided into two general classes: novolacs and resoles. Novolac resins are generally characterized as being formaldehyde deficient. That is to say that the ratio of formaldehyde to phenolic groups is <1. Resole resins are generally characterized as being formaldehyde rich. That is to say that the ratio of formaldehyde to phenolic groups is >1. Both novolacs and resoles may incorporate a variety of phenolic compounds, alone or in combination, including but not limited to phenol, resorcinol, bisphenols, phloroglucinol, cresols, alkyl phenols, phenol ethers, tannins, and lignins. Similarly, other aldehydes may be substituted in whole or in part for formaldehyde, including but not limited to acetaldehyde, propionaldehyde, cyclohexanedicarboxaldehydes, benzaldehydes, furfural, and other aryl or heterocyclic aldehydes.

[0005] Novolac resins are usually cured (crosslinked, hardened) through the use of formaldehyde, formaldehyde-donating hardener compounds, or formaldehyde equivalent compounds. Hexamethylenetetramine (hexa) and paraformaldehyde are often used commercially to cure novolac resins. In addition to a source of formaldehyde, heating and the presence of a catalyst are usually employed to accelerate the rate and extent of curing. Catalysts may include inorganic bases such as sodium or potassium hydroxide, Lewis acids such as zinc chloride, or amines such as triethylamine.

[0006] Resoles, being formaldehyde rich, do not require additional formaldehyde to cure. Heat alone or heating in the presence of a catalyst—usually an acid—are all that are required.

SUMMARY OF INVENTION

[0007] The invention herein disclosed comprises the use of oxazolidines, nitroalcohols, nitroamines, immes, aminonitroalcohols, hexahyudropyrimidines, nitrones, hydroxylamines, nitro-olefins and nitroacetals to serve as hardeners and/or as catalysts for curing phenolic resins. These hardeners include both completely new compositions as well as known compounds found to have unexpected activity. The hardeners are effective in curing a wide range of phenolic resins, including novolacs and resoles. Through the judicious selection of these hardeners, used either alone or in various combinations, it is possible to advantageously vary the processing parameters of these phenolic resin systems. Lower curing temperatures, controlled curing rates, and reduced post-cure cycles are advantageous improvements as compared to standard hexa-cured novolac or acid-catalyzed resole systems. These process improvements and reduction in cycle time have obvious economic benefits.

[0008] The hardeners and catalysts described in this invention can be applied in any application where phenolic resins are used, including but not limited to adhesives, molding compounds, foundry materials, abrasives, friction materials, insulation, laminates, coatings, pultrusion, prepregs, electronics, composites, fire resistant, and flame-retardant end uses.

DETAILED DESCRIPTION OF INVENTION

[0009] The invention includes novel curing agents, i.e., hardeners and catalysts, drawn from a wide variety of existing and new oxazolidines, nitroalcohols, nitroacetals, nitro-olefins, nitroamines, hexahydropyrimidines, aminonitroalcohols, nitrones, hydroxylamines, and imines, as described below. The hardeners and catalysts are selected from the group consisting of pyrrolidine/2-Methyl-2-nitro-1,3-propanediol (PYRR/NMPD), diethylamine/2-Methyl-2-nitro-1,3-propanediol (DEA/NMPD), 2-furfural/2-Methyl-2-nitro-1,3-propanol (FUR/NMP), vanillin-isopropylhydroxylamine (IPHA) nitrone, 2-Methyl-2-nitro-1,3-propanediol-bis-diethylamine (NMPD-bis-DEA), Cyclohexanedicarboxaldehyde diimine (CHDA-A), 2-dimethylamino-2-hydroxymethyl-1,3-propanediol (DMTA), dimethylamine-2-Methyl-2-nitro-1,3-propanediol (DMA-NMPD), bis-(2-nitroisobutoxy)methane (NMP acetal), 5-nitro-5-hydroxymethyl-1,3-bis(isopropyl)hexahydropyrimidine (PYRIM) and formaldehyde-based nitrones from hydroxylamine, including hydroxylamine (HA), N-isopropylhydroxylamine (IPHA), N-propylhydroxylamine (PHA), hydroxylamines N-ethylhydroxylamine (EHA), N-t-butylhydroxylamine (tBuHA), and N-benzyl hydroxylamine (N-BzHA).

EXAMPLES

[0010] Oxazolidines Zoldine® ZT-55 and ZT-65 (5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane), Bioban® CS-1246 (5-ethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane), Bioban® CS-1135 (4,4-dimethyl-1-oxa-3-azacyclopentane), Amine CS-1991™ (5-methyl-1-aza-3,7-dioxabicyclo[3.3.0]octane), Zoldine® BBA (3-ethyl-2-isopropyl-1-oxa-3-azacyclopentane), and Bioban® N-95 (mixture of ZT, 5-hydroxymethoxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane, and higher hydroxyalkoxymethyl oligomers), nitroalcohols tris(hydroxymethyl)-nitromethane (TN), 2-methyl-2-nitropropanol (NMP), and 2-methyl-2-nitro-1,3-propanediol (NMPD), and the hydroxylamines N-isopropylhydroxylamine (IPHA), N-ethylhydroxylamine (EHA), N-propylhydroxylamine (PHA), and N-t-butylhydroxylamine (tBuHA) were all obtained from Angus Chemical Company. The β-methyl-β-nitrostyrene, N,N-diethylhydroxylamine (DEHA), diethylamine (DEA), dimethylamine (DMA), isopropylamine (IPA), hexamethylenetetramine (HEXA), N-cyclohexylhydroxylamine (N-CyhexHA), N-benzylhydroxylamine (N-BzHA), hydroxylamine (HA), and common acids, bases, lab reagents and solvents were all commercial samples obtained from Aldrich Chemical Company. Formcel™ was obtained from Celanese. Durez PF novolac resin Varcum 29-607, Plenco PF novolac resin 13360, and Dynea PRF novolac resin 1204 were all commercially available materials. Other materials were synthesized as indicated below.

[0011] GC Analyses:

[0012] GC analyses were performed using a Hewlett Packard Model 5890A gas chromatograph with FID detector on a 30 meter×0.25 mm 1μ film DB-5 column.

[0013] DSC Analyses:

[0014] DSC analyses were performed using a TA Instruments Model Q100 differential scanning calorimeter. The DSC scans were run from 25° C. to 400° C. at $\Delta T=10°$ C./minute with a nitrogen flow of 50 cc/minute. Samples were prepared by dissolving the resin and hardener components in excess ethanol, then removing the solvent under vacuum at room temperature. Non-hermetic, aluminum sample pans were used. A small hole was punctured in the top before crimping.

[0015] Gel Time Determinations:

[0016] The gel times of resin formulations were determined by the manual hot plate method.

[0017] A hot plate is preheated to 160° C. A small sample of the resin formulation is placed on the hot surface, and a timer is started. The sample melts and is "stroked" with a spatula until the gel point is reached—i.e., the thickening melt no longer "threads" as the spatula is stroked through it. At this point the timer is stopped. The elapsed time is recorded as the gel time. Reported values are averages of multiple determinations.

Example 1

Synthesis of PYRR/NMPD

[0018] PYRR/NMPD: 2-Methyl-2-nitro-1,3-propanediol (NMPD; 27.02 g, 0.20 moles) and pyrrolidine (14.22 g, 0.20 moles) were charged to a 250 mL flask. The mixture was stirred at room temperature under a nitrogen blanket. After about 30 minutes, an exotherm to about 40° C. was observed, and the pale yellow solution became turbid. When the exotherm subsided, the reaction mixture was heated at 60° C. for 3 hours, then at 70° C. for 12 hours. The product mixture was diluted with an equal volume of ethanol and toluene, then the solvents were removed by rotary evaporation to azeotrope off the water. The yield of PYRR/NMPD as a clear, amber oil was 33.92 g. GC analysis indicated the presence of 13 area % of unreacted NMPD.

Example 2

Synthesis of DEA/NMPD

[0019] DEA/NMPD: NMPD (13.52 g, 0.10 moles) and diethylamine (DEA; 10.34 mL, 7.31 g, 0.10 moles) were charged to a 100 mL flask. The mixture was stirred at room temperature to give a clear, yellow solution. The solution was stirred at room temperature under a nitrogen blanket for 6 days. The solution was then diluted with an equal volume of toluene, and the solvent was removed by rotary evaporation to azeotrope off the water. A yellow oil was isolated. Some white crystals of unreacted NMPD separated from the product on standing at room temperature. The NMPD was removed by filtration. The yield of DEA/NMPD as a clear, yellow oil was 12.45 g. GC analysis showed the oil contained <3 area % of NMPD.

Example 3

Synthesis of FUR/NMP

[0020] FUR/NMP: Nitroethane (NE; 7.51 g, 0.10 moles), 2-furfural (19.22 g, 0.20 moles), and tetrahydrofuran (THF; 50 mL) were charged to a 250 mL flask. Amberlyst A-21 ion exchange resin (10 g) was then added. After stirring at room temperature under a nitrogen blanket for 2 weeks, the reaction mixture was filtered. The resin was washed on the filter with THF and the washings were combined with the filtrate. The solvent was removed by rotary evaporation to give 16.46 g of dark brown oil. GC/MS analysis indicated that the product was a mixture of ca. 14 area % of unreacted 2-furfural, ca. 55 area % of FUR/NMP product, and ca. 11 area % of the nitro-olefin. The crude product mixture was purified by chromatography on a silica gel column (Merck, Grade 9385, 230-400 mesh). The column was eluted with methylene chloride to remove first the nitro-olefin, and then the purified FUR/NMP product. The yield of FUR/NMP as an amber oil was 11.26 g. GC analysis indicated that all of the nitro-olefin had been removed.

