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(54) Title: WATER BASED LIGNIN EPOXY RESINS, METHODS OF USING AND MAKING THE SAME

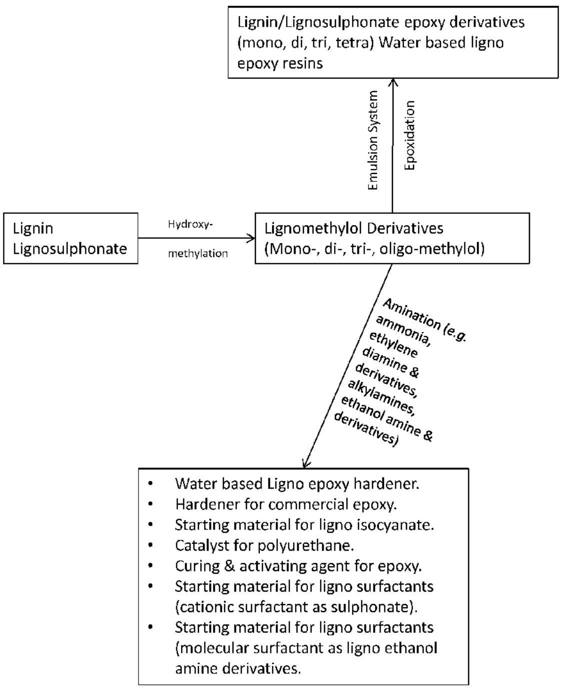

Figure 1

(57) Abstract: Water based lignoepoxy resins, and methods for their preparation and use are provided. Methods of making lignoepoxy resins without the use of volatile organic compounds are also provided.

WO 2014/021887 A1

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WATER BASED LIGNIN EPOXY RESINS, METHODS OF USING AND MAKING THE SAME

FIELD

[0001] Water based lignin epoxy resins, water based ligno amine hardeners and lignin based catalysts and activators, methods of making, and uses thereof are provided.

BACKGROUND

[0002] Epoxy resins are one of the important classes of polymeric resins used in various fields of applications such as electrical industries, adhesives, coating, as well as composite material with various reinforcing materials such as carbon fibres, Aramide, Kevlar, polyesters and fibre glass and as concrete polymer additives.

[0003] Most of the epoxy resins are from petrochemical resources, the non-renewable resources with growing costs. The epoxy resin industry generates considerable pollution since more than 60% of the epoxy resins consumed require organic solvents and diluents such as xylenes, toluene, petroleum ethers, oils and volatile organic compounds (VOC).

[0004] Several types of additives and activators are used with epoxy resins such as phenols and tertiary amines as curing activators. The polluting nature of phenols and tertiary amines is well established due to their extremely high reactivity and volatility. Accordingly, most current European standards require phenol free and zero volatile organic content (VOC) for industrial products.

[0005] Lignin is an aromatic polyphenol that is a naturally occurring renewable product. Lignin can be obtained as a waste by-product of the paper industry. Millions of tonnes are produced industrially at a significant environmental and economic cost to the industry. Currently, lignin waste must be transformed from black liquor to semi-solid waste (about 85% lignin) and then dumped or burned, all at significant cost (economically and environmentally).

[0006] Lignin represents 15-35% of wood, and accordingly is the most abundant renewable organic material on the earth. Pulping industries separate cellulose from the wood composition leaving lignin and hemicelluloses as waste by-products known as black liquor. In the sulphite process pulp industries the main by-product is lignosulphonate. The global annual production capacity is about 1.8-2.0 million tons. Each ton of pulping products produces 330-540 kg of lignosulphonate. Most of the lignosulphonate (66%) produced in pulping industries is burned (resulting in significant SO_2 pollution) and 34% is treated and dumped which is costly.

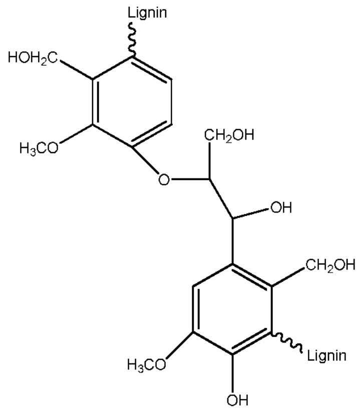
[0007] Therefore, there is a need to develop water based lignins that do not have the economic or environmental costs associated with the prior use and handling of lignins. The embodiments provided herein satisfy this need as well as others.

SUMMARY OF THE INVENTION

[0008] Embodiments provide methods of making a lignomethylol or a lignosulphonatemethylol, the method comprising contacting a lignin or a lignosulphonate with formaldehyde or paraformaldehyde or glyoxal under conditions sufficient to produce the lignomethylol or the lignosulphonatemethylol.

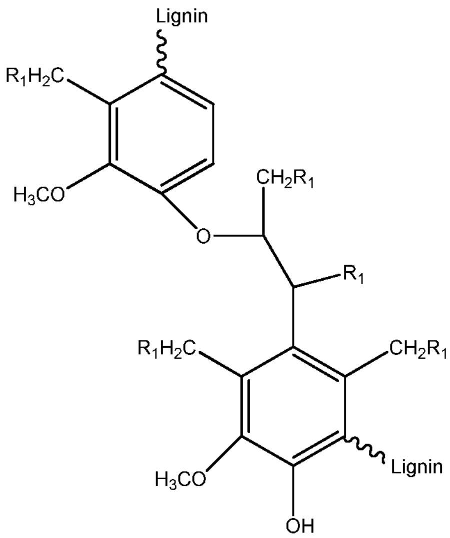
[0009] In some embodiments, methods comprising epoxidizing the lignomethylol or the lignosulphonatemethylol under basic pH conditions to produce a lignomethylol epoxy or a lignosulphonatemethylol epoxy are provided.

[0010] In some embodiments, the lignomethylol has a formula of:



[0011] In some embodiments, methods are provided that comprise contacting the lignomethylol or the lignosulphonate methylol with ammonia or other diamino compounds to produce aminolignin derivatives.

[0012] In some embodiments, the aminolignin derivative has a formula of Formula I,



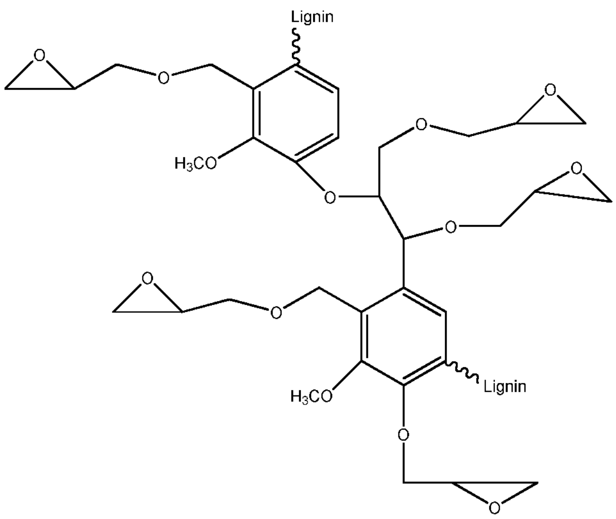
wherein each R_1 is independently selected from the group consisting of NH_2,--$NHCH_2CH_2NH_2$, diethylenetriamine, trieethylenetetraamine, tetraethylenepentaamine, hydroxylamine, hydrazine, monoethanoloamine, diethanolamine, and triethanolamine.

