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(54) Title: NOVEL CATALYST FOR PRODUCTION OF OXAZOLIDINE COMPOUNDS (57) Abstract Significant improvements in the utility of oxazolidone and polyoxazolidone compounds and in their manufacture can be achieved using a novel catalyst in the reaction between a hindered isocyanate and an epoxy, forming oxazolidone ring structures. The novel catalyst of the invention promotes the efficient and rapid formation of oxazolidone and polyoxazolidone compounds. The use of hindered isocyanate in the reaction prevents formation of side reaction products such as isocyanate trimer, allophanate and biuret.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

NOVEL CATALYST
FOR PRODUCTION OF OXAZOLIDINE COMPOUNDS

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Field of the Invention

The invention relates to the catalyzed reaction of epoxy and hindered isocyanate to produce oxazolidone and polyoxazolidone compounds that can be used as adhesives, sealants, caulks, coatings, including powder coatings and other applications of reactive curing chemistry. These compounds have structural or engineering uses, can be used in preregs, in injection molded articles, etc., and in any other area where thermoplastics or thermosetting resins have utility. The focus of the invention is on the catalyzed reaction of a compound having an epoxide and a hindered isocyanate in the production of oxazolidone compounds.

In particular, the catalyzed reaction of interest can be used to: (1) form linear thermoplastic polyoxazolidone polymers; (2) form epoxy-terminated oxazolidone prepolymers that can be cured with conventional epoxy curing agents; (3) form other oxazolidone-containing materials such as oxazolidone-containing vinyl monomers and polymers thereof, epoxy curing adhesives, etc. The oxazolidone compounds produced in this invention provide significantly improved utility, lifetime, and curing properties because of the substantial absence of isocyanurate compounds generated by a competing trimerization reaction of isocyanate compounds.

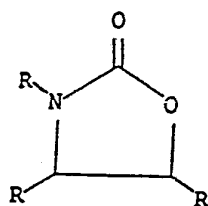
Background of the Invention

Epoxy compounds and isocyanate compounds are known to react to form oxazolidones. The reaction is also known to form substantial quantities of undesirable by-products. A major by-product results from the trimerization of

isocyanates to isocyanurate, allophanate and biuret compounds, which are highly functional and typically give rise to highly crosslinked and brittle polymers. A reaction product free of such impurity exhibits improved thermal and mechanical properties compared to one containing a higher proportion of isocyanurate compounds.

Oxazolidones are heterocyclic ring systems containing nitrogen and oxygen functionality, which can be generically represented by the following formula (I):

10



I

Most conventional catalysts used in preparing such compounds do not efficiently and cleanly drive the reaction to completion.

In large part, the catalysts available in the prior art are of low activity, are generally difficult and unsafe to handle, are not available in commercial quantities, are used only in solvent, or are otherwise unacceptable for a commercial setting. Some also promote epoxy polyether formation.

Ashida, U.S. Patent No. 4,066,628 teaches the use of a catalyst selected from the group consisting of ZnR_2 , $Zn(OCOR)_2$, ZnX and AlR_3 wherein R is an alkyl group having 1 to 12 carbon atoms and X is an organic bidentate group. The preparation of oxazolidones from an organic isocyanate and an epoxide using a quaternary ammonium halide and an alcohol as cocatalysts is disclosed in Schramm, U.S. Patent No. 3,313,747. Zinc chloride and ferric chloride have been proposed as catalysts for the foregoing reaction [K. Gulbins and K. Hamann, *Angew. Chem.*, **70**, 705 (1958)]. Zinc bromide has been proposed as a catalyst for the reaction of an epoxide, 3-phenoxy-1,2-propylene, and phenylisocyanate

in dimethylformamide, with only 33% yield of the oxazolidone [Sandler, J. Polymer Science, Part A-1, 5, 1481 (1967)]. Lithium chloride has been found by K. Gulbins to be a catalyst for the reaction between an aromatic

5 isocyanate and an aromatic epoxide [Chem. Ber., 93, 1875, (1960)]. Lithium n-butoxide has been found by R. R. Deleone to be an oxazolidone catalyst [J. Polymer Science, Part A-1, 8, 609, (1970)]. An adduct of lithium bromide and tributyl phosphine oxide has been reported by J. E.

10 Herweh and W. J. Kauffman to be an oxazolidone catalyst [Tetrahedron Letters, no. 12, 809, (1971)]. Glasgow, U.S. Patent No. 3,702,839 (November 14, 1972) discloses that a phosphonium salt is an oxazolidone catalyst. S. Kimura and H. Samejima (Japanese Patent Public Disclosure 48-70797,

15 September 25, 1973) disclose that monomer-soluble catalysts selected from the group consisting of specific organic metal chelates, alkyl glycidyl ammonium salts, trialkyl (triaryl or tricycloalkyl) borates, and trialkyl (or triaryl) phosphines are oxazolidone catalysts. Y. Iseda

20 and F. Odaka et al. (Japanese Patent Public Disclosure 49-37999, April 9, 1974) disclose that epoxy-soluble quaternary ammonium compounds and/or lithium halide-phosphine oxide complexes are oxazolidone catalysts. Ashida, U.S. Patent No. 3,817,938 (June 18, 1974) discloses

25 that alkoxides or phenoxides of metals of Group IIA or IIIA of the Periodic Table are oxazolidone catalysts. M. J. Marks et al., U.S. Patent No. 4,658,007 (April 14, 1987) disclose the preparation of an oxazolidone-containing polymer or precursor from a polyepoxide and a

30 polyisocyanate using an organoantimony iodide catalyst. We are also aware of DiSalvo, U.S. Patent No. 4,424,316; Goel, U.S. Patent No. 4,613,660; and Waterman, U.S. Patent No. 4,731,428, each of which relates to the reaction of epoxy compounds and isocyanate compounds in the preparation of

35 curing materials.

Standard catalyst systems do not efficiently drive the oxazolidone forming reaction. Further, standard isocyanates such as MDI and TDI form unwanted reaction by-products. In view of these facts, a substantial need exists for a reaction system including isocyanate reactants and catalyst that cooperate to smoothly form oxazolidone without substantial formation of reaction by-product.