Example 4

Synthesis of Vanillin-IPHA Nitrone

[0021] Vanillin-IPHA Nitrone: Vanillin (30.43 g, 0.20 moles), isopropylhydroxylamine (IPHA; ANGUS lot 5-H-93; 15.02 g, 0.20 moles) and methanol (50 mL) were charged to a 500 mL flask. The mixture was stirred at room temperature under a nitrogen blanket to give a clear, yellow solution. After a few minutes, a slow exotherm began, with a temperature of ca. 45° C. being reached in about 20 minutes. Shortly after the exotherm began to subside, crystalline solids began to separate from the reaction mixture. The reaction slurry was allowed to stir at room temperature overnight. The white crystalline solid product was isolated by filtration. The product was washed on the filter with a total of 100 mL of isopropanol. After drying, the yield of vanillin-IPHA nitrone product was 34.00 g. MP=178-179° C.

Example 5

Synthesis of NMPD-bis-DEA

[0022] NMPD-bis-DEA: NMPD (ANGUS lot ZD-06024; 27.08 g, 0.20 moles) and DEA (41.2 mL, 29.13 g, 0.40 moles) were dissolved with stirring in 40 g of distilled water in a 250 mL flask. An exotherm to about 45° C. occurred over about 10 minutes. The turbid reaction mixture solution was stirred at room temperature overnight. The reaction mixture was saturated with sodium chloride, then the layers were separated. The aqueous layer was extracted twice with equal volumes of ether. The extracts were combined and were dried over anhydrous magnesium sulfate. After filtering, the solvent was removed from the solution to give a quantitative yield of NMPD-bis-DEA as a clear yellow liquid product. GC analysis showed the product contained <3 area % of NMPD.

Example 6

Synthesis of CHDA-bis-IPHA Nitrone

[0023] CHDA-bis-IPHA nitrone: Cyclohexanedicarboxaldehyde (CHDA; mixture of 1,4 and 1,3 isomers; Dow XUR-YM-2002108630; 14.02 g, 0.10 moles) and IPHA (ANGUS lot CEC200101840-54; 15.02 g, 0.20 moles) were stirred under nitrogen with 25 g of methanol in a 250 mL flask. An exotherm to ca. 50° C. ensued as the IPHA dissolved. The exotherm quickly cooled, resulting in a clear colorless solution. The solution was stirred at room temperature for several days. The solvent was removed from the solution by rotary evaporation. Toluene was added to the resulting paste, then the mixture was subjected to rotary evaporation again to remove water as an azeotrope. The resulting CHDA-bis-IPHA nitrone was an off-white solid. The yield was 23.3 g (92%). Because it was a mixture of isomers, the product exhibited a broad melting range of 130-140° C.

[0024] The product could be recrystallized from 10:1 toluene—isopropanol to give more discrete isomer fractions having narrower melting ranges.

Example 7

Synthesis of CHDA-A

[0025] CHDA-A: This adduct was made by the reaction of CHDA with an excess of aqueous ammonium hydroxide solution.

Example 8

Synthesis of DMTA

[0026] DMTA: This aminoalcohol was made by the reductive methylation of TN by a modification of the method described in U.S. Pat. No. 2,363,466.

Example 9

Synthesis of DMA-NMPD

[0027] DMA-NMPD: NMPD (ANGUS lot ZD-06024; 13.57 g, 0.10 moles) was dissolved in aqueous DMA (40 wt. %, 12.6 mL, 4.53 g, 0.10 moles) with stirring at room temperature under nitrogen. Within about 30 minutes the solution became very turbid and darker yellow in color. After 5 days at room temperature the reaction mixture was a white, waxy solid. The product was slurried with methanol and toluene, then the solvents were removed by rotary evaporation. The yield of off-white DMA-NMPD was 15.4 g (95%). MP was 73-77° C. GC analysis showed about 4 area % of NMPD.

Example 10

Synthesis of NMP Acetal

[0028] NMP acetal: This compound was prepared according to the method described in U.S. Pat. No. 2,415,046.

Example 11

Synthesis of PYRIM

[0029] PYRIM: TN (15 g, 0.1 moles), IPA (12 g, 0.2 moles), and 36 wt. % aqueous formaldehyde (7 mL, 0.1 moles) were mixed in a flask. The mixture was cooled in an ice bath to avoid loss of the amine. It was then stirred at room temperature for 30 minutes, then it was kept at 5° C. overnight. The solid product that separated was isolated by filtration and dried in air for 4 hours. The yield of 5-nitro-5-hydroxymethyl-1,3-bis(isopropyl)hexahydropyrimidine (PYRIM) as a tan solid was 22 g (91%). MP=116-117° C.

Example 12

Synthesis of Formaldehyde-Based Nitrones

[0030] FORMALDEHYDE-BASED NITRONES: Formaldehyde-based nitrones from hydroxylamine (HA), IPHA, PHA, EHA, tBuHA, and N-benzylHA were all prepared by the general procedure described below:

[0031] IPHA (7.51 g, 0.10 moles; ANGUS lot CEC200101840-54) was dissolved in 15 g of methanol, then Formcel™ (55 wt. % formaldehyde in methanol; 5.45 g, 0.10 moles; Celanese lot T-2529 (Jan. 11, 2001)) was added. The clear colorless solution was stirred at room temperature for a few minutes. GC analysis showed complete conversion to the nitrone. The resulting solution was 31 wt. % in nitrone.

Example 13

Synthesis of PF Resole Resin

[0032] PF RESOLE RESIN RS20020437871: A resin kettle was charged with phenol (47 g, 0.5 moles), aqueous formaldehyde (37 wt. %, 80 mL, 32.06 g, 1.0 mole) and 100 mL of 4 N sodium hydroxide solution. The solution was stirred under nitrogen. An exotherm to ca. 60° C. was observed upon mixing. This subsided over about 1 hour. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then heated at 90-95° C. for 1 hour. After cooling to room temperature, the mixture was brought to pH 7 with hydrochloric acid. During this neutralization the temperature of the reaction mixture was kept at ca. 15° C. by cooling the kettle in ice water. After neutralization, the reaction mixture was allowed to settle. The upper, aqueous layer was decanted from the lower, resole layer. The resole was diluted with ca. 400 mL of acetone, and the solution was dried over anhydrous magnesium sulfate. The dried solution was filtered, then the solvent was removed by rotary evaporation at room temperature. The yield of resole as a clear brown liquid was 39.0 g.

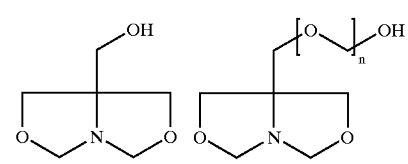
Example 14

Comparative DSC Data Survey

[0033] The objective of this work was to explore the potential for hardeners (methylene donors) and catalysts/accelerators to cure PF and PRF novolac resins. Hexamethylenetetramine (hexa) was used as the baseline for comparison since it is the hardener used most extensively in this industry.

[0034] Specific Examples of the Classes of Hardeners Cited in the Data

OXAZOLIDINES (OX)



F.W. 145.15 ZT [6542-37-6]

F.W. 175.18 (for n=1) N-95 [143350-39-4]

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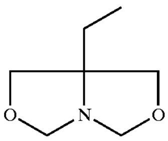
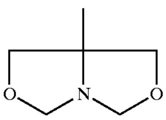


F.W. 143.18
CS-1246
[7747-35-5]



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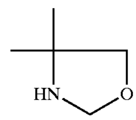
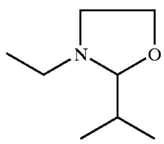
CS-1991
[7747-34-4]

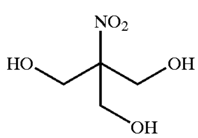


F.W. 101.14
CS-1135
[51200-87-4]

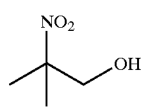


F.W. 143.22
ZOLDINE BBA
[127334-11-6]

NITROALCOHOLS (NA)

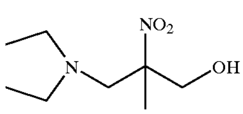


F.W. 151.11
TN
[126-11-4]

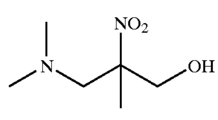


NMP
[76-39-1]
F.W. 119.12

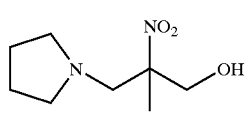
AMINONITROALCOHOLS (ANA)



F.W. 190.24
DEA-NMPD
(new compound - no CAS#)



F.W. 162.18
DMA-NMPD
(new compound - no CAS#)



F.W. 188.22
PYRR-NMPD
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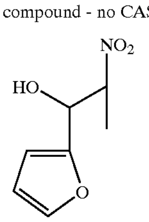
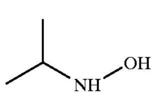
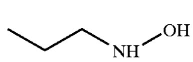


F.W. 171.15
FUR-NMP
(new compound - no CAS#)

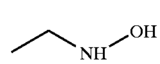
HYDROXYLAMINES (HA)



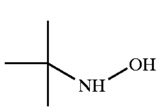
IPHA
[5080-22-8]
F.W. 75.11



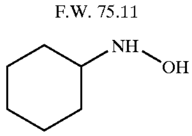
PHA
[627-38-3]
F.W. 75.11



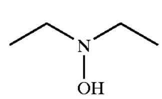
EHA
[624-81-7]
F.W. 61.08



tBuHA
[16649-50-6]
F.W. 89.13



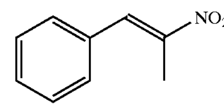
N-CyhexHA
[2211-64-5]
F.W. 115.17



DEHA
[3710-84-7]
F.W. 89.14

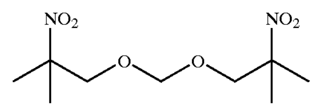
-continued

NITROOLEFINS (NO)