[0013] In some embodiments, methods comprising drying the water soluble aminolignin are provided.

[0014] In some embodiments, methods comprising contacting the amino lignin with anethanolamine, a hydroxycarboxylic acid salt, a polyhydroxycarboxylic acid, an isocyanate terminated polyalkylene oxide,an epichlorohydrine, a hydroxycarboxylic acid salt, or a polyhydroxylic acid salt to produce a surfactant are provided.

[0015] In some embodiments, methods comprising contacting the aminolignin with epichlorohydrine at a temperature of about 0-10 °C to produce a ligno aminoepoxy resin are provided.

[0016] In some embodiments, the ligno aminoepoxy resin has a formula of:



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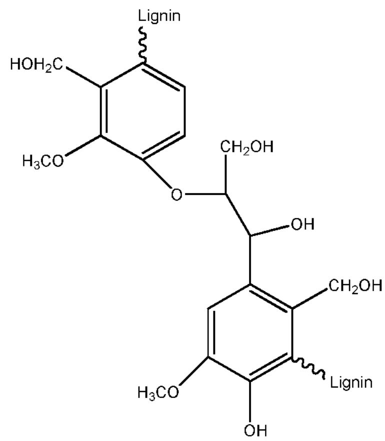
[0017] In some embodiments, methods comprising contacting the ligno amino resin with phosgene, carbon monoxide, or carbon dioxide to produce a lignoisocyanate derivatives are provided.

[0018] In some embodiments, a product produced by any method described herein does not comprise a volatile organic compound.

[0019] In some embodiments, methods of curing an ligno amino epoxy resin, the method comprising contacting the ligno aminoepoxyresin with a water soluble aminolignin according to their epoxy equivalent weight for a sufficient time at room temperature until the resin is cured are provided.

[0020] In some embodiments, compositions comprising one or more of amino lignin derivatives, lignoethylenediamine derivatives, lignodiethylenetriaminederivatives, lignotriethylenetetramine derivatives, lignoethanolamine derivatives, lignodiethanolaminederivatives, lignotriethanolaminederivatives, lignohydrazine derivatives, lignohydroxylamine derivatives, or lignoisophoronediamine derivatives, or any combination thereof are provided.

[0021] In some embodiments, a composition has a formula of



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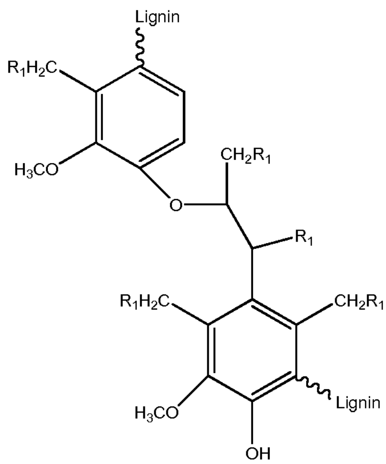
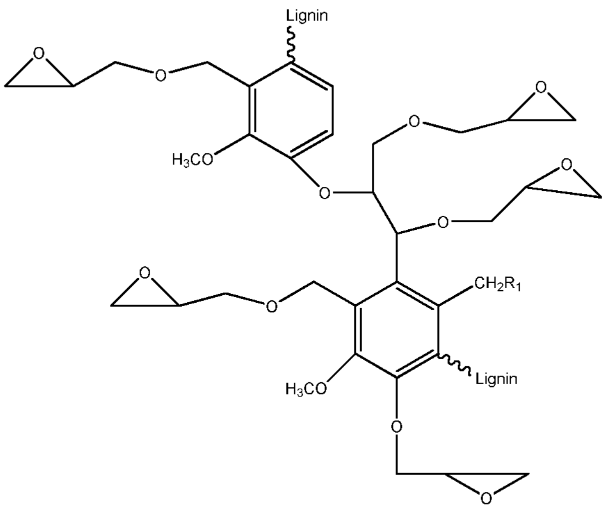
[0022] In some embodiments, the composition has a formula of Formula I,



I,

wherein each R_1 is independently selected from the group consisting of NH_2, $NH_2CH_2CH_2NH_2$, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine, hydroxylamine, hydrazine, monoethanoloamine, diethanolamine, and triethanolamine.

[0023] In some embodiments, the composition has a formula of



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BRIEF DESCRIPTION OF DRAWINGS

[0024] Figure 1 shows a general schematic of representative embodiments provided herein.

DETAILED DESCRIPTION

[0025] This description is not limited to the particular processes, compositions, or methodologies described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and it is not intended to limit the scope of the embodiments described herein. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. In some cases, terms with commonly understood meanings are defined herein for clarity and/or for ready reference, and the inclusion of such definitions herein should not necessarily be construed to represent a substantial difference over what is generally understood in the art. However, in case of conflict, the patent specification, including definitions, will prevail.

[0026] It must also be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise.

[0027] As used in this document, terms “comprise,” “have,” and “include” and their conjugates, as used herein, mean “including but not limited to.” While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0028] The embodiments provide, for example, an improved and more efficient chemical reaction used to transform lignin pulping industry waste to methylol lignin derivatives, methylol lignosulphonate (*e.g.*, mono, di, trimethylols) then transferred to epoxy resins using an emulsion system procedure for epoxidation of lignin, lignin methylol, and methylol lignosulphonate (*e.g.*, mono, di, tri and oligo) resulting in epoxy resins with high epoxy index, water based,self-emulsifying, stable epoxy system.

[0029] Embodiments, provided herein, provide amination of the lignin, lignosulphonate and methylollignosulphonate to produce water soluble aminolignin derivatives. These can be used, for example, as curing agents for water based epoxy resins.

[0030] The present disclosure also provides reactions to transform the lignoamine derivatives via an epoxidisation reaction to form novel water based lignoamine epoxy resins. In some embodiments, the lignoepoxy derivatives do not require addition of any phenolic activatoror triamines commonly used with most epoxy resins because the lignophenolic groups behave as activators for epoxy resins. Treatment of lignin with acid producesactive polyphenols with high activating efficiency as modified lignin starting material for both water based lignoepoxy resins and for other commercial epoxy resins. This is performed without the need for volatile polluting phenols and triamines. An example of the processes that are provided is shown in Figure 1.

[0031] The embodiments provided herein provide significant surprising advantages over existing technologies. For example, the present embodiments produce water based lignoepoxy resins without the use of volatile organic compounds as solvents or diluents. In contrast, most commercial epoxy resins for coating and other applications use aromatic organic solvents and diluents. The water based lignoepoxy resins produced herein, however, can be produced from lignin and lignosulphonate that can be recovered from, for example, pulping industry waste. In contrast, prior commercial epoxy resins were based upon the use petrochemical resources, such as oil. The water based lignoepoxy resins are less expensive to make, and safer for the environment because of the absence of volatile organic compounds. The water based lignoepoxy resins produced according to the methods described herein are already active and do not require the use of toxic volatile phenols or volatile tertiary amines as curing activators. This is because ligno poly phenols can act as curing activators and the activation can be induced, for example, by the addition of excess amount of ligno polyphenols. The water based lignoepoxy resins are safe, nonvolatile, nontoxic, highly active curing agents that are produced from lignin waste and are, therefore, a sustainable resource. In contrast, prior epoxy curing agents were amines or polyamines, which are volatile, toxic, and/or carcinogenic and are not produced from a sustainable resource. The presently described water based lignoepoxy resins are more flexible for industrial application because they can be tailored to produce several types of monomers, raw materials, additives, or surfactants

[0032] The presently described cured resins derived from the water based lignoepoxy resins have a higher glass transition temperature than most common commercial epoxy resins, which provides more uses. Additionally, the presently described embodiments produced epoxy resins that have high epoxy index. In some embodiments, the epoxy index is about, or at least3.2%.