Summary of the Invention

10 We have found a system, including isocyanate reactant and catalyst, that can be used in the rapid and efficient production of oxazolidone compounds without the concurrent formation of trimer isocyanurate impurities. The system involves the catalyzed reaction of an epoxy-
15 containing compound and a hindered isocyanate. The catalyst comprises zinc halide (ZnX_2), such as zinc iodide, zinc bromide, and zinc chloride. The in-situ production of a zinc halide catalyst can also be utilized in the process of the invention. For example, zinc iodide can be produced
20 through the reaction of a zinc compound and an iodide compound (a non-limiting example of an in situ preparation is: $ZnA + 2 MI \rightarrow ZnI_2 + 2 MA$, wherein M is a monovalent metal cation and A is a monovalent displaceable anion). We have found that the hindered isocyanate of this invention
25 will not trimerize under the reaction conditions disclosed. Further, the novel catalysts smoothly convert isocyanate and epoxy to oxazolidone. The effects together result in high yields of oxazolidone free of unwanted reaction by-products. The catalyst system is stable and is soluble and
30 active in hot-melt and solvent-free systems, is tolerant of water and atmospheric impurities, requires no special handling, and is easily blended into the system.

A first aspect of the invention comprises a process for the preparation of oxazolidone compounds in the presence of

a zinc halide catalyst system. A second aspect of the invention comprises a linear polyoxazolidone polymer comprising the product of reaction of a polyepoxy compound and a hindered polyisocyanate compound in the presence of the zinc halide catalyst system. A further aspect of the invention comprises an epoxy-terminated prepolymer prepared from a polyepoxy compound and the product of the reaction of a hindered polyisocyanate and hydroxy-terminated prepolymer, i.e., polymeric polyol. A still further aspect comprises a vinyl monomer having an oxazolidone or polyoxazolidone functionality and vinyl polymers made using such a monomer having pendant oxazolidone functionality. A final aspect of the invention is a functional material such as an adhesive, sealant, coating, potting compound, powder coating etc., with an oxazolidone or polyoxazolidone compound of the invention.

Detailed Description of the Invention

The invention provides an improved process for the preparation of oxazolidone and polyoxazolidone products comprising the reaction of a hindered organic isocyanate compound and an epoxy compound in the presence of an effective amount of a catalyst compound comprising a zinc halide, i.e., ZnCl_2 , ZnBr_2 , and ZnI_2 , or an in situ generated zinc halide. The invention provides for an efficient production of oxazolidone compounds that are substantially free of trimer isocyanurate and other impurities due to the presence of hindered isocyanate. Preferably the oxazolidone and polyoxazolidone materials are produced by the process of the invention such that there is less than about 1 wt-% of the isocyanurate compound present.

The term "in situ generated zinc halide" indicates the inclusion of zinc and halide-containing reactants, in the reaction mixture of the isocyanate and the epoxy compound,

that can react sufficiently rapidly to form a zinc halide to catalyze the formation of the oxazolidone. In preparing the polyoxazolidones by the reaction of an organic polyisocyanate with a polyepoxy compound, the relative
5 amounts of the organic polyisocyanate and the polyepoxy can be adjusted to produce the desired reaction products.

The hindered isocyanate-epoxide reaction, catalyzed by the zinc halide catalyst system of the present invention, is preferably carried out in the melt form in an absence of
10 solvent at an elevated temperature in the range of about 80° C to about 250° C for a period of time up to about 10 hours. Choice of the zinc halide catalyst can vary depending on the desired product, solubility of the catalyst in the reactants, and the process conditions.
15 Preferably the catalyst is ZnI_2 , which is the most widely useable of the zinc halides in the preparation of linear oxazolidones, vinyl monomers and polymers containing oxazolidone functionality, or oxazolidone prepolymers.

The catalyst is present in an amount sufficient to
20 affect formation of the polyoxazolidone ring in a sufficiently short period of time to be of commercial interest. The exact amount of catalyst present in any particular instance can vary depending on desired product and the process conditions, but preferably it is present in
25 the reaction mixture in an amount within the range of about 0.01 to about 4 wt-% based on the total weight of organic and inorganic reactants. More preferably, the amount of catalyst present is in the range of about 0.1 to 2 wt-%. The oxazolidone product formed from the reaction of the
30 polyepoxide and polyisocyanate in the presence of a zinc halide catalyst typically contains less than about 0.2 wt-% of a zinc halide catalyst residue.

The term "oxazolidone compound" as used in this application includes both monomer or small molecule
35 compounds and polymers having repeating oxazolidone polymer

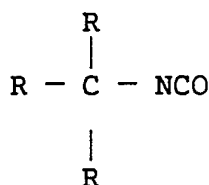
backbone structures or vinyl polymers with pendant oxazolidone groups. The general representation of an oxazolidone compound is shown above in Formula I.

The term "hindered organic isocyanate" as used herein and in the claims is taken to mean an organic compound containing one or more isocyanate groups (-NCO) wherein the nitrogen atom of the isocyanate compound is directly attached to a tertiary carbon atom. The tertiary carbon atom can be a carbon atom in an aliphatic group and can also be an aliphatic ring carbon atom. These aliphatic carbon atoms can also be substituents on aromatic ring systems. Non-limiting examples of such a tertiary bonded isocyanate group are shown in the following formulae:

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II(a)

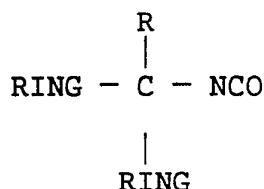
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II(b)

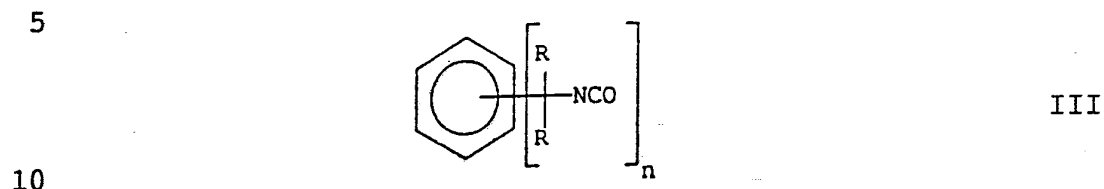
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wherein R is a C₁₋₁₂ alkyl, aryl, etc., group. The above formulae show the isocyanate group attached to a tertiary alkyl carbon, II(a), and within a ring system, II(b), having a tertiary carbon (the unfilled valences representing the ring). The tertiary carbon or ring carbon can be a portion of an inorganic compound having virtually any structure or substituent.

Hindered isocyanate compounds for use in this invention include aliphatic and aromatic compounds with a hindered

isocyanate substituent wherein the tertiary carbon is attached to an aromatic ring structure represented by the following formula (III):



wherein R is a C₁₋₁₂ alkyl, aryl, etc., group, the aromatic ring is merely a representation of a substituted ring or multiring system, and preferably n = 1-3.