B-methyl-B-
nitrostyrene
F.W. 163.17
[705-60-2]

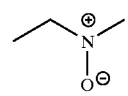
NITROACETALS (NAc)



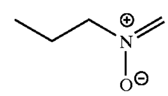
NMP acetal
F.W. 2025.25
[6263-70-3]

NITRONES (NIT)

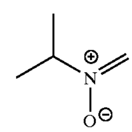
HCHO-HA
nitrone
F.W. 44.03



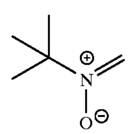
HCHO-EHA
nitrone
F.W. 73.09



HCHO-PHA
nitrone
F.W. 87.12



HCHO-IPHA
nitrone
F.W. 87.12



HCHO-tBuHA
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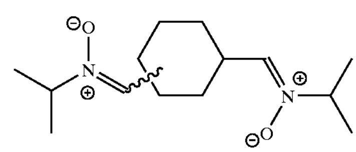
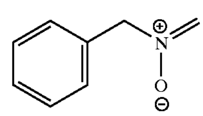
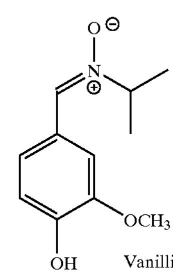
F.W. 101.14



CHDA-bis-IPHA
nitrone
F.W. 254.37

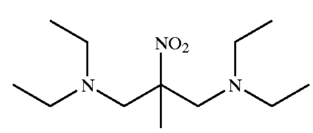


HCHO-N-BzHA
nitrone
F.W. 135.16



Vanillin-IPHA
nitrone
F.W. 209.24

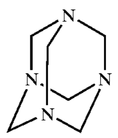
NITROAMINES (NAm)



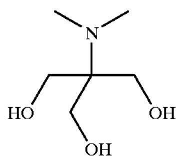
NMPD-bis-DEA
F.W. 245.36
(new compound - no CAS#)

-continued

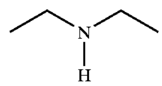
AMINES (Am)



HEXA
[100-97-0]
F.W. 140.19

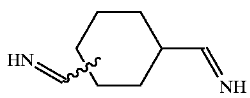


DMTA
[1112-24-9]
F.W. 149.19



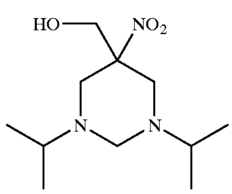
DEA
[109-89-7]
F.W. 73.14

IMINES (Im)



CHDA-A
F.W. 154.25
(new compound - no CAS#)

HEXAHYDROPYRIMIDINES (PYRIM)



PYRIM
[229477-36-5]
F.W. 245.32

[0035] The data (see Table 1 below) showed that the behavior of both of the PF novolac resins evaluated (Durez 29-607 and Plenco 13360) gave essentially the same performance with the various hardeners/catalysts tested. This indicated that the variations in cure behavior were a function of the hardener/catalyst and not of the resin. It was therefore reasonable to expect that a given hardener or catalyst would give similar performance with any PF novolac.

[0036] The PRF resin (Dynea 1204) by virtue of its resorcinol content was more reactive than the PF novolac resins. This is a well-known property. The purpose for including it here was to determine the differences in performance between PF and PRF resins with these new hardeners/catalysts.

[0037] Overall, with PF novolacs, the oxazolidines (OX), nitroalcohols (NA), nitro acetals (NAc), nitrones (NIT) and the aminonitroalcohols (ANA) appear to act as methylene (formaldehyde) donors. The nitroolefins (NO) are incorporated, but not as effectively as the methylene donors.

[0038] The hydroxylamine IPHA is not capable of acting as a methylene donor. However, it exhibits catalytic activity when paired with other methylene donors such as TN and ZT, by lowering the curing onset and peak temperatures compared to the corresponding formulations without IPHA.

[0039] Paraformaldehyde is more typically used than hexa as a hardener in PRF novolac resin formulations. Hexa was used here, however, to better allow comparisons of the new hardeners/catalysts with the PF novolac resins.

[0040] Because of its resorcinol content, the PRF novolac resin generally exhibits higher reactivity than PF novolacs and its reactivity with OXs and ANAs in this study are different. For example, CS-1135 reacted vigorously and exothermally with the PRF novolac upon mixing at room temperature. TN and NMP acetal were more reactive with the PRF novolac than in the PF resins.

[0041] In contrast, the ANAs appeared to be much poorer methylene donors here. The 3° amine groups present in the ANAs appear to act as catalysts in the PF novolac formulations, but this catalytic activity is overshadowed by the higher reactivity already provided by the resorcinol groups.

TABLE 1

LOW TEMPERATURE CURING PHENOLIC RESINS COMPARATIVE DSC DATA

TA Instruments Model Q100 DSC
Run Conditions: 10 C. / minute from 25 C. to 400 C. with N2 at 50 cc / min

CLASS:

Am = amine	NA = nitroalcohol	NIT = nitrone
OX = oxazolidine	NAm = nitroamine	Im = imine
HA = hydroxylamine	NO = nitroolefin	PYRIM = hexahydropyrimidine
ANA = aminonitroalcohol	NAc = nitroacetal	

HARDENER			CURING EVENTS			
			ONSET / PEAK C.	ONSET / PEAK C.	ONSET / PEAK C.	ONSET / PEAK C.
(CLASS)	WT. %	RESIN	(HEAT, J/g)	(HEAT, J/g)	(HEAT, J/g)	(HEAT, J/g)
Hexa	5.39	Durez 29-607 PF novolac	140 / 153 (69)	218 / 227 (3)	244 / 255 (72)	
(Am -		Plenco 13360 PF novolac	141 / 152 (122)	ca. 200 / 228 (132)		
baseline)		Dynea 1204 PRF novolac	104 / 122 (113)	239 / 285 (18)		
ZT-55	29.08	Durez 29-607 PF novolac	151 / 193 (137)	286 / 316 (44)		
(OX)		Plenco 13360 PF novolac	150 / 191 (241)	294 / 321 (54)		
		Dynea 1204 PRF novolac	ca. 140 / 169 (98)	272 / 299 (73)		
CS-1246	14.13	Durez 29-607 PF novolac	142 / 183 (161)	309 / 341 (30)		
(OX)		Plenco 13360 PF novolac	143 / 181 (162)	299 / 338 (48)		
		Dynea 1204 PRF novolac	89 / 163 (114)	305 / 327 (15)		