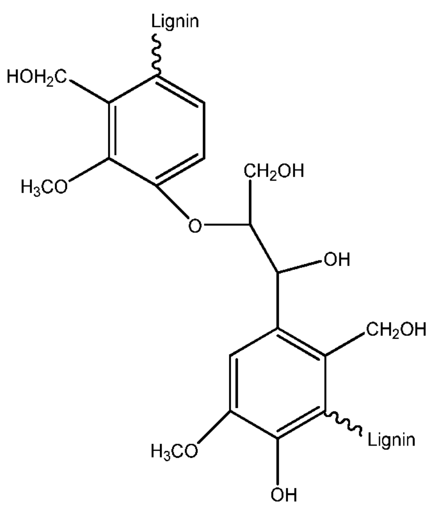
[0033] Accordingly, methods for producing the water based lignoepoxy and related resins are provided. The resins can then be used in a variety of applications.

[0034] Embodiments described herein provide methods of making a lignomethylol or a lignosulphonate methylol. In some embodiments, the method comprises contacting a lignin or a lignosulphonate with an aldehyde under conditions sufficient to produce the lignomethylol or the lignosulphonate methylol. Examples of the aldehyde include, but are not limited to, formaldehyde,paraformaldehyde or glyoxal, or any combination thereof. The lignomethylols or lignosulphonate methylols can be, for example, mono, di, tri and tetra methylol. The lignomethylols or lignosulphonate methylols can be produced by, for example, converting the basic alkaline solution of lignin or lignosulphonate to their methylolic resin. The conversion can be performed, for example, by a condensation reaction with the aldehyde. The conditions for the condensation can be modified according to the specific lignin or lignosulphonate and the resin to be made. The conditions that can be varied include, but are not limited to, temperature, pH,reactant ratio and time of reaction. In some embodiments, the reaction conditions are those listed in Table 1-3, which is shown below.

[0035] In some embodiments, the method further comprises epoxidizing the lignomethylol or the lignosulphonate methylol under basic pH conditions to produce a lignomethylol epoxy or a lignosulphonate methylol epoxy. In some embodiments, the reaction occurs by contacting the methylol with epichlorohydrine at 60-70 ºC in the emulsion system. In some embodiments, the emulsion system comprises butanone,water, and epichlorohydrine (ratio of about 1:1:1) in the presence of 2% emulsifier at pH of about 9-10.

[0036] In some embodiments, the basic pH conditions are a pH of about9 to about 11, about 9.5 to about 10.5, or about 10. The reaction can occur, for example, in the presence of epichlorohydrin to form an epoxy. In some embodiments, the epoxidizing step is performed at a temperature of about 50 to about 80, about 60 to about 80, about 70 to about 80, about 60 to about 70, about 60 to about 65, or about 65 to about 70ºC. In some embodiments, the epoxidizing is performed in an emulsion system. In some embodiments, the emulsion system comprises ketone, water, epichlorohydrine and emulsifier. In some embodiments, the weight ratio of the butanone:water:epichlorohydrine is 1:1:1. In some embodiments, the emulsion system comprises the emulsifier such as cetrimide (cetyltrimethylammonium bromide)or other nonionic surfactants. In some embodiments, the emulsion system can consist of butanone, water, and epichlorohydrine (ratio 1:1:1) in the presence of 2% emulsifier at pH 9-10. In some embodiments, the pH of the solution is controlled by the addition of a sodium hydroxide solution. In some embodiments, the sodium hydroxide solution is a 20% sodium hydroxide solution.

[0037] In some embodiments, the lignomethylol has a formula of



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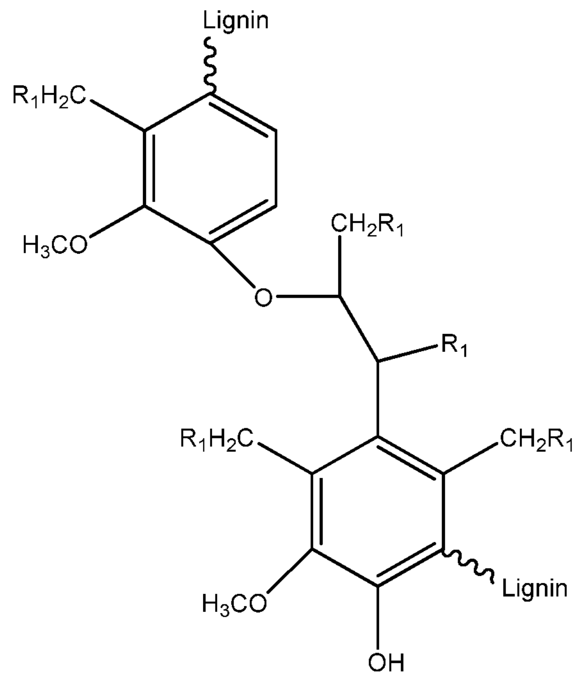
[0038] In some embodiments, the method also comprises contacting the lignomethylol or the lignosulphonate methylol with an amino compound to produce an aminolignin derivative. In some embodiments, the aminolignin derivative is water soluble. In some embodiments, the amino compound is ammonia. In some embodiments, the amino compound is a diamino compound. In some embodiments, the ammonia is ammonia gas under pressure, such as with an autoclave reaction system. Other examples of amino compounds that can be used include, but are not limited to, ethylene diamine, diethylenetriamine, tetraethylenepentamine, monoethanolamine, diethanolamine, triethanolamine, alkylamines (mono, di, or tri alkylamines), isophorone diamine, hydroxylamine, and hydrazine. The amino compound can be in the form of a liquid or solution.

[0039] In some embodiments, the aminolignin derivative has a formula of Formula I,



I,

wherein each R_1 is independently selected from the group consisting of NH_2, $NH_2CH_2CH_2NH_2$, diethylenetriamine, trieethylenetetraamine, tetraethylenepentaamine, hydroxylamine, hydrazine, monoethanoloamine, diethanolamine, and triethanolamine. In some embodiments, each R_1 is identical to one another.