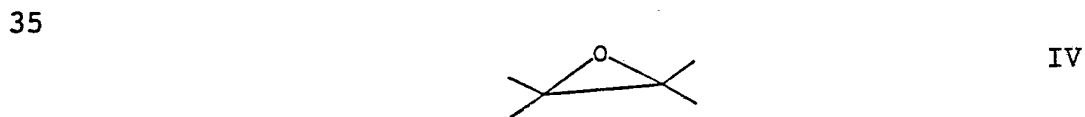
15 The preferred compounds are isocyanate compounds formed on aromatic ring structures wherein the hindered isocyanate group can be substituted meta, ortho, or para to a vinyl group or to a second hindered isocyanate group. Such compounds include hindered aromatic diisocyanate compounds

20 and vinyl-substituted hindered monoisocyanate aromatic monomers. Representative examples of the most preferred isocyanate compounds comprises m-TMI and m-TMXDI [known as 3-isopropenyl(α,α -dimethylbenzyl)isocyanate and 1,3-bis(α -isocyanatoisopropyl)benzene, respectively]. The isocyanate

25 compound referred to as m-TMXDI is also known as tetramethylxylenediisocyanate. Also beneficial and preferred would be the para isomers of these compounds, i.e., 4-isopropenyl(α,α -dimethylbenzyl)isocyanate and 1,4-bis-(α -isocyanatoisopropyl)benzene, respectively. Most

30 preferred are the hindered aromatic diisocyanate compounds.

The term "epoxy" as used herein and in the appended claims is taken to mean a compound containing one or more epoxy groups, i.e., oxirane rings, generally represented by the following formula (IV):



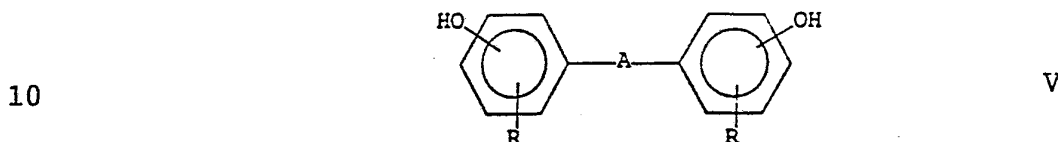
Useful epoxides can contain aromatic, aliphatic, or cycloaliphatic groups. They can be mono- or polyepoxides. Herein "poly-" functional compounds include within their scope difunctional compounds. Examples of useful monoepoxy compounds are phenyl glycidyl ether, allyl glycidyl ether, and epichlorohydrin. Suitable polyepoxides include the resinous reaction products of an epihalohydrin with, for example, bisphenol A (2,2-bis(4-hydroxyphenyl)propane), bisphenol F (bis(4-hydroxyphenyl)methane), or halogenated derivatives thereof. Such materials are available commercially under the tradenames DER™ and EPON™ from Dow Chemical Company and Shell Chemical Company, respectively.

Epoxide compounds with two or more epoxy groups define a preferred class of materials. Although some polyepoxides can have as many as 100 or more epoxy groups, it is more preferred that the functionality of the polyepoxide be relatively low, i.e., from about 2 to 10, and most preferably from about 2 to about 4. Epoxides with lower functionality are preferable and advantageous for certain applications because they typically give rise to less highly crosslinked polymers, which tend to have better physical and thermal properties as well as being more easily processed. For example, diepoxides are used in combination with diisocyanates to form linear thermoplastic polymers. A preferred group of diepoxides include the diglycidyl ethers of bisphenol A, bisphenol F, hydrogenated bisphenol A, butanediol, neopentylglycol, and mixtures thereof.

A useful group of epoxy compounds are aromatic in nature. These include, for example, glycidyl ethers of polyhydric mononuclear and fused-ring polynuclear phenols such as resorcinol, hydroquinone, pyrocatechol, saligenin, phloroglucinol, 1,5-dihydroxynaphthalene, 1,6-

dihydroxynaphthalene, 1,7-dihydroxynaphthalene, and the like.

This group of aromatic epoxy compounds also includes the glycidyl ethers of nonfused ring polynuclear phenols, which can be prepared from the reaction of epichlorohydrin or epibromohydrin and a nonfused-ring polynuclear phenol represented by the general formula (V):



wherein R represents 0 to 4 substituents selected from the class consisting of halogen and lower alkyl, and A is a bridging group selected from the class consisting of alkylene, substituted alkylene, carbonyl, ether, sulfide, sulfone, and a single covalent bond. Herein, "lower alkyl" means an alkyl group containing from one to six carbon atoms.

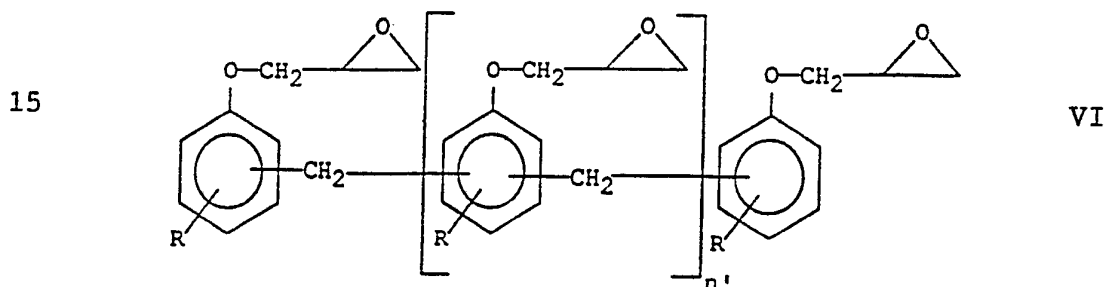
20 Typical examples of such nonfused-ring epoxy compounds are diglycidyl ethers of the following phenolic compounds:
 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxybiphenyl,
 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)methane
 (bisphenol F), 2,2-bis(4-hydroxyphenyl)butane (bisphenol
 25 B), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), 1,1-bis(4-hydroxyphenyl)propane, 3,3-bis(4-hydroxyphenyl)pentane, 2-(3-hydroxyphenyl)-2-(4-hydroxyphenyl)butane, 1-phenyl-1-(2-hydroxyphenyl)-1-(3-hydroxyphenyl)propane, 1-phenyl-1,1-bis(4-hydroxyphenyl)butane, 1-phenyl-1,1-bis(4-hydroxyphenyl)pentane, 1-tolyl-1,1-bis(4-hydroxyphenyl)ethane, bis(3-bromo-4-hydroxyphenyl)methane, 2,2-bis(3-bromo-4-hydroxyphenyl)propane, bis(3-bromo-4-hydroxyphenyl)diphenylmethane, 1,1-bis(3-bromo-4-hydroxyphenyl)-1-(2,5-dibromophenyl)ethane, bis(3,5-

30

35

dibromo-4-hydroxyphenyl)methane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, bis(3,5-dibromo-4-hydroxyphenyl)diphenylmethane, 1,1-bis(3,5-dibromo-4-hydroxyphenyl)-1-(2,5-dibromophenyl)ethane, bis(3-bromo-4-hydroxyphenyl)sulfone, bis(3,5-dibromo-4-hydroxyphenyl)sulfone.