TABLE 1-continued

LOW TEMPERATURE CURING PHENOLIC RESINS COMPARATIVE DSC DATA

CS-1135 (OX)	22.29	Durez 29-607 PF novolac	65 / 98 (36)	128 / 175 (68)	304 / 351 (19)	
		Plenco 13360 PF novolac	60 / 115 (141)	ca. 150 / 153 (110)	267 / 321 (46)	
		Dynea 1204 PRF novolac	(gels on mixing)			
CS-1991 (OX)	15	Durez 29-607 PF novolac	100 / 118 (9)	134 / 183 (129)	295 / 336 (41)	
		Plenco 13360 PF novolac	90 / 187 (232)	287 / 329 (65)		
		Dynea 1204 PRF novolac	123 / 157 (73)	305 / 323 (17)		
DEA-NMPD (ANA)	25	Durez 29-607 PF novolac	97 / 113 (99)	139 / 205 (124)		
		Plenco 13360 PF novolac	93 / 118 (39)			
		Dynea 1204 PRF novolac	ca. 110 / 173 (371)	150 / 167 (19)	185 / 204 (48)	
PYRR-NMPD (ANA)	25	Durez 29-607 PF novolac	100 / 112 (80)	127 / 159 (80)	161 / 181 (150)	234 / 251 (134)
		Plenco 13360 PF novolac	ca. 100 / 130 (112)	125 / 166 (478)		
		Dynea 1204 PRF novolac	130 / 172 (223)	ca. 225 / 239 (149)		
Vanillin-IPHA (NIT)	25	Durez 29-607 PF novolac	203 / 230 (143)			
		Plenco 13360 PF novolac	200 / 232 (238)			
		Dynea 1204 PRF novolac	198 / 232 (209)			
TN / IPHA (NA - HA)	5.55 / 8.27	Durez 29-607 PF novolac	151 / 156 (179)			
		Plenco 13360 PF novolac	142 / 153 (363)			
		Dynea 1204 PRF novolac	78 / 105 (209)	163 / 193 (25)	ca. 225 / 242 (46)	302 / 346 (10)
ZT-55 / IPHA (OX - HA)	14.54 / 8.27	Durez 29-607 PF novolac	136 / 167 (138)	285 / 332 (34)		
		Plenco 13360 PF novolac	126 / 173 (139)	ca. 200 / 210 (67)	297 / 338 (66)	
		Dynea 1204 PRF novolac	77 / 104 (39)	161 / 211 (90)	286 / 304 (42)	
N-95 (OX)	25	Durez 29-607 PF novolac	164 / 197 (145)	297 / 329 (37)		
		Plenco 13360 PF novolac	152 / 184 (163)	293 / 325 (78)		
		Dynea 1204 PRF novolac	80 / 170 (267)	ca. 260 / 302 (75)		
TN (NA)	11.11	Durez 29-607 PF novolac	198 / 208 (254)			
		Plenco 13360 PF novolac	206 / 214 (421)			
		Dynea 1204 PRF novolac	83 / 107 (259)	156 / 211 (51)		
TN / ZT-55 (OX - NA)	5.55 / 14.54	Durez 29-607 PF novolac	172 / 191 (182)			
		Plenco 13360 PF novolac	181 / 191 (424)			
		Dynea 1204 PRF novolac	103 / 164 (212)	278 / 310 (32)		
PYRR-NMPD (ANA)	15 / 15	Durez 29-607 PF novolac	79 / 114 (122)	ca. 145 / 168 (276)		
		Plenco 13360 PF novolac	80 / 131 (128)	ca. 150 / 168 (454)		
		Dynea 1204 PRF novolac	107 / 174 (469)	ca. 230 / 304 (220)		
FUR-NMP (ANA)	25	Durez 29-607 PF novolac	208 / 251 (156)			
		Plenco 13360 PF novolac	186 / 255 (227)			
		Dynea 1204 PRF novolac	90 / 117 (100)	ca. 140 / 145 (87)	ca. 230 / 241 (85)	
B-methyl-B-nitrostyrene (NO)	25	Durez 29-607 PF novolac	245 / 268 (60)			
		Plenco 13360 PF novolac	241 / 276 (85)			
		Dynea 1204 PRF novolac	ca. 65 / 98 (305)			
NMP acetal (NAc)	25	Durez 29-607 PF novolac	123 / 163 (19)	181 / 196 (48)	266 / 290 (43)	
		Plenco 13360 PF novolac	241 / 293 (102)			
		Dynea 1204 PRF novolac	ca. 200 / 272 (658)			
Zoldine BBA (OX)	25	Durez 29-607 PF novolac	232 / 283 (46)			
		Plenco 13360 PF novolac	205 / 277 (189)			
		Dynea 1204 PRF novolac	72 / 112 (49)	295 / 315 (23)		
CS-1135 / IPHA (OX - HA)	15 / 8	Durez 29-607 PF novolac	134 / 155 (20)	191 / 223 (39)	279 / 345 (36)	
		Plenco 13360 PF novolac	83 / 108 (68)	139 / 158 (68)	281 / 331 (52)	
		Dynea 1204 PRF novolac	70 / 110 (163)	ca. 150 / 2121 (297)		
N-95 / IPHA (OX - HA)	15 / 8	Durez 29-607 PF novolac	137 / 159 (264)	290 / 329 (49)		
		Plenco 13360 PF novolac	142 / 168 (171)	293 / 339 (68)		
		Dynea 1204 PRF novolac	69 / 105 (157)	ca. 150 / 213 (265)	ca. 280 / 304 (59)	
Vanillin-IPHA nitrone / IPHA (NIT - HA)	15 / 5	Durez 29-607 PF novolac	167 / 191 (81)	ca. 200 / 232 (202)		
		Plenco 13360 PF novolac	171 / 190 (197)	ca. 215 / 232 (184)		
		Dynea 1204 PRF novolac	82 / 110 (288)	ca. 170 / 238 (305)		
CS-1246 / IPHA (OX - HA)	12.0 / 8.0	Durez 29-607 PF novolac	130 / 168 (301)	268 / 330 (63)		
		Plenco 13360 PF novolac	118 / 169 (308)	276 / 325 (87)		
		Dynea 1204 PRF novolac	64 / 109 (157)	ca. 160 / 213 (226)	ca. 280 / 319 (33)	
CS-1991 / IPHA (OX - HA)	12.0 / 8.0	Durez 29-607 PF novolac	128 / 167 (332)	266 / 329 (70)		
		Plenco 13360 PF novolac	82 / 162 (259)	260 / 333 (107)		
		Dynea 1204 PRF novolac	68 / 114 (114)	122 / 182 (334)	ca. 270 / 318 (43)	
ZT-55 / TN / (OX - NA)	10.0 / 5.0 /	Durez 29-607 PF novolac	ca. 130 / 156 (353)	ca. 265 / 310 (161)		
		Plenco 13360 PF novolac	129 / 157 (327)	ca. 255 / 305 (63)		
		Dynea 1204 PRF novolac	ca. 100 / 182 (293)			

TABLE 1-continued

LOW TEMPERATURE CURING PHENOLIC RESINS COMPARATIVE DSC DATA

B-methyl-B-Nitrostyrene/ TN (NO - NA)	10.0 / 10.0	Durez 29-607 PF novolac	210 / 217 (333)	ca. 145 / 154 (259)		
		Plenco 13360 PF novolac	203 / 213 (322)			
		Dynea 1204 PRF novolac	76 / 104 (219)			
B-methyl-B-Nitrostyrene/ TN / IPHA (NO - NA - HA)	10.0 / 5.0 / 5	Durez 29-607 PF novolac	63 / 78 (21)	147 / 175 (141)	ca. 200 / 229 (232)	
		Plenco 13360 PF novolac	137 / 160 (246)	ca. 205 / ca. 245 (196)		
		Dynea 1204 PRF novolac	73 / 110 (321)	ca. 168 / 222 (216)		
DEA-NMPD / TN (ANA - NA)	10.0 / 5.0	Durez 29-607 PF novolac	125 / 177 (146)	154 / 170 (5)	211 / 232 (3)	317 / 341 (5)
		Plenco 13360 PF novolac	92 / 103 (13)			
		Dynea 1204 PRF novolac	62 / 80 (21)	96 / 172 (417)		
DEA-NMPD / TN / IPHA (ANA - NA - HA)	10.0 / 5.0 / 5	Durez 29-607 PF novolac	73 / 90 (15)	114 / 127 (84)	ca. 205 / 222 (43)	
		Plenco 13360 PF novolac	75 / 93 (21)	102 / 120 (55)	ca. 175 / 216 (32)	
		Dynea 1204 PRF novolac	71 / 156 (445)	ca. 220 / 247 (148)		

Example 15

Comparative DSC Data Survey

[0042] In order to demonstrate the utility of this invention, a series of formulations were prepared by dissolving a commercially available PF novolac resin (Varcum 29-607 available from Durez Corp.) in ethanol along with the hardener/catalyst system to be evaluated. The solvent was then removed in a vacuum oven at ambient temperature. The resulting solid resin formulation was evaluated using a differential scanning calorimeter (DSC; TA Instruments Model Q100) to observe curing onset and peak temperatures and heats of curing for the curing events taking place. The DSC scans were run at $\Delta T=10°$ C./minute from 25° C. to 400° C. Hexamethylenetetramine (hexa) was used as a baseline since it is the hardener most commonly used in the industry. The results of these DSC analyses are shown in the below Table 2.

[0043] The DSC results using hexa as the hardener show two exothermic curing events of nearly equal heat emission (measured as joules per gram, J/g). The ANGUS hardeners CS-1135 oxazolidine and the new nitroaminoalcohols DEA/NMPD and PYRR/NMPD showed dramatic lowering in the peak temperatures of both of the curing events. Significant cost savings may be realized through the use of lower mold temperatures allowed by using the hardeners of the invention. The combination of ZT-55 oxazolidine with new nitroaminoalcohol PYRR/NMPD resulted in almost all of the curing event taking place at <200° C. Advantageously, this provides cost savings through the elimination or dramatic reduction in the need for thermal post-curing. Oxazolidines ZT-55, CS-1991, and CS-1246, nitroalcohol TN, vanillin-IPHA nitrone, and the formulation of TN with ZT-55 all showed essentially all of the curing taking place in the 180-230° C. range. A further advantage indicated in these results is improved resin pot life at intermediate temperatures to allow for blending, resin transfer to molds, etc., followed by rapid cure at higher mold tempertures.

[0044] Unexpectedly, the HAs of the invention have been shown to have a catalytic/accelerator effect on other methylene donors. Further, the function and utility of nitrone (NIT) intermediates as curing agents was unexpected. The ability of HAs to improve upon the performance of hexa is a truly novel and significant breakthrough.

[0045] The question of use levels is somewhat complicated. Hexa is used as a hardener at levels of from about 3% to as much as 15 or 20% based on resin weight. The use level depends upon the end use application, the cured resin properties desired in that application, and the processing conditions to be used.

[0046] Similarly, the ANGUS-based hardeners/methylene donors disclosed herein (OX, NA, NIT, ANA, NAm, NAc, PYRIM) can be used at different levels to achieve different processing behaviors and end use properties. As a guideline for use, we have assembled a table of "formaldehyde equivalents" for hexa and the various methylene donors we have disclosed. This table enables a user to determine how much of a chosen hardener is needed to provide the same equivalents of formaldehyde that would be provided by a given amount of hexa. In general, these new ANGUS-based hardeners would be expected to be used at from about 0.1 wt. % to as much as 75 wt. % based on resin weight.

[0047] It should be noted that the objective of this invention was not only to discover new hardeners and catalysts that can be cured at lower temperatures than hexa-based formulation. In a broader sense, the objective was to discover new hardeners and catalysts that would lead to broader control over the processing of phenolic resins. Low temperature cure and/or a reduction in post cure baking time are certainly of value in terms of energy savings and increase in throughput. But an increase in pot life stability of a resin system can also provide significant benefits to an end user. Examples include injection molding, filament winding, and pultrusion applications in which the resin is often a melt rather than a solution. In these applications the ability to provide a resin formulation that will not advance while in the melt but will rapidly cure at an elevated cure temperature will result in more consistent parts, less resin waste, and less machine down-time to clean out advanced resin.

[0048] Finally, the hardeners and catalysts discovered in this invention can be used in any of the applications in which phenolic resins are used, including, molding compounds, foundry materials, abrasives, friction materials, insulation, adhesives, coatings, prepregs, electronics, laminates, filament winding, pultrusion, composites, and fire resistant and flame-retardant end uses.