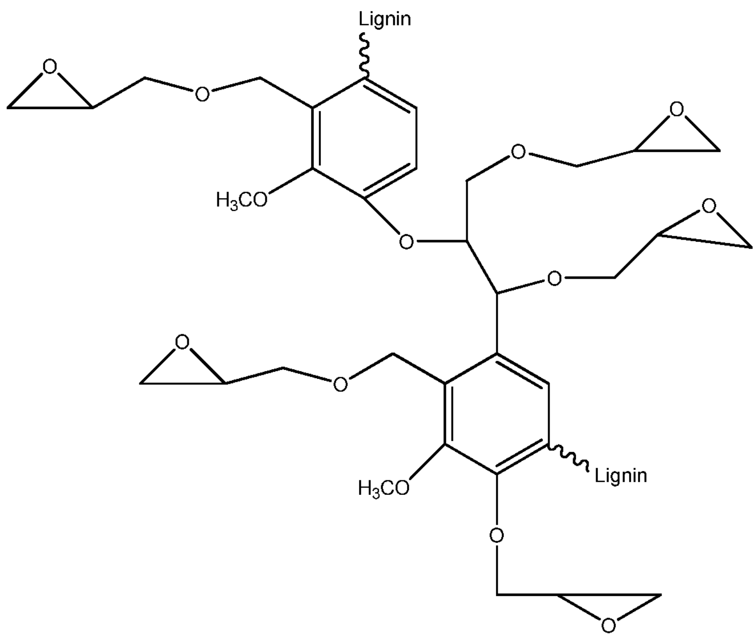
[0040] In some embodiments, the methylol compound is contacted with ammonia gas. In some embodiments, the methylol compound is contacted with ammonia gas under pressure of about 1 to 2 atm. In some embodiments, the reaction occurs at a temperature of about 60 to about 80 °C. In some embodiments, the reaction is allowed to occur for about 1 to about 3 or about 2 to about 3 hours. The reaction will lead to the production of a lignoamine resins. Other lignoamine derivatives can be prepared by, for example, dissolving the ligno methylols in the amino compounds. The solutions can then be heated with, for example, continuous mixing at 60 to 80°C for about 2 to 3 hours. The unreacted amine compound can be separated and recycled, thus leading to cost savings by ensuring that the reagent is efficiently used.

[0041] In some embodiments, the ligno amine derivatives can then be transformed into their aminoglycidyl ether derivatives. In some embodiments, the aminolignin that is produced is not dry and contains water. Therefore, in some embodiments, the method further comprises drying the aminolignin. The aminolignin can be dried until the water content is reduced by about, or at least, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 96, 97, 98, or 99%. In some embodiments, the aminolignin is dried until the water content is less than 0.1%.by using drying agents such as, but not limited to, molecular sieves.or drying under vacuum for some solid ligno amine derivatives.

[0042] In some embodiments, the method further comprises contacting the amino lignin with a compound to produce a surfactant. In some embodiments, the amino lignin is contacted with ethanolamine(*e.g.*, mono,di,and tri),a hydroxycarboxylic acid salt, a polyhydroxycarboxylic acid, an isocyanate terminated polyalkylene oxide, an epichlorohydrine, a hydroxycarboxylic acid salts, or polyhydroxylic acid salts, to produce a surfactant.

[0043] In some embodiments, the method comprises contacting the aminolignin with epichlorohydrine at a temperature of about 0 to about 10 ºC to produce a ligno aminoepoxy resin. In some embodiments, the aminolignin is contacted with epichlorohydrine at a pH of about 9 to about 10. In some embodiments, the pH of the solution is controlled by the addition of a sodium hydroxide solution or other basic solution. In some embodiments, the sodium hydroxide solution is a 20% sodium hydroxide solution. In some embodiments, the resin is produced in an emulsion system.

[0044] In some embodiments, the resin has a formula of



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[0045] In some embodiments, the emulsion system comprises ketone, water, and epichlorohydrine. Examples of ketones that can be used include, but are not limited to, butanone,2-pentanone,2-hexanone,2-isohexanone and the like. In some embodiments, the ratio of the ketone to water to epichlorohydrine is 1:1:1weight ratio. In some embodiments, the reaction is performed in the presence of an emulsifier. Examples of the emulsifier iscetrimide, or molecular surfactants In some embodiments, the emulsifier is1-3% weight % of the reactants. In some embodiments, the mixture is mixed for about, or at least, 1, 2, 3, 4, or 5 hours. The emulsified epoxy can then be used as a water based system specifically for epoxy derived from low molecular weight lignin.In some embodiments, the emulsion is demulsified. In some embodiments, the water is separated and the ketone and the unreacted epichlorohydrine are isolated and can be reused. The ketone and unreacted epichlorohydrine can be isolated by distillation under reduced pressure. Reduced pressure can be, for example, about 0.1mm Hg.

[0046] In some embodiments, the method further comprises contacting the lignoaminoresin with phosgene, carbon monoxide, or carbon dioxide to produce a polyisocyanate. In some embodiments, the lignoaminoresin is dissolved in diethylketone or ethylacetate. The gases (*e.g.* phosgene, carbon monoxide, or carbon dioxide, or any combination thereof) can be passed through (*e.g.*bubbled) the solution. In some embodiments, the excess unreacted gas can be flushed or removed out by passing through dry nitrogen gas and/or decomposing the unreacted gases by contacting with KOH or other suitable basic solution and/or can be separated and recycled. The polyisocyante (*e.g.* lignoisocyante) and derivatives thereof can be used as a foamed hydrogel active gradient,polyurethane active gradient,crosslinking agent, and interpenetrating polymer network (IPN).

[0047] Methods of curing lignoamino epoxy resins are also provided. In some embodiments, the method of curing comprises contacting the ligno aminoepoxyresin with a water soluble aminolignin. The method comprises, in some embodiments, contacting an amount of each according to their epoxy equivalent weight ("EEW"). For example, for a commercial epoxy resin that has an epoxy equivalent weight of 190, then when it is cured with amine hardener with an amine equivalent weight 114,then each 190 g of epoxy will require 114 g of the hardener as curing agent. The reaction can then be cured at room temperature. The cured product can be, for example, a coating film.

[0048] In some embodiments, compositions comprising one or more of the following are provided: amino lignin derivatives (*e.g.*, monoamino lignin, diaminolignin, triaminolignin, oligoaminolignin), lignoethylenediamine derivatives (*e.g.*, mono, di, tri, and oligoethylenediamine derivatives), lignodiethylenetriamine derivatives (*e.g.*, mono, di, tri and oligo derivatives), lignotriethylenetetramine derivatives (*e.g.*, mono, di, tri and oligo derivatives), lignoethanolamine derivatives (*e.g.*, mono, di, tri and oligomonoethanolamine derivatives), lignodiethanolamine derivatives (*e.g.*, mono, di, tri and oligodiethanolamine derivatives), lignotriethanolamine derivatives (*e.g.*, mono, di, tri and oligo-tri, ethanolamine derivatives), lignohydrazine derivatives, which were found to be decomposed to lignoamine derivatives,lignohydroxylamine derivatives, (*e.g.*, mono,di, tri and oligohydroxylamine derivatives),or lignoisophoronediamine derivatives (*e.g.*, mono, di, tri and oligoisophoronediamine derivatives), or any combination thereof.

[0049] The compounds described herein can be used for many applications. For example, the water based ligno epoxy resins and water based lignoamine hardeners that can be used as environmentally safe with zero volatile organic content (VOC) alternatives for resins used in coatings,floorings, adhesives, binders, additives, lubricants,and thermosetting resins. Accordingly, in some embodiments, a coating, a flooring, an adhesive, a binder, an additive, a lubricant, and a thermosetting resin comprising one or more of the compounds described herein are provided.