The glycidyl ethers of novolac resins can also be used as the epoxy compound of the invention. The novolac resins are the products obtained by the acid condensation of phenol, or substituted phenol, with formaldehyde. The glycidyl ethers of such resins can be represented by the following general formula (VI):



20 wherein n' has an average value of about 0 to 20, preferably 1 to 12; R represents from 0 to 4 substituents each independently selected from halogen, lower alkyl, aryl, and aralkyl groups, and preferably selected from halogen and lower alkyl groups. The above formula is highly idealized and is an approximation only. The compounds are prepared by the condensation of formaldehyde with phenolic compounds. Such a preparation method provides a wide variety of branched/unbranched systems with a variety of differing molecular weights, all of which are approximately represented by the above standard representation in the art.

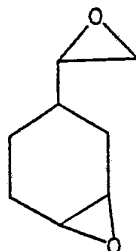
Furthermore, dicyclopentadiene dioxide epoxies can be used. Such materials have the following formula (VII):



VII

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Additionally, vinylcyclohexene dioxide, for example,
the compound having the formula (VIII):

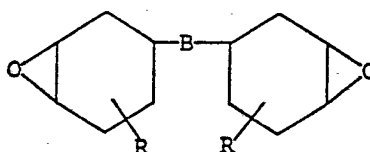


VIII

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15 can be used in the invention.

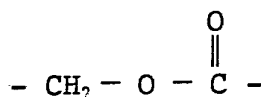
Dicyclohexyloxide carboxylates can also be used as the
epoxy compound of the invention. Such compounds are
represented by the general formula (IX):



IX

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wherein R in each instance represents from 0 to 9 lower
25 alkyl groups and B represents a divalent bridging radical
selected from the class consisting of the following formula
(X, XI, and XII):



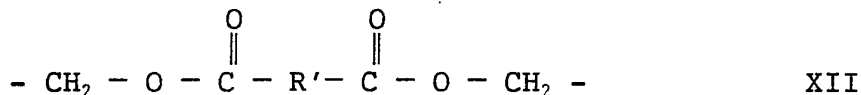
X

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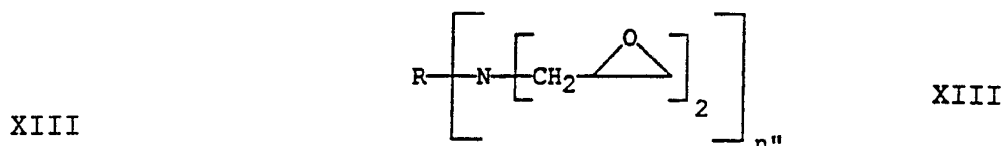


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wherein R' is selected from the class consisting of lower alkylene, lower oxyalkylene, arylene, etc. Examples of the
 15 dicyclohexyloxide carboxylates are 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl)maleate, bis(3,4-
 20 epoxycyclohexylmethyl)succinate, ethylene[bis(3,4-epoxy-6-methylcyclohexane carboxylate)], and the like.

The glycidyl derivatives of aromatic primary amines can be used as the epoxy compound of the invention. These compounds are represented by the following formula (XIII):

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wherein n'' is an integer of 1 to 3; R is an aromatic residue of valency n'' and is selected from the class consisting of aromatic residues such as phenyl, phenylene, diphenylene, etc. Illustrative of such compounds are the
 35 N,N-diglycidyl derivatives of aniline, 2,4-tolylene diamine, 2,6-tolylene diamine, m-phenylene diamine, p-phenylene diamine, 4,4'-diaminodiphenyl, 4,4'-diaminodiphenylmethane, 2,2-bis(4-aminophenyl)propane, 2,2-bis(4-aminophenyl)butane, 4,4'-diaminodiphenyl sulfate,

4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, and 1,5-diaminonaphthalene, and similar methylene bridged polyphenyl polyamines from about 35 wt-% to about 85 wt-% of methylene dianilines. The remaining part of said mixture consists of triamines and polyamines of higher molecular weight. Such polyamine mixtures are formed through the condensation reaction of aniline and formaldehyde.

As stated above, epoxide compounds with two or more epoxy groups define a preferred class of starting materials. With respect to functionality, aromatic epoxides define a preferred class of starting materials, and the glycidyl ethers of nonfused-ring polynuclear phenols define a more preferred class. Examples of this class are listed above.

The catalyst used in the present invention comprises a zinc halide (ZnX_2 , wherein $\text{X} = \text{Cl}, \text{Br}, \text{I}$). In the reaction of a hindered isocyanate and an epoxy, these catalysts efficiently produce substantially quantitative yields of an oxazolidone compound, without the formation of any significant amount of isocyanurate compounds. These catalysts, particularly ZnI_2 , make the oxazolidone preparation commercially feasible, at least in part because they are relatively safe to use, easily handled, and relatively economical. ZnI_2 is also preferred because it is the most widely useable of the catalysts in the formation of the oxazolidone monomers and polymers of the invention. For example, in the preparation of linear oxazolidone polymers, the solubility of ZnBr_2 in the epoxy-isocyanate reactant mixture generally needs to be considered for effective catalytic activity.