TABLE 2

RESIN SYSTEM					CURING EVENTS			
					PEAK TEMP, C. /	PEAK TEMP, C. /	PEAK TEMP, C. /	PEAK TEMP, C. /
SUPPLIER	PRODUCT NUMBER	TYPE	HARDENER	WT. %	TOTAL HEAT, J/g	TOTAL HEAT, J/g	TOTAL HEAT, J/g	TOTAL HEAT, J/g
Durez	29-607	PF novolac	ZT-55 / IPHA	14.54 / 8.27	167 / 138			332 / 34
			DEA/NMPD	25	97 / 99	205 / 124		
			PYRR/NMPD	25	112 / ca 80 159 / ca 80	ca 181 / ca 150	ca 251 / ca 45	(tr @ 322)
			N-95	25		197 / 145		329 / 37
			B-methyl-B-nitrostyrene	25			268 / ca 40	ca 330 / ca 20
			NMP acetal	25	163 / 19	196 / 48	290 / 34	327 / 9
			Vanillin / IPHA nitrone	25	103 / 11 139 / 15	230 / 143		325 / 16
			PYRR/NMPD / ZT-55	15 / 15	114 / 122 168 / 122	192 / 108		321 / 2

Example 15

Extensive Hardener/Catalyst Survey with Durez PF Novolac 29-607

[0049] A broader variety of hardeners/catalysts were evaluated alone and in combination. The results obtained in the comparative survey remain valid as shown in Table 3.

TABLE 3

LOW TEMPERATURE CURING PHENOLIC RESINS Durez PF Novolac 29-607

SUMMARY OF DSC DATA

TA Instruments Model Q 100 DSC
Run Conditions: 10 C. / minute from 25 C. to 400 C. with N2 at 50 cc / min.

CLASS:

Am = amine	NA = nitroalcohol	NIT = nitrone
OX = oxazolidine	NAm = nitroamine	Im = imine
HA = hydroxylamine	NO = nitroolefin	PYRIM = hexahydro-pyrimidine
ANA = aminonitroalcohol	NAc = nitroacetal	

RESIN SYSTEM			CURING EVENTS				
HARDENER	WT. %	CLASS	ONSET / PEAK C. (HEAT, J/g)	ONSET / PEAK C. (HEAT, J/g)	ONSET / PEAK C. (HEAT, J/g)	ONSET / PEAK C. (HEAT, J/g)	GEL TIMES SEC (MIN) 160 C.
HEXA	5.39	Am-base-line	140 / 153 (69)	218 / 227 (3)	244 / 255 (72)		154
ZT	29.08	OX	151 / 193 (137)	286 / 316 (44)			
CS-1246	14.13	OX	142 / 183 (161)	309 / 341 (30)			133
CS-1135	22.29	OX	65 / 98 (36)	128 / 175 (68)	304 / 351 (19)		56
CS-1991	15	OX	100 / 118 (9)	134 / 183 (129)	295 / 336 (41)		78
Zoldine BBA	25	OX	232 / 283 (46)				
N-95	25	OX	164 / 197 (145)	297 / 329 (37)			
TN	11.11	NA	198 / 208 (254)				
IPHA	16.55	HA	147 / 159 (39)	235 / 267 (65)			
DEA-NMPD	25	ANA	97 / 113 (99)	139 / 205 (124)			
	15	ANA	88 / 108 (37)	ca. 128 / 179 (62)	ca. 205 / 222 (111)		
DMA-NMPD	25	ANA	111 / 211 (292)				39
	15	ANA	107 / 194 (265)				
FUR-NMP	25	ANA	208 / 251 (156)				
PYRR-NMPD	25	ANA	100 / 112 (80)	127 / 159 (80)	161 / 181 (150)	234 / 251 (134)	121
NMPD-bis-DEA	15	NAm	85 / 108 (76)	ca. 160 / 185 (6)	ca. 190 / 239 (137)		
B-methyl-B-Nitro-styrene	25	NO	245 / 268 (60)				
NMP acetal	25	NAc	123 / 163 (19)	181 / 196 (48)	266 / 290 (43)		
Vanillin	25	NIT	203 / 230 (143)				(>60)
IPHA nitrone	15	NIT	193 / 233 (209)	321 / 342 (12)			
CHDA-bis-IPHA nitrone	15	NIT	181 / 215 (276)				(41.75)

TABLE 3-continued

LOW TEMPERATURE CURING PHENOLIC RESINS Durez PF Novolac 29-607

HCHO-IPHA nitrone	15	NIT	87 / 104 (9)	ca. 150 / 173 (76)	ca. 230 / 252 (50)	ca. 300 / 342 (43)	
HCHO-PHA nitrone	15	NIT	80 / 126 (21)	ca. 140 / 162 (31)	180 / 224 (260)		
HCHO-tBuHA nitrone	15	NIT	ca. 90 / ca. 125 (ca. 10)	146 / 172 (62)	ca. 195 / 248 (151)		
HCHO-EHA nitrone	15	NIT	102 / 159 (57)	174 / 229 (238)			
HCHO-HA nitrone	15	NIT	ca. 100 / 107 (100)	ca. 115 / 164 (85)	ca. 160 / 223 (304)		(>30)
HCHO-N-BzHA nitrone	15	NIT	82 / 116 (27)	ca. 140 / 154 (24)	179 / 231 (124)		209
CHDA-A	15	Im	88 / 107 (7)	ca. 145 / 213 (144)			(31.25)
Hexa / IPHA	6.0 / 6.0	Am - HA	128 / 178 (164)	ca. 185 / 217 (262)			
Hexa / IPHA	8.6 / 5.0	Am - HA	147 / 158 (56)	198 / 228 (106)			94
Hexa / IPHA	8.6 / 2.5	Am - HA	148 / 164 (33)	215 / 230 (78)			97
Hexa / IPHA	8.6 / 1.0	Am - HA	146 / 166 (17)	196 / 220 (54)			97
Hexa / PHA	6.0 / 6.0	Am - HA	93 / 112 (12)	126 / 151 (27)	149 / 208 (194)		
Hexa / PHA	8.6 / 5.0	Am - HA	153 / 164 (7)	202 / 209 (10)	ca. 215 / 230 (113)		143
Hexa / PHA	8.6 / 1.0	Am - HA	154 / 166 (13)	199 / 208 (17)	ca. 250 / 255 (108)		152
Hexa / PHA	8.6 / 0.5	Am - HA	151 / 167 (15)	227 / 263 (68)			140
Hexa / PHA	8.6 / 0.1	Am - HA	151 / 165 (15)	224 / 283 (77)			145
Hexa / DEHA	8.6 / 5.0	Am - HA	151 / 162 (17)	192 / 215 (29)			113
Hexa / DEHA	8.6 / 1.0	Am - HA	152 / 165 (16)	223 / 252 (17)			143
Hexa / N-Cy-hex HA	8.6 / 2.5	Am - HA	92 / 116 (24)	ca. 145 / 162 (38)	ca. 180 / 235 (82)		
Hexa / NMPD bis-DEA	8.6 / 2.0	Am - NAm	89 / 165 (48)	ca. 205 / 218 (28)			145
CS-1135 /	15.0 / 8.0	OX - HA	134 / 155 (20)	191 / 223 (39)	279 / 345 (38)		
IPHA	10.0 / 5.0	OX - HA	71 / 107 (61)	ca. 128 / 152 (50)	ca. 160 / 182 (39)	ca. 330 / 357 (29)	83
CS-1246 / IPHA	12.0 / 8.0	OX - HA	130 / 168 (301)	268 / 330 (63)			
CS-1246 / IPHA	12.0 / 1.0	OX - HA	139 / 172 (133)	313 / 343 (25)			133

TABLE 3-continued

LOW TEMPERATURE CURING PHENOLIC RESINS Durez PF Novolac 29-607						
CS-1246 / DEHA	12.0 / 1.0	OX - HA	145 / 173 (104)	289 / 342 (42)		105
CS-1991 / IPHA	12.0 / 8.0	OX - HA	128 / 167 (332)	266 / 329 (70)		
N-95 / IPHA	15.0 / 8.0	OX - HA	137 / 169 (264)	290 / 329 (49)		
ZT / IPHA	14.54 / 8.27	OX - HA	136 / 167 (138)	285 / 332 (34)		
CS-1135 / DMTA	10.0 / 5.0	OX - Am	93 / 142 (87)	226 / 289 (146)		
TN / IPHA	5.55 / 8.27	NA - HA	151 / 156 (179)			
TN / IPHA	14.4 / 2.0	NA - HA	189 / 203 (234)			303
TN / IPHA	12.8 / 5.0	NA - HA	151 / 156 (88)	ca. 175 / ca. 180 (85)		170
TN / IPHA	12.8 / 1.0	NA - HA	192 / 204 (283)			483
TN / IPHA	12.8 / 0.5	NA - HA	198 / 209 (299)			(>7)
TN / IPHA	12.8 / 0.1	NA - HA	207 / 216 (243)			(>7)
TN / PHA	5.0 / 5.0	NA - HA	145 / 167 (237)			
TN / PHA	12.8 / 5.0	NA - HA	149 / 179 (323)			(>7)
TN / PHA	12.8 / 1.0	NA - HA	188 / 206 (299)			(7.00)
TN / PHA	12.8 / 0.5	NA - HA	196 / 206 (522)			(>8)
TN / PHA	12.8 / 0.1	NA - HA	205 / 215 (244)			(14.25)
TN / DEHA	12.8 / 2.0	NA - HA	163 / 185 (222)			198
TN / N-Cy-hex HA	12.8 / 5.0	NA - HA	151 / 172 (293)			193
TN / ZT	5.55 / 14.54	NA - OX	172 / 191 (182)			
TN / DMTA	10.0 / 5.0	NA - Am	105 / 119 (15)	125 / 144 (178)	ca. 245 / 283 (74)	
NMP / DEA	8.0 / 7.0	NA - Am	197 / 243 (184)			
TN /	14.4 / 10.0	NA - Im	148 / 183 (241)			110
CHDA-A	14.4 / 5.0	NA - Im	103 / 196 (321)			105
	10.0 / 5.0	NA - Im	91 / 114 (14)	c34 / 168 (314)		
TN / NMPD-	12.8 / 2.0	NA - NAm	157 / 184 (190)			85
bis-DEA	12.8 / 1.0	NA - NAm	158 / 164 (311)			110
	5.0 / 10.0	NA - NAm	81 / 105 (83)	ca. 145 / 174 (111)	ca. 220 / 243 (115)	42
TN / B-methyl-B-Nitro-styrene	10.0 / 10.0	NA - NO	210 / 217 (333)			
Vanillin-IPHA nitrone / TN	15.0 / 5.0	NIT - NA	167 / 191 (81)	ca. 200 / 232 (202)		