EXAMPLES

Example 1: Preparation of lignoepoxy resin

[0050] A 500 ml flanged top five neck reaction vessel fitted with mechanical stirrer,thermometer,condenser and separating funnel was immersed in thermo stated oil bath. The vessel was charged with 75 g of methylol lignin with number of methylol groups about 3 (prepared from low molecular weight lignin under condition described in Table 1) was dissolved in 100 g of butanone. 100g of epichlorohydrine was added and 100g of distilled water was added. The system was flashed with nitrogen for 10 minutes with mixing. 2 g of cetrimide surfactant was added with efficient mixing and the temperature was raised to 60 C. Then 50 ml of 20 % sodium hydroxide was added portion wise over three hours to keep the pH at 9-10. The reaction was continued for one hour. Samples were taken each 30 minutes for curing test.At the end of the reaction the butanone and the excess of unreacted epichlorohydrine was distilled off. The residue was found to contain two components water soluble lignoepoxy resin52% and insoluble residue 48% solid lignoepoxy resins.(the yield was 85% based on methylol lignin)

[0051] The two fraction were characterized by instrumentation such as IR, NMR, and DSC. Both components were found to undergo curing with hardeners or thermal curing when examined by DSC.The epoxy equivalent found from titration with HBr was found to be 2-3.2 g equivalent for the last three fractions.

Example 2: Preparation of lignomethylolsulphonate epoxy resin

[0052] The same procedure as described in Example 1was performed using lignomethylolsulphonate instead of lignomethylol without using the emulsifier as lignomethylolsulphonate acts as self-emulsifying material. The reaction provided a higher ratio of water soluble to the solid lignoepoxy resin.

Example 3: Effect of stoichiometric ratio of NaOH /lignomethylol on the yield and epoxy equivalent

[0053] The effect of stoichiometric ratio of NaOH /lignomethylol was investigated using the same procedure described in Example 1. It was found that increasing the NaOH/Lignomethylol by 10-20% enhances the epoxy equivalent by 10-15%. Exemplary results are shown in Table 2.

Table 2: Exemplary experimental data obtained in the epoxidation of lignomethylols and lignosulphonate methylols at reaction conditions that gave optimum results.

Reactants/epichlorohydrine	Temp. ºC	pH	Time /hours	Epoxy equivalent (g/eq.wt	Yield
Methylolated lignin	60	9	3	2.8	87
	70	10	3.5	3.2	82
Lignosulphonated methylols	60	9	3	2.1	92
	70	10	3.5	2.4	84

Example 4: Effect of reaction time on the yield and epoxy equivalent

[0054] The same procedure as described in Examples 1-3 was used. Fractions were taken each 30 minutes up to 6 hours. Analysis of the samples indicate that extending the addition time (3-4 hours) increases the epoxy equivalent and lignoepoxy yield by 10- 15%. Yield and epoxy equivalent starts to decrease after 4 hours due to the epoxy ring opening polymerization. Samples of the obtained data are shown in Table 2.

Table 1 shows exemplary conditions used in the preparation of lignomethylols and lignosulphonate methylols

Wt ratio Lignin: aldehyde	Tempe rature . °C	Reaction time (h)	pH	CH_2OH/ Structural unit of lignin.	Average of 3 exp	Number of CH_2OH
3.6:1*	65-70	3.0	9-10	2.84-3.3	2.86	3.0

Example 5: Preparation of lignoamine hardener

[0055] A three necked reaction vessel fitted with condenser,mechanical stirrer and thermometer was immersed in thermostated oil bath and was charged with 100 g of lignomethylols (number of methylol groups about 3 (prepared under the exemplary conditions described in Table 1),200g water,33g ethylene diamine, and 5g (10 % NaOH) was added drop wise to maintain the pH at 9-10.The system was heated to 60 °C.The reaction was continued for three hours. The system was brought to reflux for an additional one hour. The unreacted ethylene diamine was distilled off,and the viscous residue lignoamine derivative (hardener) was water soluble with dark color.The hardener was used as curing agent for epoxy resin both commercial and the lignoepoxy resins that were prepared according to Examples1-3.All the sample were cured after 16 hours (*e.g.*overnight).

Example 6: Preparation of amino lignin hardener

[0056] 250ml laboratory autoclave was charged with 20 g of lignomethylol ,100 ml water ,3 g NaOH, the reactor was closed firmly and compressed ammonia gas was introduced .The reaction was carried out at 60 C under two atmosphere pressure for 3 hours.The product was separated and tested for curing commercial epoxy resin and ligno epoxy resins prepared in examples 1-4.All the samples tested were found to be cured overnight.

Example-7: Preparation of lignohydrazine hardeners

[0057] The autoclave was charged with 20 g lignomethylol,100 g water, 2g NaOH,and 30 g 20% hydrazine solution in water.The reactor was secured then the system was heated gradually with continuous mixing to 60 °C.The reaction was continued for 3 hours. The product was separated and tested for curing.The product was found to have similar structure and hardening efficiency to the hardeners prepared in Example 6,indicating that hydrazine has decomposed to ammonia which then reacted with methylol lignin,or the hydrazine lignin derivative was formed first then it decomposed to lignoamine and ammonia.

Example 8: Preparation of lignoethanolamine hardener

[0058] The reaction vessel was charged with 100g lignomethylol,100g water,3g NaOH, and 35g of mono ethanolamine,the reaction was brought to reflux for two hours,then cooled to room temperature the unreacted ethanol amine was distilled off ,the highly viscous semisolid product was tested for curing commercial epoxy resin and lignoepoxy resins prepared in Examples 1-4,the hardener showed very low curing efficiency at ambient temperature ,but underwent fully cured at 70 ºC for 6 hours.

Example 9: Preparation of lignoisocyanate derivatives

[0059] In a closed phosegenation system 25g of lignoamine derivative prepared according to Example 6 was dissolved in 100 g of dichloromethane. 30 g of triethylamine was added as a HCl acceptor. The reaction vessel was immersed in a cooling bath to maintain the temperature at 25-30 ºC.Phosgene, produced instantly using simple Kip system by adding concentrated sulphuric acid to chloroform, was bubbled slowly at 1 g per 10 minutes through the reaction system with continuous mixing and under extremely dry condition.At the end of the reaction the system was flushed with N_2 gas to remove the unreacted and dissolved phosgene. The outlet gas was bubbled through alcoholic KOH to decompose the phosgene.

[0060] The residual product was soluble in methylene chloride.Evaporation of methylene chloride gave highly viscous dark colored lignoisocyanate derivatives,the product was tested to cure some commercial polyols used in polyurethane technology.

[0061] Polyisocyanate products can be prepared by replacing phosgene with CO_2 or CO in an autoclave under high pressure.

Example 10: Curing of lignoepoxy resin with the lignoamino hardeners

[0062] Several curing experiments were carried out by mixing stoichiometric ratios of ligno amine prepared in Example 5 with lignoepoxy from those described in Examples 1-4 or with commercial epoxy. The curing of the samples was investigated by DSC. The glass transition temperature of the cured samples was found to be much higher than standard commercial epoxy resins and their hardeners by about 10-20 °C. The values found for some resins ranged between 80-120 °C.For example, when the lignoamino hardener was used for curing Bisphenol-A diglycidylepoxy resins, the glass transition of the cured product increased by about 10 °C.