The zinc halides can also be generated in situ in the reaction mixture comprising the epoxy and isocyanate compounds. This is accomplished by the addition of a zinc compound and an appropriate number of equivalents of a

halide compound to the reaction mixture. The zinc and halide compounds react with sufficient rapidity to form a catalytic amount of zinc halide (ZnX_2) in situ before any substantial isocyanurate formation can occur. Useable zinc compounds include zinc acetate, zinc carbonate, zinc stearate, zinc naphthenate, zinc trifluoroacetate, zinc tetrafluoraborate, etc. Suitable halide compounds include, for example, potassium iodide, sodium iodide, copper (II) iodide, silver iodide, magnesium iodide, their respective bromide and chloride salts, etc. A particularly useful in situ combination is $\text{Zn}(\text{OAc})_2$ and KI. The relative amounts of halide compound and zinc compound can be easily determined using conventional reaction calculations.

The relative amounts of the hindered isocyanate and the epoxy can be calculated by knowledge of the number of active epoxy groups in the epoxy compound, the number of active isocyanate groups in the isocyanate compound, and the desired end result. That is, the relative proportions of the epoxide and hindered isocyanate employed typically control the type of product formed. For example, if a stoichiometric excess of the isocyanate is used, an isocyanate-terminated oxazolidone compound results. Furthermore, the molecular weight of the resultant polymer can be controlled by the relative amounts of the starting materials. The use of relatively equivalent amounts of the epoxide and hindered isocyanate is a means of providing higher molecular weight polyoxazolidones. In general, however, the reaction of the present invention is conducted at a ratio of about 0.2 to 20 equivalents of epoxy functionality per equivalent to -NCO functionality and in the presence of an effective catalytic amount of a zinc halide or in situ generated zinc halide compound.

Substantially Linear Polymers Prepared
Using the Oxazolidone Reaction

The preferred polyoxazolidone compounds of the invention are linear polymers made by reacting primarily
5 diepoxy compounds with hindered diisocyanate compounds. The diepoxy compounds and diisocyanate compounds are as described above. The linear oxazolidone polymer compounds of the invention can be prepared by simply mixing a diepoxy compound at elevated temperature with a hindered
10 diisocyanate compound in the presence of the ZnX_2 catalyst system. The quantity of zinc halide catalyst, e.g., the zinc iodide or in situ generated zinc iodide, employed can vary over a wide range depending on the process conditions. Preferably, the amount of catalyst is within the range of
15 about 0.01% to about 4% by weight of the combined organic and inorganic reactants. More preferably, about 0.1 to 2 wt-% of the catalyst is used. Preferably, the catalyst used in the preparation of linear oxazolidone polymers is ZnI_2 , at least in part because it is the most effective for
20 a wide variety of reactant mixtures.

The linear oxazolidone polymers can take the form of a viscous liquid or a solid depending on the molecular weight. Molecular weights of the invention can vary from about 400 to 5,000 or higher, with molecular weights of
25 about 500,000 possible. The polymeric compounds of the invention can be molded under heat and pressure as a thermoplastic or they can be further cured through the use of conventional curing, polymerization, or crosslinking agents. The cured polymeric compositions of the invention
30 are well suited for structural applications such as gears, bearings, tires, ball joint liners, heel lifts, and for insulating and cushioning foams, coatings including powder coatings, potting, and encapsulation.

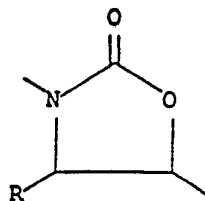
In the preparation of the linear oxazolidone polymers,
35 a diepoxy compound and a hindered diisocyanate compound of

the invention are preferably reacted at a ratio of about 0.2 to 5 equivalents of epoxy per equivalent of -NCO. More preferably, in the formation of the linear oxazolidone polymers, the hindered diisocyanate compound is reacted
5 with the diepoxy compound at a ratio of about 0.5 to 2 equivalents of epoxy per equivalent of -NCO.

Most preferably, approximately equimolar proportions of diepoxy and hindered diisocyanate compounds are used if a purely thermoplastic nonreactive material is desired. In
10 order to increase molecular weight, a stoichiometry of about 1:1 between the hindered diisocyanate and diepoxy compounds is used and the reaction is run for greater than about 2 hours at a temperature above 125°C.

The polymer reaction product is an alternating polymer
15 where the residues alternate between residues arising from the diepoxy compound with residues arising from the diisocyanate compound. The linear polymer can be represented by the formula: $(-A - R' - A - R'')_n$, wherein A is an oxazolidone residue having the formula (XIV):

20



XIV

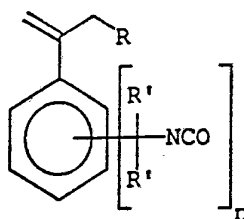
25 wherein R' is a residue derived from the hindered diisocyanate compound used in the formation of the oxazolidone and R'' comprises a residue derived from the diepoxy compound used in forming the oxazolidone; and wherein n is an integer of 1 to 1,000. The polymer
30 terminus can comprise either free epoxy or free isocyanate groups. Slight excesses of isocyanate compound or epoxy compound would tend to result in a majority of the polymers having isocyanate end groups or conversely an excess of epoxy end groups, respectively.

35

After the formation of the linear oxazolidone polymers is complete, the terminal -NCO or epoxy reactive functionality can be quenched using conventional reagents that can react and neutralize the reactive character of the functional group. Such reactions leave the linear oxazolidone polymer as a thermoplastic material which can be injected, formed into a film, sheet, pellet, extruded into a shaped extrusion, pultruded with a reinforcing fiber, or applied to any other typical thermoplastic end use.

Vinyl Monomers and Polymers
Containing Oxazolidone Residues

Vinyl monomers containing oxazolidone residues can be manufactured by the following reaction sequence. A vinyl monomer having hindered mono-, di-, or triisocyanate functionality of the formula (XV):



XV

wherein each R' is independently a C₁₋₆ alkyl, R is H or R', and n = 1-3, can be reacted with a mono- or polyepoxy (which includes diepoxy) compound to form a vinyl monomer having an oxazolidone moiety and one or more terminal vinyl groups. The vinyl monomer having hindered isocyanate functionality as depicted by Formula XV and the epoxy compound are combined at a ratio of about 0.8 to 1.2 equivalents of epoxy group per equivalent of isocyanate functionality. More preferably, the reactants are combined at a ratio of about 1 to 1 equivalents of epoxy functionality per equivalent of isocyanate functionality.