TABLE 3-continued

LOW TEMPERATURE CURING PHENOLIC RESINS Durez PF Novolac 29-607						
CHDA-bis-IPHA nitrone TN	10.0 / 14.4	NIT - NA	172 / 183 (232)			260
CHDA-bis-IPHA nitrone DEA-NMPD	10.0 / 5.0	NIT - ANA	181 / 216 (114)			
DEA-NMPD / TN	10.0 / 5.0	ANA - NA	125 / 177 (146)			66
DMA-NMPD / TN	10.0 / 5.0	ANA - NA	112 / 125 (52)	ca. 140 / 193 (233)		
DMA-NMPD / TN	2.0 / 14.4	ANA - NA	169 / 191 (157)			238
DEA-NMPD / IPHA	10.0 / 5.0	ANA - HA	86 / 110 (48)	ca. 125 / 138 (46)	ca. 175 / 237 (125)	
DEA-NMPD / PHA	10.0 / 5.0	ANA - HA	95 / 111 (22)	119 / 139 (53)	ca. 170 / 217 (139)	
PYRR-NMPD / ZT	15.00 / 15.00	ANA - OX	79 / 114 (122)	ca. 145 / 168 (276)		91
DEA-NMPD / CS-1135 / IPHA	10.0 / 10.0 / 5	ANA-OX-HA	ca. 105 / 119 (43)	ca. 130 / 138 (33)	ca. 175 / 204 (117)	ca. 240
DEA-NMPD / TN / IPHA	10.0 / 10.0 / 5	ANA-NA-HA	73 / 90 (15)	114 / 127 (84)	ca. 205 / 222 (43)	150
DMA-NMPD / TN / IPHA	10.0 / 5.0 / 5	ANA-NA-HA	ca. 100 / 108 (17)	123 / 127 (53)	ca. 160 / 165 (105)	
	9.0 / 10.0 / 1	ANA-NA-HA	91 / 106 (14)	122 / 158 (84)		43
	2.0 / 14.4 / 1	ANA-NA-HA	171 / 192 (243)			115
TN / IPHA / DMA-NMPD	2.0 / 12.8/ 1	ANA-NA-HA	181 / 201 (181)			130
ZT / TN / IPHA	10.0 / 5.0 / 5	OX-NA-HA	ca. 130 / 156 (353)			121
	5.0 / 12.8 / 2	OX-NA-HA	165 / 187 (187)			195
CS-1246 / TN IPHA	7.0 / 7.0 / 1	OX-NA-HA	153 / 177 (149)			148
B-methyl-B-nitro-styrene/ TN / IPHA	10.0 / 5.0 / 5	NO-NA-HA	63 / 78 (21)	147 / 175 (141)	ca. 200 / 229 (232)	291
PYRIM / IPHA	17.5 / 2.0	PYRIM - HA	118 . 130 (50)	ca. 145 / 158 (184)		58
PYRIM / TN / IPHA	4.6 / 12.8 / 2	PYRIM-NA-HA	106 / 122 (16)	133 / 147 (217)		78
	2.0 / 12.8 / 1	PYRIM-NA-HA	167 / 184 (234)			97

[0050] In addition, the following observations can be made:

[0051] Oxazolidines (OX)

[0052] The ability of an oxazolidine to act as a methylene donor is a function of its structure.

[0053] Oxazolidines derived from aldehydes other than formaldehyde show low activity (Zoldine BBA).

[0054] Bis-oxazolidines such as ZT and CS-1991 are poorer methylene donors than mono-oxazolidines such as CS-1135. They have a greater affinity for formaldehyde. It is expected that mono-oxazolidines in which the N—H was replaced by N—R would also be poorer methylene donors.

[0055] While N-95 has a higher formaldehyde equivalent weight than ZT, it has comparable reactivity. The additional formaldehyde content is not in a more active form.

[0056] CS-1135 and CS-1991 are more effective methylene donors than hexa by DSC, and CS-1135, CS-1991, and CS-1246 showed shorter gel times than a hexa formulation containing the same formaldehyde equivalent.

[0057] The combination of an oxazolidine (ZT) with a nitroalcohol (TN) did not improve performance. No synergy was realized.

[0058] The combination of oxazolidines with hydroxylamines (HA) seemed to result in a lowering in the temperature of the second curing event seen by DSC, but had little positive effect on the initial curing events. This behavior was corroborated by the lack of improvement in gel times. Both N-alkyl and N,N-dialkyl HAs showed similar performance.

[0059] The 3° amine DMTA showed DSC performance similar to HAs.

[0060] The combination of ANAs with OX improved both DSC performance and gel time, but used in combination with HAs were similar to HAs alone.

[0061] The combination of OXs with NAs and HAs showed improved DSC and gel time performance when OX was the predominant methylene donor.

[0062] Aminonitroalcohols (ANA)

[0063] The ANAs DEA-NMPD AND PYRR-NMPD had lower DSC cure onset and peak temperatures and shorter gel times than the hexa baseline formulation.

[0064] The combination of the ANA DEA-NMPD with the nitroalcohol (NA) TN had lower DSC cure onset and peak temperatures and shorter gel time than the hexa baseline formulation. Poorer results were obtained with DMA-NMPD.

[0065] The DSC performance of ANAs in the presence of HAs was better than with ANAs alone.

[0066] Formulations containing ANAs, NAs, and HAs had better DSC and gel time performance than ANA-NA or ANA-HA formulations.

[0067] Overall, ANAs appear to act as both catalysts by virtue of their Mannich base 3° amine group and as methylene donors through both their nitroalcohol group and their Mannich base group.

[0068] Nitroalcohols (NA)

[0069] NAs alone are weak methylene donors in PF novolac resin formulations.

[0070] The combination of NAs with HAs did show improved DSC and gel time performance although these formulations did not perform better than the hexa baseline formulation.

[0071] The combination of NAs with amines (Am) showed improved DSC performance with DMTA but not with DEA. It can be surmised that stronger base strength gives better performance.

[0072] The imine (Im) CHDA-A in combination with the NA TN gave better DSC performance and shorter gel times than the hexa baseline formulation.

[0073] Combinations of nitroamines (NAm) with NA gave DSC and gel time results that were similar to those obtained with ANAs and NAs. Performance was better than with the hexa baseline formulation.

[0074] Nitroamines (NAm)

[0075] The low DSC curing onset and peak temperatures observed with NMPD-bis-DEA confirmed the hypothesis that the Mannich base groups of both the ANAs and NAms act as both catalysts and as methylene donors. Performance was better than hexa baseline.

[0076] NMPD-bis-DEA is effective in generating low DSC cure temperatures and short gel times even at catalytic concentrations (1-2%).

[0077] Hexahydropyrimidines (PYRIM)>

[0078] PYRIM are effective methylene donors.

[0079] Formulations of PYRIM with HAs gave better DSC and gel time performance than the hexa baseline formulation.

[0080] Formulations of PYRIM with HAs and NAs gave better DSC and gel time performance than the hexa baseline formulation.

[0081] Nitrones (NIT)

[0082] NIT derived from IPHA and CHDA or vanillin are methylene donors and are about as effective as NAs.

[0083] The performances of the IPHA nitrones of CHDA or vanillin are not improved by formulation with NAs or ANAs.

[0084] The formaldehyde nitrones of EHA, PHA, IPHA and tBuHA all gave better DSC performances than the hexa baseline formulation.

[0085] The DSC performances of the formaldehyde-IPHA and the formaldehyde-PHA nitrones were comparable to those of the TN-IPHA and TN-PHA formulation. This strongly supports the intermediacy of nitrones in NA-HA formulations.

[0086] Nitroolefins (NO)

[0087] NOs are incorporated at high reaction temperatures.

[0088] Formulation of NA with NO gives DSC performance comparable to the NA alone. No synergy was observed.

[0089] Formulations of NO with both NA and HA gave DSC and gel time results that were comparable to NA-HA formulations. No synergy was observed.

[0090] Nitroacetals (NAc)

[0091] The DSC performance of NAcs were comparable to those of NAs.

[0092] Hydroxylamines (HA)

[0093] The performance of this class of compounds is discussed in combination with the other classes. HA alone was not effective in curing PF novolac.

[0094] Imines (Im)

[0095] CHDA-A alone was comparable in performance to TN.

[0096] CHDA-A was effective in improving the DSC and gel time performance of NA formulations. Performance was better than hexa baseline.

[0097] Hexa-Based Formulations (Am)

[0098] HAs were found to be effective methylene transfer agents even in hexa formulations. This is a completely novel and unexpected result, but it does fit the performance of HAs seen above.