Example11: Emulsion ligno epoxy resin for coating application

[0063] The emulsion lignoepoxy prepared according to Examples 1and 2 were cured with equivalent amount of lignoamino hardener, which was prepared according to Example -5, (5 g of ligno epoxy emulsion+1.5 g of lignoamino hardener) and mixed and applied to concrete a surface,and left to cure at ambient temperature overnight. A dark brown colored shiny coated surface was obtained.

Example 12. Curing of lignoepoxy emulsion by commercial hardener

[0064] 5 g of ligno epoxy emulsion was cured with 0.9 g of commercial hardener /Parchem product 8050. The emulsion was applied to concrete surface and left overnight. The coated surface showed improved abrasion properties as compared to surface coating of Example 10.

[0065] From the foregoing, it will be appreciated that various embodiments of the present disclosure have been described herein for purposes of illustration, and that various modifications may be made without departing from the scope and spirit of the present disclosure. Accordingly, the various embodiments disclosed herein are not intended to be limiting.

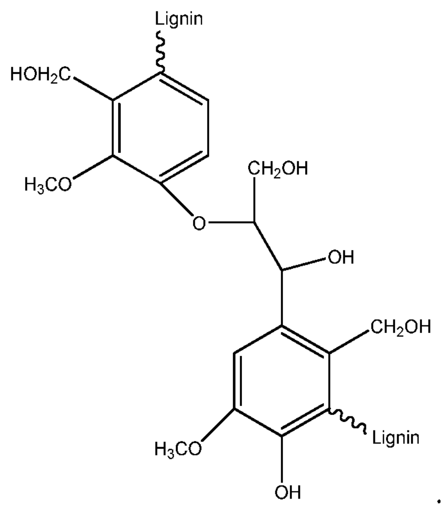
CLAIMS

What is claimed is:

1. A method of making a lignomethylol or a lignosulphonate methylol, the method comprising contacting a lignin or a lignosulphonate with formaldehyde or paraformaldehyde or glyoxal under conditions sufficient to produce the lignomethylol or the lignosulphonate methylol.

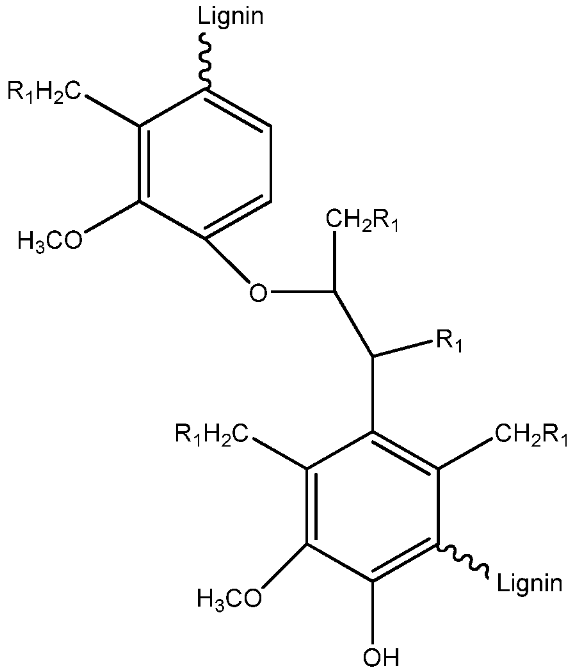
2. The method of claim 1, further comprising epoxidizing the lignomethylol or the lignosulphonate methylol under basic pH conditions to produce a lignomethylol epoxy or a lignosulphonate methylol epoxy.

3. The method of claim 1, wherein the lignomethylol has a formula of:



4. The method of claim 1, further comprising contacting the lignomethylol or the lignosulphonate methylol with ammonia or an amino compound to produce aminolignin derivatives.

5. The method of claim 4, wherein the aminolignin derivative has a formula of Formula I,



,

wherein each R_1 is independently selected from the group consisting of NH_2,--$NHCH_2CH_2NH_2$, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine, hydroxylamine, hydrazine, monoethanoloamine, diethanolamine, and triethanolamine.

6. The method of claim 4, wherein the amino compound is a monoethanolamine, a monoalkylamine, dialkylamine, trialkyl amine ,ethylene diamine, diethylenetriamine,tetraethylene pentamine, monoethanol amine, diethanolamine, triethanolamine, isophorone diamine,hydroxylamine, or hydrazine.

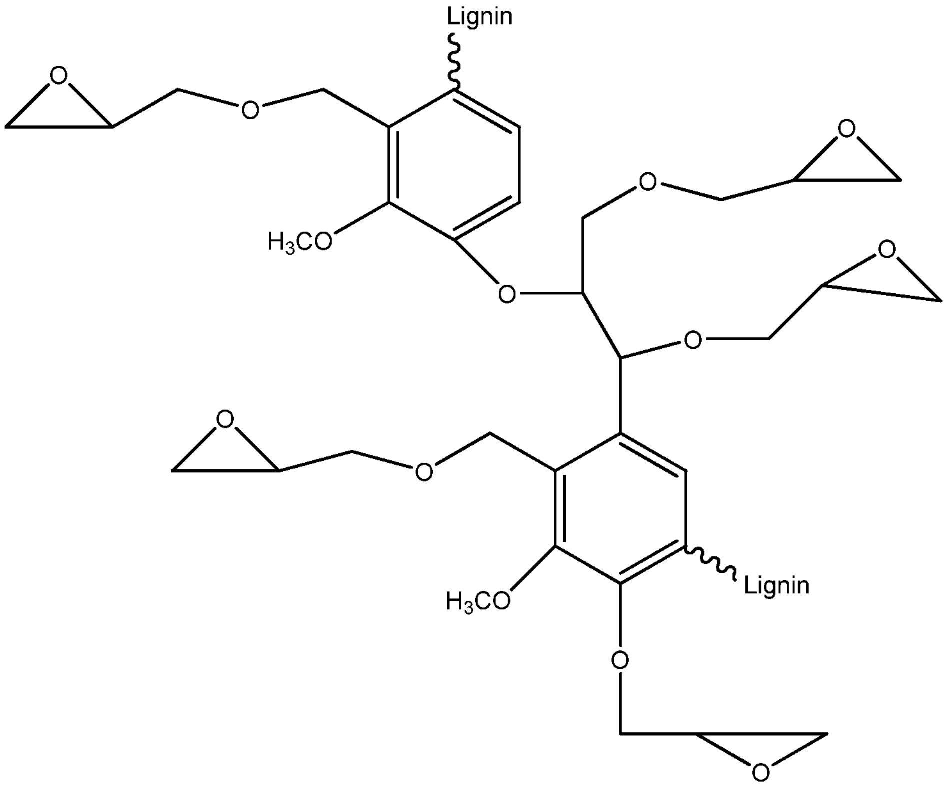
7. The method of claim 4, further comprising drying the water soluble aminolignin.