Preferred oxazolidone monomers are oxazolidone monomers prepared from aromatic vinyl monomers having one or two

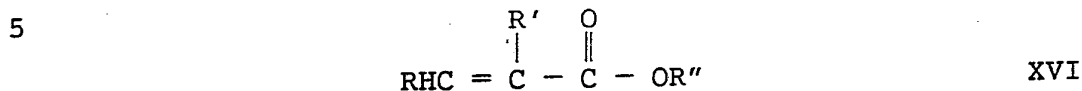
pendant hindered isocyanate groups. The more preferred oxazolidone-containing monomers are oxazolidone monomers prepared from aromatic vinyl monomers having a single pendant hindered isocyanate groups. Representative
5 examples of such a monomer are meta- and para-TMI, also known as 3-isopropenyl(α,α -dimethylbenzyl)isocyanate and 4-isopropenyl(α,α -dimethylbenzyl)isocyanate, respectively.

Such a hindered isocyanate compound is then reacted with an approximately equivalent amount of a mono- or
10 polyepoxy compound, such as phenyl glycidyl ether, allyl glycidyl ether, epichlorohydrin, diglycidyl ether of butanediol, among others as discussed above. Preferably, the monoisocyanate compound is reacted with a diepoxy compound selected from the group consisting of diglycidyl
15 ethers of bisphenol A, bisphenol F, hydrogenated bisphenol A, butanediol, neopentylglycol, or mixtures thereof. The resultant products are divinyl monomers containing oxazolidone functionality with terminal vinyl substituents. For structural representations of certain of these
20 compounds see Examples 6 and 7 below.

Such a reaction can also be repeated to generate a linear polyoxazolidone substituent on the vinyl monomer. The vinyl monomers formed using the above described chemistry can be combined in typical vinyl polymerization
25 chemistry to form vinyl polymers having oxazolidone or polyoxazolidone groups in the backbone. Such vinyl monomers and polymers are useful as crosslinking agents, polymerizable adhesion promoters, etc.

The vinyl polymers of the invention can be obtained by
30 polymerizing the oxazolidone-containing vinyl monomer with other vinyl monomers such as ethylene, propylene, styrene, acrylonitrile, vinyl acetate, vinyl chloride, maleic acid, acrylic acid, methacrylic acid, acrylamide, an ester of

α,β -unsaturated carboxylic acids and alcohols of the formula (XVI):



- 10 wherein R may be H, CH₃, C₂H₅; R' may be H or an alkyl group ranging from CH₃ to C₄H₉; and R'' may be derived from: (i) CH₃ to C₄H₉ straight chain alcohols; (ii) saturated or unsaturated cyclic alcohols containing up to 20 carbon atoms; (iii) C₃H₇ to C₁₆H₃₇ branched alkyl or C₅H₁₁ to C₂₂H₄₅ straight chain alkyl alcohols; and (iv) alkoxy or aryloxy alkyl alcohols, etc.

The esters formed with the straight chain alcohols defined above which are useful as hydrophobic monomers include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate or butyl methacrylate. Esters formed with saturated or unsaturated cyclic alcohols described above which are useful as hydrophobic monomers include cyclohexyl acrylate, cyclohexyl methacrylate, benzyl acrylate, benzyl methacrylate, isobornyl acrylate, isobornyl methacrylate, adamantyl acrylate, adamantyl methacrylate, furfuryl acrylate and furfuryl methacrylate. Esters of branched alkyl or straight chain higher alkyl alcohols described above which are useful as hydrophobic monomers include 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isobutyl acrylate, isobutyl methacrylate, isooctyl acrylate, isooctyl methacrylate, dodecylacrylate, dodecyl methacrylate, octadodecyl acrylate and octadodecyl methacrylate. Esters of alkoxy or aryloxy alkyl alcohols useful as hydrophobic monomers include methoxyethyl acrylate, methoxyethyl methacrylate, ethoxyethyl acrylate, ethoxyethyl methacrylate, propoxyethyl acrylate,

propoxyethyl methacrylate, butoxyethyl acrylate, butoxyethyl methacrylate, phenoxyethyl acrylate, and phenoxyethyl methacrylate.

Hydrophilic monomers can be copolymerized with the hydrophobic monomers described above in forming the copolymers. Suitable hydrophilic monomers include: (i) N-substituted acrylamides or methacrylamides; (ii) α,β -unsaturated carboxylic acids; and (iii) hydroxyalkyl acrylates and methacrylates and their homologs. N-substituted acrylamides or methacrylamides useful as hydrophilic monomers include diacetone acrylamide and its homologs as described in U.S. Patent No. 3,277,056, dimethyl acrylamide, butyl acrylamide, octyl acrylamide, and isobutyl methyl acrylamide. The α,β -unsaturated carboxyl acid hydrophilic monomers include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid.

The hydroxyalkyl acrylate and methacrylate hydrophilic monomers and their homologs include hydroxyethyl acrylate and methacrylate, diethylene glycol monoacrylate and monomethacrylate, triethylene glycol monoacrylate and monomethacrylate, polyethylene glycol monoacrylate and monomethacrylate of molecular weight up to 1000, linear or branched hydroxypropyl acrylate and methacrylate, dipropylene glycol monoacrylate and monomethacrylate, tripropylene glycol monoacrylate and monomethacrylate, tetrapropylene glycol monoacrylate and monomethacrylate, and polypropylene glycol monoacrylate and monomethylacrylate of molecular weight up to 1000.

Suitable solvents or carriers in which said hydrophobic and hydrophilic monomers may be polymerized include ethyl acetate, amyl acetate, butyl acetate, butyl cellosolve acetate, cellosolve acetate, methyl cellosolve acetate, acetone, methyl ethyl ketone, methyl isobutyl ketone, butyl

cellosolve, cellosolve, methyl cellosolve, ethyl alcohol, isopropyl alcohol, butyl alcohol, toluene, and xylene. Other solvents may also be used as carriers as will be appreciated by those skilled in the art. Suitable carriers may also include any one or a mixture of any of the foregoing solvents in any proportion.

Generally, the process for preparing the copolymer involves mixing the hydrophobic and hydrophilic monomers in a suitable solvent/carrier selected from those set forth hereinabove to form a uniform mixture, and inducing polymerization. Polymerization may be induced by conventional initiators such as peroxides and the like, or by irradiation or redox systems. Polymerization usually occurs at temperatures between about 0° C and 120° C, and preferably at the reflux temperature of the solvent/carrier.

Prepolymer Chemistry

Prepolymers useful in the oxazolidone systems of this invention comprise viscous liquid, semisolid and solid prepolymers. Typically these are made by first forming an isocyanate-terminated prepolymer comprising the reaction product of a polymeric polyol having at least two hydroxy (-OH) groups and the hindered polyisocyanate compound of the invention. Subsequently this isocyanate-terminated prepolymer is reacted with a polyepoxy compound to form an epoxy capped oxazolidone containing prepolymer.