[0099] IPHA in particular appears to perform catalytically with hexa. Formulations containing a fixed level of hexa with 5.0, 2.5, and 1.0% of IPHA all gave the same gel time.

[0100] PHA, DEHA, and N-CyhexHA were less effective than IPHA, but were still improved over the baseline hexa formulation.

[0101] Formulations of NAm with hexa were only marginally improved over the baseline hexa formulation.

Example 16

Hardener/Catalyst Study with PF Resole

[0102] PF resole resins are made with an excess of formaldehyde. Hence, they do not require a methylene donor to effect curing. Typically, they are cured by heat alone, or with heat and an acid catalyst.

[0103] The data shown above indicated that HAs were effective methylene transfer agents. Since resole resins are formaldehyde rich, it begged the question to determine whether HAs could effectively cure resole resins via similar methylene group transfer.

[0104] In order to evaluate the effects of the HAs alone, a resole resin was synthesized free of residual acid or base.

[0105] The results of this preliminary study (Table 4) showed the following:

[0106] IPHA increased the gel time of the resole resin. Gel time increased with increasing IPHA concentration.

[0107] OX increased the gel times of the resole resin. The less reactive ZT gave longer gel time than the more reactive CS-1135. This is probably a function of base strength.

[0108] TN gave a gel time intermediate between ZT and CS-135. The addition of IPHA to TN actually increased gel time further.

[0109] Resole resin catalyzed with oxalic acid had a shorter gel time than the uncatalyzed resin.

[0110] The gel times for oxalic acid—IPHA formulations increased in gel time, with longer gel time at higher IPHA concentration.

[0111] However, this increased gel time behavior, although unexpected, may actually be of great benefit: it may be a means of effectively improving the working pot life of resole resin formulations without impairing their performance.

TABLE 4

LOW TEMPERATURE CURING PHENOLIC RESINS PF RESOLE STUDIES - correlation of DSC data with Gel Time data

RESOLE: RS200204378-71

>>TA Instruments Model Q 100 DSC
Run Conditions: 10 C. / minute from 25 C. to 400 C. with 50 cc / min. N2
>>Gel Times determined using the hot plate method

>>CLASS:

Am = amine	NA = nitroalcohol	NIT = nitrone
OX = oxazolidine	NAm = nitroamine	Im = imine
HA = hydroxylamine	NO = nitroolefin	PYRIM = hexahydropyrimidine
ANA = aminonitroalcohol	NAc = nitroacetal	

			DSC CURING EVENTS				
HARDENER	WT. %	CLASS	ONSET / PEAK TEMP, C. / (HEAT, J/g)	ONSET / PEAK TEMP, C. / (HEAT, J/g)	ONSET / PEAK TEMP, C. / (HEAT, J/g)	ONSET / PEAK TEMP, C. / (HEAT, J/g)	GEL TIMES SEC (MIN) 160 C.
None	None	(none)	147 / 177 (195)	ca. 200 / 235 (281)			63
IPHA	1	HA	ca. 150 / 191 (224)	ca. 215 / 228 (220)			77
	5	HA	157 / 180 (155)	ca. 205 / 237 (103)			92
	10	HA	164 / 182 (192)	ca. 215 / 236 (94)	ca. 325 / 331 (18)		108

TABLE 4-continued

LOW TEMPERATURE CURING PHENOLIC RESINS PF RESOLE STUDIES - correlation of DSC data with Gel Time data

ZT	10	OX	165 / 191 (289)	ca. 220 / 238 (168)			127
CS-1135	10	OX	117 / 134 (11)	155 / 173 (111)	ca. 205 / 236 (174)	ca. 310 / 319 (34)	85
TN	5	NA	ca. 150 / 185 (160)	ca. 218 / 244 (233)			108
TN / IPHA	5.0 / 1.0	NA - HA	154 / 192 (192)	ca. 225 / 240 (170)			119
Oxalic acid	1	Acid					48
Oxalic acid /	1.0 / 1.0	Acid / HA					53
IPHA	1.0 / 10.0	Acid / HA					143

[0112]

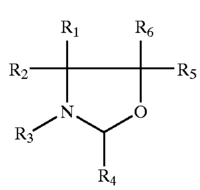
					MOLES HCHO AVAILABLE	
HARDENER	CHEMICAL FAMILY	PHYSICAL FORMS	ACTIVES % W/W	MOLECULAR WEIGHT	Per gram*	Per pound*
Hexamethylenetetra mine	Amine	Solid	100	140.19	0.0428	19.41
Formalin	Aldehyde	Liquid	37 (Aq)	30.03	0.0123	5.59
TN	Nitroalcohol	Solid	100	151.11	0.0199	9.01
NMPD	"	"	"	135.11	0.0148	6.73
NMP	"	"	"	119.12	0.0084	3.81
ZT-100	Oxazolidine	"	"	145.15	0.0138	6.26
ZT-55	"	Liquid	55 (Aq)	145.15	0.0076	3.44
CS-1246	"	"	100	143.18	0.0140	6.35
CS-1991	"	"	"	129.15	0.0155	7.04
CS-1135	"	"	78 (Aq)	101.14	0.0077	4.49
DMA - NMPD	Aminonitroal cohol	Solid	100	162.18	0.0123	5.60
DEA - NMPD	"	Liquid	"	190.24	0.0105	4.76
PYRR - NMPD	"	"	"	188.22	0.0106	4.82
NMPD-bis-DEA	Nitroamine	"	"	245.36	0.0082	3.70
HCHO - EHA	Nitrone	"	34 (MeOH)	73.09	0.0047	2.11
HCHO - PHA	"	"	31 (MeOH)	87.12	0.0036	1.61
HCHO - IPHA	"	"	31 (MeOH)	87.12	0.0036	1.61
HCHO - tBuHA	"	"	30 (MeOH)	101.14	0.0030	1.35
Vanillin - IPHA nitrone	"	Solid	100	209.24	0.0048	2.17
CHDA- bis-IPHA nitrone	"	"	"	254.37	0.0079	3.57
CHDA-A	Imine	"	"	138.21	0.0145	6.58

*Product as supplied

[0113]

PHENOLIC RESIN HARDENERS

Oxazolidines:



$R_1, R_2, R_3, R_4, R_5, R_6$ = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

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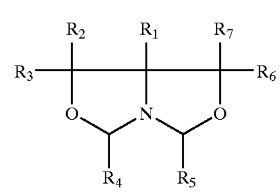

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$ = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

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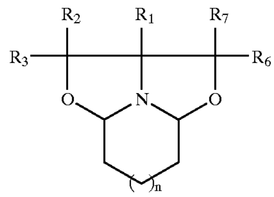
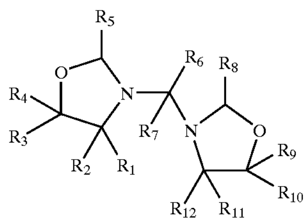
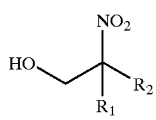


n = integer from 1 to 6
R_1, R_2, R_3, R_4, R_5 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

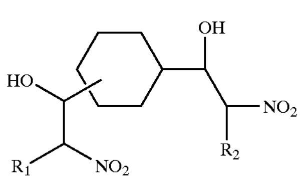


R_1 to R_{12} = same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalklene

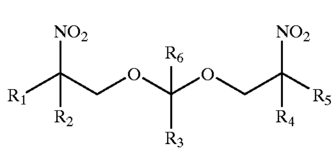
Nitroalcohols, Nitroacetals:



R_1, R_2 = may be the same or different, selected from H, C_1–C_{12} linear or branced alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



1,2-, 1,3-, and 1,4-isomers
R_1, R_2, = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



R_1 to R_6 = may be the same or different, selected from H, C_1–C_{12}linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

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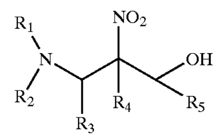
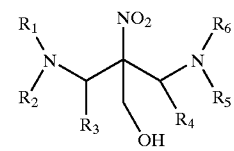
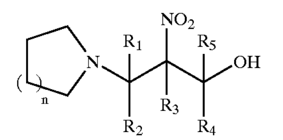
Aminonitroalcohols:



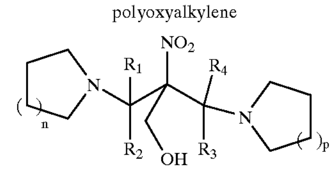
R_1, R_2, R_3, R_4, R_5 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



R_1, R_2, R_3, R_4, R_5 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

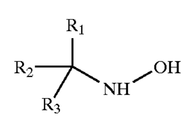


n = integer from 1 to 6
R_1 to R_5 = same or different, selected from H, C_1–C_{12} linear or branched alkyl oralkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

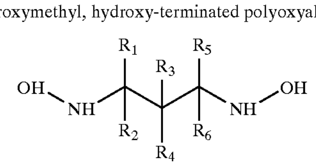


n, p = same or different = integer from 1 to 6
R_1 to R_4 = same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl,heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

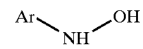
Nitro-olefins, Hydroxylamines:



R_1, R_2, R_3 = may be the same or different, selected from H, C_1–C_{12} linear, cyclic or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



R_1 to R_6 = may be the same or different, selected from H, C_1–C_{12} linear or branched or cyclic alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



Ar = phenyl or substituted aryl

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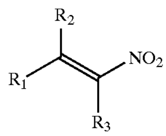
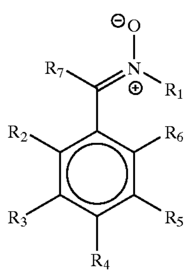
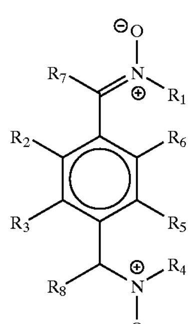