8. The method of claim 4, further comprising contacting the amino lignin with anethanolamine, a hydroxycarboxylic acid salt, a polyhydroxycarboxylic acid, an isocyanate

terminated polyalkylene oxide,an epichlorohydrine, a hydroxycarboxylic acid salt, or a polyhydroxylic acid salt to produce a surfactant.

9. The method of claim 4, further comprising contacting the aminolignin with epichlorohydrine at a temperature of about 0-10 ºC to produce a ligno aminoepoxy resin.

10. The method of claim 9, wherein the ligno aminoepoxy resin has a formula of:



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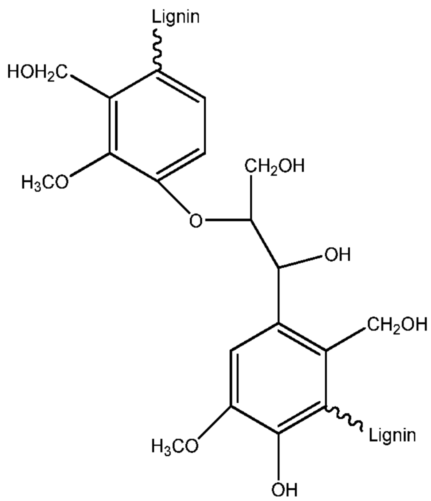
11. The method of claim 9, further comprising contacting the ligno amino resin with phosgene, carbon monoxide, or carbon dioxide to produce a lignoisocyanate derivatives.

12. The methods of any one of claims 1-11, wherein a product produced by the methods does not comprise a volatile organic compound.

13. A method of curing an ligno amino epoxy resin, the method comprising contacting the ligno aminoepoxyresin with a water soluble aminolignin according to their epoxy equivalent weight for a sufficient time at room temperature until the resin is cured.

14. A composition comprising one or more of amino lignin derivatives, lignoethylenediamine derivatives, lignodiethylenetriaminederivatives, lignotriethylenetetramine derivatives, lignoethanolamine derivatives, lignodiethanolaminederivatives, lignotriethanolaminederivatives, lignohydrazine derivatives, lignohydroxylamine derivatives, or lignoisophoronediamine derivatives, or any combination thereof.

15. The composition of claim 14, wherein the composition has a formula of



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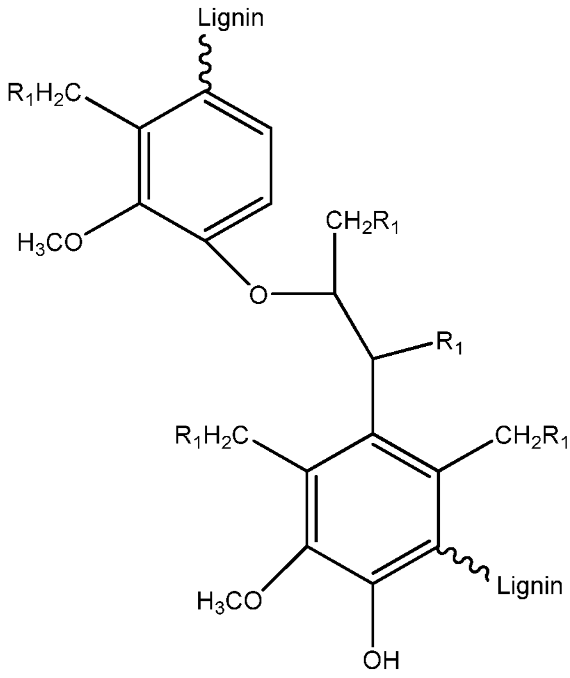
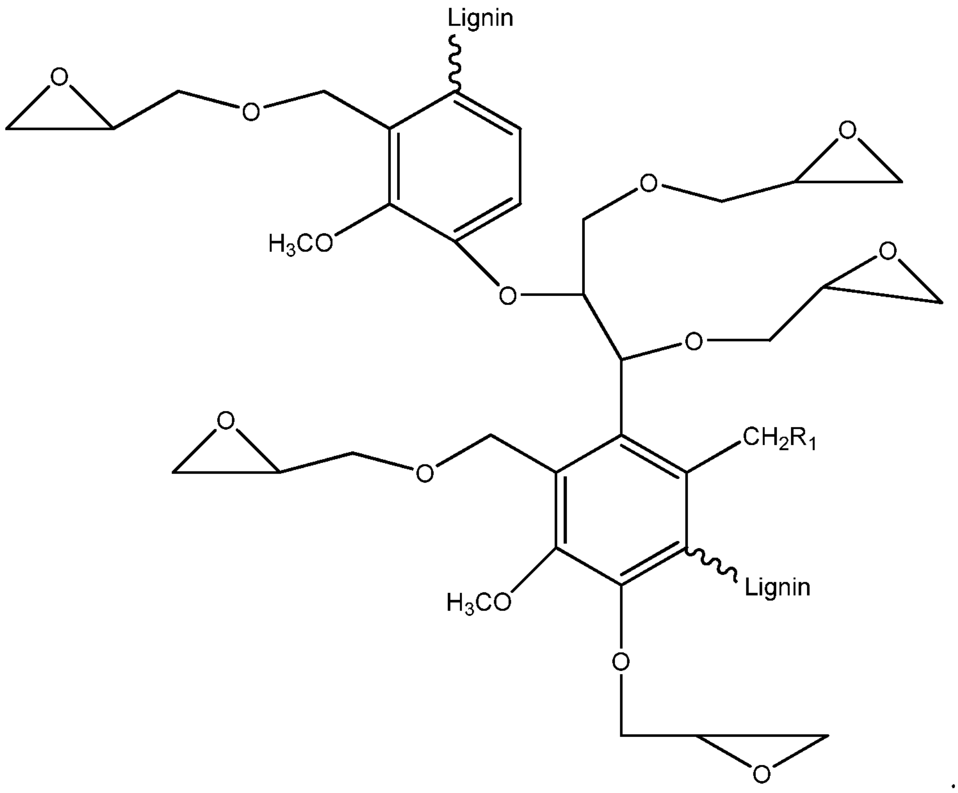
16. The composition of claim 14, wherein the composition has a formula of Formula I,



I,

wherein each R_1 is independently selected from the group consisting of NH_2, $NH_2CH_2CH_2NH_2$, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine, hydroxylamine, hydrazine, monoethanoloamine, diethanolamine, and triethanolamine.