In the reaction forming the isocyanate-terminated prepolymer there is greater than 1 (i.e.) about 1.1 to 5 equivalents of -NCO per equivalent of hydroxy functionality in the polymeric polyol. The reaction is typically carried out neat at an elevated temperature in the range of about 80° C to about 250° C for a period of time up to about 10 hours. In the reaction between the polyepoxy compound and the isocyanate-terminated prepolymer there is preferably greater than 1 (i.e.) about 1.1 to 10 equivalents of epoxy

functionality per equivalent of -NCO functionality. This reaction is carried out in the presence of a zinc halide catalyst under the reaction conditions outlined above for the isocyanate-epoxide reaction of the invention.

- 5 Polyhydroxy compounds suitable for forming the prepolymers of the invention are generally fluid compositions at room temperature and have a molecular weight and hydroxy functionality which will result in a prepolymer of manageable viscosity. Typically a suitable
10 polyhydroxy compound can have a molecular weight less than about 20,000 or typically less than 10,000, preferably in the range of 1,000 to 6,000, most preferably for reasons of reactivity viscosity controlling commercial availability of about 2,000 to 5,000. The hydroxy functionality of the
15 compounds typically range from about 2-4. The higher hydroxy functionalities can result in prepolymers of unacceptably high viscosity. We have found that brominated or phosphorylated polyols used alone or in combination with standard polyols can enhance flame resistant properties.
- 20 Preferred polyhydroxy compounds, i.e., polyols, include polyoxyalkylene compounds having at least two hydroxy groups in the molecule. Examples of such compounds are polyethylene glycols, polypropylene glycols, polytetramethylene glycols, polybutylene glycols,
25 polybutadiene diols and triols, low molecular weight hydroxy-containing polyesters, hydroxy-containing polyester amides, polyalkylene ether glycol compounds, hydroxy-containing oils, including tongue oil and their alkyl modifications, most preferred hydroxy-containing compounds
30 are polymeric diols or triols of a molecular weight resulting in the desired viscosity for the end product. The hindered isocyanate compounds and the epoxy compounds used for forming the prepolymers of this invention are recited above.

The epoxy-terminated oxazolidone-containing compounds, polymers, and prepolymers of the invention can be cured with typical epoxy reactive compounds. In the most typical situation, the epoxy compound reacts with a compound having
5 a free reactive hydrogen compound. The following examples of compositions are illustrative of this.

(1) Compositions can be prepared from an admixture which can comprise (a) an epoxy-terminated oxazolidone compound and (b) a polyfunctional amine, i.e., an amine
10 having at least two active amino hydrogen atoms which can be on the same nitrogen atom or different nitrogen atoms, preferably in an amount sufficient to provide between about 0.2 to 4.0 amino hydrogen atoms per epoxy group of said oxazolidone and preferably between about 0.5 to 2.0 amino
15 hydrogen atoms per epoxy group. Suitable polyfunctional amines include monoamines, diamines, triamines, and higher polyamines such as 2-ethylhexylamine, aniline, phenethylamine, cyclohexylamine, 2-aminohexanol, 1,3-diamino-2-propanol, ethylenediamine, butylenediamine,
20 xylylenediamine, hexamethylenediamine, dihexylenetriamine, diethylenetriamine, triethylenetetraamine, p,p'-sulfonyldiamine, p,p'-methylenedianiline, 4,4'-methylenedianiline, and the like.

(2) Curable compositions can be prepared from an
25 admixture which can comprise (a) an epoxy-terminated oxazolidone compound and (b) a polycarboxylic acid. Illustrative polycarboxylic acids which can be employed include aliphatic, aromatic, and cycloaliphatic polycarboxylic acids such as oxalic acid, malonic acid,
30 glutaric acid, maleic acid, suberic acid, citraconic acid, 1,2-cyclohexanedicarboxylic acid, phthalic acid, 1,8-naphthalenedicarboxylic acid, 3-carboxycinnamic acid, 1,2,4-butanetricarboxylic acid, 1,2,4-hexanetricarboxylic acid, 1,2,4-benzenetricarboxylic acid, and the like;
35 polycarboxy polyesters, i.e., polyesters containing more

than one carboxy group per molecule, such as polycarboxylic acids of the type exemplified above.

(3) Curable compositions can be prepared from an admixture which can comprise (a) an epoxy-terminated oxazolidone compound and (b) a polyol, i.e., an organic compound having at least two hydroxy groups which are alcoholic hydroxy groups, phenolic hydroxy groups, or both alcoholic and phenolic hydroxy groups, e.g., aliphatic and cycloaliphatic polyalcohols and polyhydric phenols. The polyol is employed in an amount which provides between about 0.2 and 4.0 active hydrogen-containing hydroxy equivalents per epoxy equivalent of said oxazolidone. The compositions can be further modified by incorporating therein a polycarboxylic acid compound such as those illustrated in Section (2) above. Typical polyols which can be employed include ethylene glycol, diethylene glycol, glycerol, polypropylene glycols, butanediol, triethanolamine, pentaerythritol, trimethylolethane bis(4-hydroxyphenyl)methane, inositol, sorbitol, trimethylol-phenol, resorcinol, pyrogallol, hydroquinone, 1,8-naphthalenediol, 2,4,6-trimethylolphenol allyl ether, cyclohexanediol, and the like.

(4) Curable compositions can be prepared from an admixture which can comprise (a) an epoxy-terminated oxazolidone compound and (b) a polycarboxylic acid such as those illustrated in Section (2) above in an amount sufficient to provide between 0.3 and 3.0 carboxy equivalents per epoxy equivalent of said isocyanate oxazolidone. A polyol of the type exemplified in Section (3) above can be employed to further modify the compositions. In these admixtures the polycarboxylic acid is a major component as compared with the polyol modifier.

(5) Curable compositions can be prepared from an admixture which can comprise (a) an epoxy-terminated oxazolidone and (b) any one of the following classes of

compounds, namely, polythiols such as the sulfur analogs of the polyols listed in Section (3) above, phenol-aldehyde condensates, urea-aldehyde condensates, melamine-aldehyde condensates, polyamines, polyamides, polycarboxylic acid halides, and the like.