R_1, R_2, R_3 = may be the same or different, selected from H, C_1–C_{12} linear, cyclic or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

Nitrones:



R_1 = selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic
R_2 to R_7 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy, C_1–C_{12} linear or branched alkyl or alkenyl oxy, phenoxy, substituted aryloxy, Cl, Br, F, trifluoromethyl, thio, C_1–C_{12} linear or branched alkyl or alkenyl thio, C_1–C_{12} linear or branched dialkylamino, diarylamino



1,2-, 1,3-, and 1,4-isomers
R_1, R_4 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic
R_2 to R_8 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy, C_1–C_{12} linear or branched alkyl or alkenyl oxy, phenoxy, substituted aryloxy, Cl, Br, F, trifluoromethyl, thio, C_1–C_{12} linear or branched alkyl or alkenyl thio, C_1–C_{12} linear or branched dialkylamino, diarylamino

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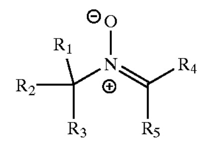
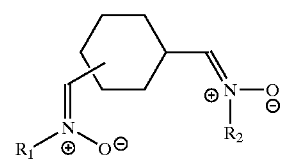
Nitrones:

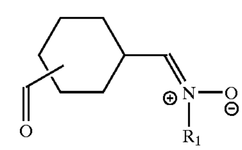


R_1 to R_5 = may be the same or different, selected from H, C_1–C_{12}linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic

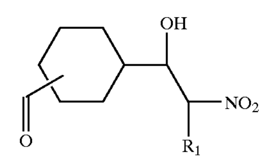


1,2-, 1,3-, and 1,4-isomers
R_1, R_2 = may be the same or different, selected from H, C_1–C_{12} alkyl or alkenyl, phenyl, substituted aryl, heterocyclic

Various Functionalities:

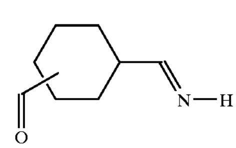


1,2-, 1,3-, and 1,4-isomers
R_1 = H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic

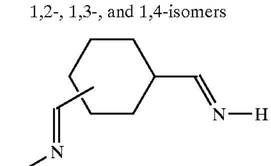


1,2-, 1,3-, and 1,4-isomers
R_1 = H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl

Various Functionalities:



1,2-, 1,3-, and 1,4-isomers



1,2-, 1,3-, and 1,4-isomers

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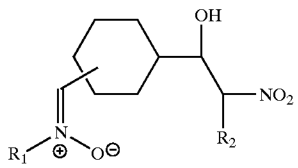
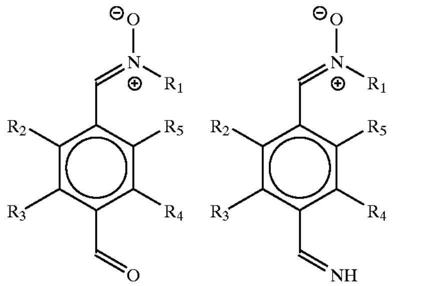
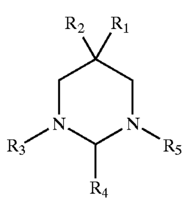


1,2-, 1,3-, and 1,4-isomers
R_1 = H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic
R_2 = H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl



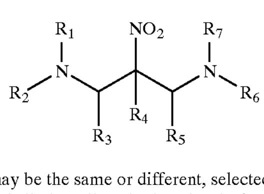
1,2-, 1,3-, and 1,4-isomers
R_1 = H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic
R_2, R_3, R_4, R_5 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxyl, linear or branched alkyl or alkenyl oxy, phenoxy, substituted arloxy, Cl, Br, F, trifluoromethyl, thio, linear or branched alkyl or alkenyl thio, C_1–C_{12} linear or branched dialkylamino, diarylamino

Hexahydropyrimidines (PYRIM):



R_1 = may be NO_2, H, c_1–C_{12} linear or branched alkyl or alkenyl phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy, c_1–C_{12} linear or branched alkyl or alkenyl oxy, phenoxy, substituted aryloxy, hydroxy-terminated polyoxyalkylene
R_2 to R_5 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

Nitroamines (NAm):



R_1 to R_7 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

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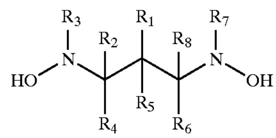
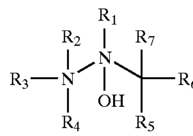
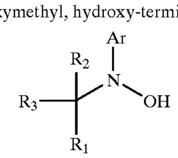
Hydroxylamines (HA):



R_1 to R_8 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



R_1 to R_7 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene



Ar = phenyl or substituted aryl
R_1 to R_3 = may be the same or different, selected from H, C_1–C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene

What is claimed is:

1. A cured phenolic resin comprising:

a. a phenolic compound;

b. an aldehyde; and

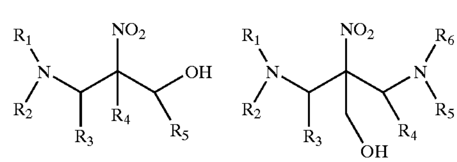
c. a curing agent selected from the group consisting of oxazolidines, nitroamines, aminonitroalcohols, imines, hexahydropyrimidines, nitroalcohols, nitrones, hydroxylamines, nitro-olefins and nitroacetals.

2. The cured phenolic resin of claim 1, wherein the phenolic compound is selected from the group consisting of phenol, resorcinol, bisphenol, phloroglucinol, cresols, alkyl phenols, phenol ethers, tannins and lignins

3. The cured phenolic resin of claim 1, wherein the aldehyde is selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, cyclohexanedicarboxaldehydes, benzaldehydes, furfural, an aryl aldehyde and a heterocyclic aldehyde.

4. A phenolic resin curing agent selected from the group consisting of oxazolidines, nitroalcohols, nitroamines, aminonitroalcohols, imines, hexahydropyrimidines, nitrones, hydroxylamines, nitro-olefins, nitroacetals and combinations thereof.

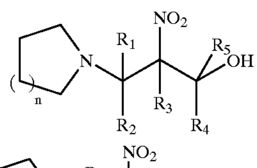
5. A curing agent composition comprising a nitroaminoalcohol having the following structures:

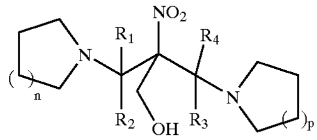


wherein R_1 to R_6 may be the same or different, selected from H, C_1—C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene.

6. The curing agent composition of claim 5 wherein the nitroaminoalcohol is selected from the group consisting of DEA/NMPD and DMA/NMPD.

7. A curing agent composition comprising a nitroaminoalcohol having the following structures:

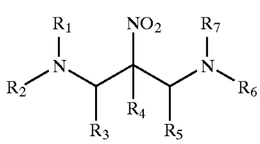




Wherein n and p are integers from 1 to 6, and R_1 to R_5 are the same or different, selected from H, C_1—C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene.

8. The curing agent composition of claim 7. Wherein the nitroaminoalcohol comprises PYRR/NMPD.

9. A curing agent composition comprising a nitroamine having the following structure:



Wherein R_1 to R_7 are the same or different, selected from H, C_1—C_{12} linear or branched alkyl or alkenyl, phenyl, substituted aryl, heterocyclic, hydroxymethyl, hydroxy-terminated polyoxyalkylene.

10. The curing agent composition of claim 7. Wherein the nitroamine is selected from the group consisting of NMPD-bis-DMA and NMPD-bis-DEA.

11. The phenolic resin curing agent of claim 4, wherein the curing agent comprises an oxazolidine selected from the group consisting of ZT-55, CS-1135, CS-1991 and CS-1246.

12. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of CS-1135 oxazolidine and DMA/NMPD.

13. The phenolic resin curing agent of claim 4, wherein the curing agent comprises the nitroalcohol, TN.

14. The phenolic resin curing agent of claim 4, wherein the curing agent comprises vanillin-IPHA nitrone.

15. The phenolic resin curing agent of claim 11, wherein the oxazolidine is combined with a nitroaminoalcohol selected from the group consisting of DEA/NMPD, DMA/NMPD and PYRR/NMPD.

16. The phenolic resin curing agent of claim 13, wherein the nitroalcohol is combined with DEA/NMPD.

17. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of a nitroaminoalcohol and a hydroxylamine.

18. The phenolic resin curing agent of claim 17, wherein the curing agent comprises a combination of a nitroalcohol, a nitroaminoalcohol and a hydroxylamine.

19. The phenolic resin curing agent of claim 13, wherein the nitroalcohol is combined with CHDA-A.

20. The phenolic resin curing agent of claim 13, wherein the nitroalcohol is combined with a nitroamine.

21. The phenolic resin curing agent of claim 4, wherein the curing agent comprises NMPD-bis-DEA.

22. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a hexahydropyrimidine.

23. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of a hydroxylamine and a hexahydropyrimidine.

24. The phenolic resin curing agent of claim 17, wherein the curing agent comprises a combination of a nitroalcohol, a hexahydropyrimidine and a hydroxylamine.

25. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a hydroxylamine-form aldehyde nitrone selected from the group consisting of N-CyhexHA, N-BzHA, EHA, PHA, IPHA and tBuHA.

26. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of a nitroalcohol, an oxazolidine, and a hydroxylamine.

27. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of a nitroaminoalcohol and a hydroxylamine.

28. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of hexamethylenetetramine and a hydroxylamine.

29. The phenolic resin curing agent of claim 4, wherein the curing agent comprises a combination of hexamethylenetetramine and a nitroamine.

* * * * *