17. The composition of claim 14, wherein the composition has a formula of


Lignin
O
O
O
O
H3CO
O
O
O
O
O
CH2R1
O
H3CO
Lignin
O
O

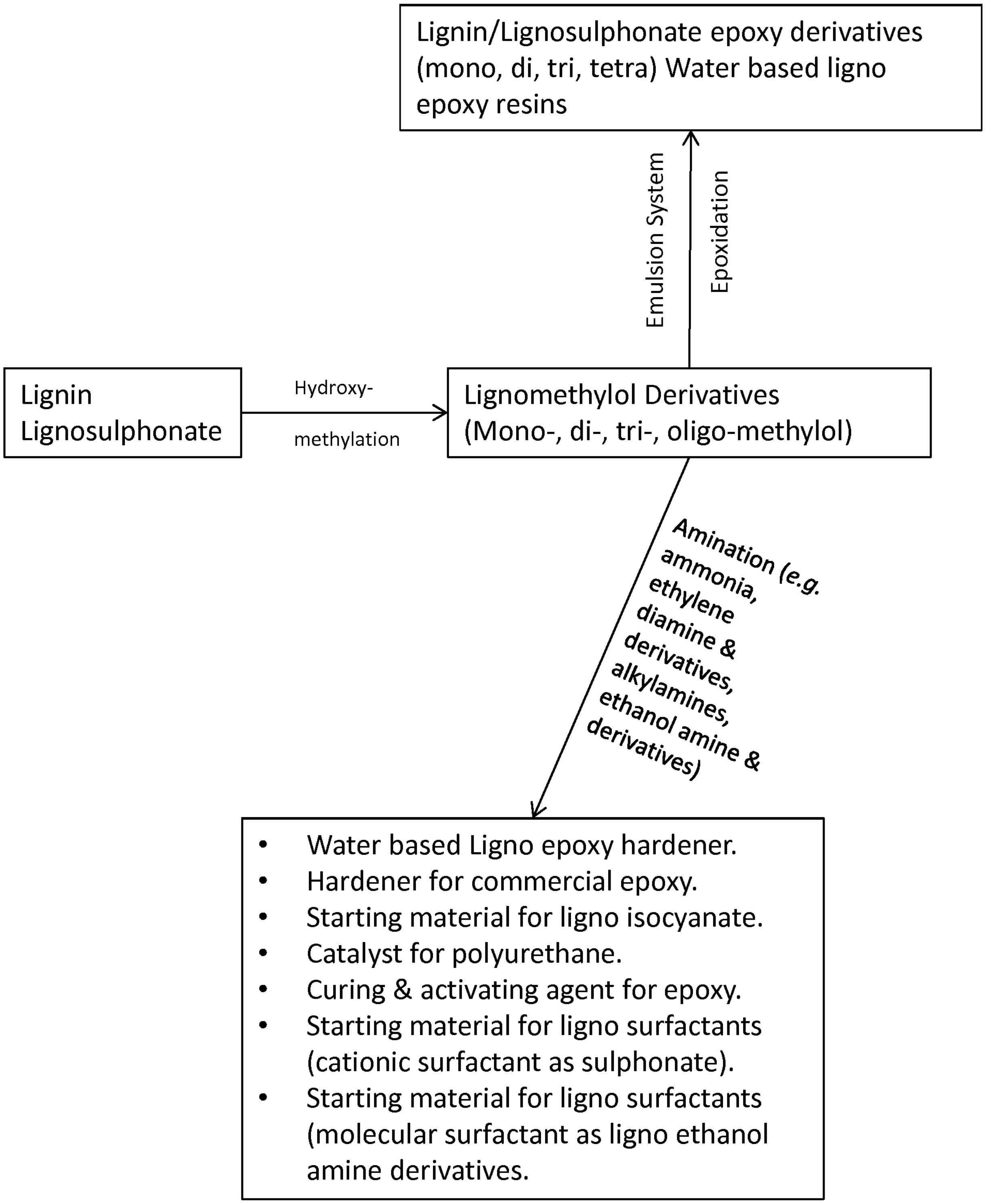

Lignin/Lignosulphonate epoxy derivatives (mono, di, tri, tetra) Water based ligno epoxy resins
Emulsion System
Epoxidation
Lignin Lignosulphonate
Hydroxy-
methylation
Lignomethylol Derivatives (Mono-, di-, tri-, oligo-methylol)
Amination (e.g. ammonia, ethylene diamine & derivatives, alkylamines, ethanol amine & derivatives)
• Water based Ligno epoxy hardener.
• Hardener for commercial epoxy.
• Starting material for ligno isocyanate.
• Catalyst for polyurethane.
• Curing & activating agent for epoxy.
• Starting material for ligno surfactants (cationic surfactant as sulphonate).
• Starting material for ligno surfactants (molecular surfactant as ligno ethanol amine derivatives.

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/49178

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08G 18/00 (2012.01)
USPC - 527/401;527/400
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 527/401
IPC: C08G 18/00 (2012.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 527/400 (See Search Words below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PUBWEST: PGPB, USPT, USOC, EPAB, JPAB
Google: Scholar/Patents: lignin epoxy resins formaldehyde amine epichlorohydrin ammonia epoxidation epoxide reaction methylolation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 4,113,675A (CLARKE et al) 12 September 1978 (12.09.1978) Col 2, ln 24-32; Col 2,ln 59-65	1 ---- 2-12
Y	US 2011/0098384 A1 (BLOUNT) 28 April 2011 (28.04.2011) para [0050];[0054]; [0058];[0060];[0063];[0064]; [0069]-[0070];[0073];[0088];[0089];[0097];[0095];[0096]	2; 4-12
Y	US 2008/0262182 A1 (FUNAOKA) 23 October 2008 (23.10.2008) Figure 23	3;5;10

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 November 2012 (27.11.2012)	19 DEC 2012

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/49178

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-12 directed to method of making a lignomethylol or a lignosulphonate methylol, the method comprising contacting a lignin or a lignosulphonate with formaldehyde or paraformaldehyde or glyoxal under conditions sufficient to produce the lignomethylol or the lignosulphonate methylol.

Group II: claim 13 directed to a method of curing an ligno amino epoxy resin, the method comprising contacting the ligno aminoepoxyresin with a water soluble aminolignin according to their epoxy equivalent weight for a sufficient time at room temperature until the resin is cured

Continued in Supplemental Box III

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
CLaims 1-12

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continued Supplemental BOX III

Group III: claims 14-17 directed to a composition comprising one or more of amino lignin derivatives, lignoethy lenediamine lignotriethy lenetetramine derivatives, derivatives, lignodiethy lenetriaminederi vati ves, lignoethanolamine derivatives, lignodiethanolaminederi vati ves, lignotriethanolaminederi vati ves, lignohydrazine deri vati ves, lignohydroxylamine derivatives, or lignoisophoronediamine derivatives, or any combination thereof.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Group III does not require contacting a lignin or a lignosulphonate with formaldehyde of Group I or contacting the ligno aminoepoxy resin with a water soluble aminolignin of Group II

Group II does not require contacting a lignin or a lignosulphonate with formaldehyde of Group I or lignoethy lenediamine/lignotriethy lenetetramine/lignodiethylenetriaminederi vatives/lignoethanolamine /lignodiethanolamine/lignotriethanolamine/lignohydrazine/lignohydroxylamine/lignoisophoronediamine derivatives of Group III

Group I does not require contacting the ligno aminoepoxy resin with a water soluble aminolignin of Group II or lignoethy lenediamine/lignotriethy lenetetramine/lignodiethy lenetriaminederi vati ves/lignoethanolamine/lignodiethanolamine/lignotriethanolamine/lignohydrazine/lignohydroxylamine/lignoisophoronediamine derivatives of Group III

The common feature of method of making/recovering lignin derivatives of Groups I-II is disclosed by US 2009/0209739 A1 (Funaoka et al.) 20 August 2009 (see para [0019]; [0029]; [0033]; [0036]), therefore the common feature is not an improvement over the prior art.