(6) Curable compositions can be prepared from latent one component systems of epoxy-functional oxazolidones. This could include curing by heat, UV, or other means. Catalysts for heat curing include dicyandiamide, BF_3 -amine salts such as BF_3 -monoethylamine, imidazoles such as 2-ethyl-4-methylimidazole, benzyldimethylamine, bicyclic amidines, bicyclic amidine salts, and other quaternary amine salts such as benzyltriethylammonium chloride.

(7) Curable compositions can be prepared from an admixture which can comprise (a) an epoxy-terminated oxazolidone and (b) a diisocyanate or isocyanate prepolymer. The isocyanates could be TMXDI, MDI (4,4'-diphenylmethane diisocyanate), TDI (tolylene diisocyanate), IPDI (isophorone diisocyanate), etc.

The epoxy-terminated oxazolidone compounds and their cured resins exhibit excellent thermal properties, good chemical and solvent stability, and excellent toughness and flexibility. They can be used in functional materials such as adhesives, coatings, sealants, caulks, and structural laminates. In preparing such materials, the compositions can include additives such as fillers, thickeners, fibers, antioxidants, pigments, surfactants, etc.

The following examples further illustrate the invention and contain the best mode.

30

Example 1

Preparation of a Linear Oxazolidone Polymer Using Zinc Iodide

Into a 50 ml glass jar, having a screw-on lid, was placed about 9.5 parts by weight of a diglycidyl ether of bisphenol A (EPONTM 828) and 6.1 parts of 1,3-bis(α -

isocyanatoisopropyl)benzene (m-TMXDI, 0.05 equivalents) with 0.2 parts by weight of zinc iodide. The glass jar was sealed and placed in an oven at 200° C. After 15 minutes of reaction time, the contents of the glass jar showed an increase in viscosity. After 20 minutes the contents of the glass jar darkened, and after 35 minutes the contents showed a further increase in viscosity. Upon a further lapse of time, the viscosity of the contents of the glass jar did not appear to change.

10 The above reactants were mixed at a 1:1 molar ratio of -NCO to epoxy groups. A hard brittle solid formed. According to IR analysis, no residual -NCO nor epoxy functionality remained. The major feature of the IR was an absorbance band at 1750 cm⁻¹ to the carbonyl absorption of an oxazolidone ring. This evidence clearly indicates the stoichiometric conversion of the reactants forming a linear oxazolidone polymer in the absence of detectable levels of isocyanurate trimer.

Example 2

20 Comparative Example

Example 1 was repeated exactly except that 0.2 parts of a di-C₁₅-alkyldimethylammonium chloride was used in place of the 0.2 parts of zinc iodide. The contents of the glass jar showed no initial reaction and the product appeared to be only slightly thickened at the end of the reaction.

Example 3

Comparative Example

Example 1 was repeated exactly except that the 0.2 parts by weight of zinc iodide was replaced by 0.2 parts by weight of 2-ethyl-4-methylimidazole. After 20 minutes, the contents of the glass jar became a dark solid mass comprising a crosslinked epoxide and free m-TMXDI.

Example 4

Preparation of an Isocyanate-Terminated Prepolymer

35 Into a 2 liter reaction vessel equipped with a reflux

condenser, nitrogen gas inlet, mechanical stirrer, and thermometer was added 183.0 g of m-TMXDI (1.5 equivalents) and 266.0 g of Polymeg™ 1000 (polyethylene glycol, 0.52 equivalents). The reaction mixture was heated to 80° C and maintained at this temperature for 2 hours. At this time the reaction mixture had a measured % NCO of 10.34%.

Example 5

Preparation of an Oxazolidone from a Prepolymer

A 250 ml three-necked round bottom flask was equipped with a reflux condenser, an inert nitrogen gas inlet, a magnetic spin bar, and a thermometer. The flask was charged with 110 ml of dimethylformamide, 19.0 gm of a diglycidyl ether of bisphenol A (0.10 equivalents, EPON™ 828), 40.8 g (0.10 equivalents based on the -NCO content) of the prepolymer of Example 4, and 0.96 g (3.0 mM) of zinc iodide. The reaction mixture was heated to 140° C and maintained at that temperature for 3 hours 30 minutes. Upon cooling, the contents of the flask gelled to a solid mass.

An inspection of the infrared spectrum of the sample showed little or no absorption at 2270 cm⁻¹, which is characteristic of free isocyanate, and a weak absorption at 910 cm⁻¹, which indicates a substantial absence of epoxy functionality. A strong absorption centered at about 1751 cm⁻¹ was observed, which indicates the presence of substantial quantities of oxazolidone functionality.

Example 6

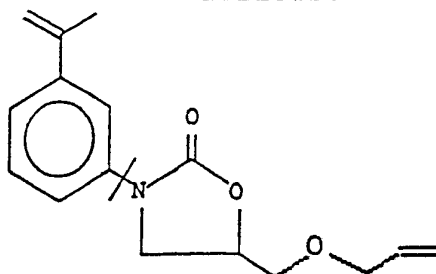
Preparation of an Oxazolidone-Containing Vinyl Monomer

Into a 50 ml glass jar equipped with a screw-on lid was placed 6.04 g 3-isopropenyl(α,α -dimethylbenzyl)isocyanate (m-TMI, 30 mM), 3.42 g allyl glycidyl ether (30 mM), and 0.1 g of zinc iodide. The jar was sealed and placed in an oven and heated for 2 hours at 125° C. At the end of the period, the material in the jar was a viscous liquid at

room temperature. The infrared spectrum taken of the material in the jar showed a complete absence of -NCO and the presence of only minor amounts of epoxy functionality. The proposed structure is as follows:

5

10



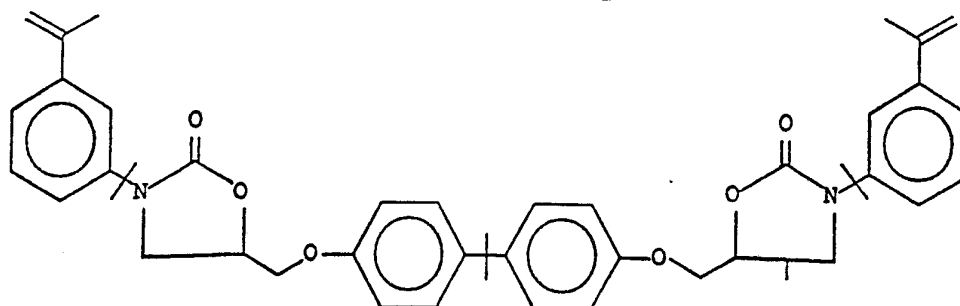
Example 7

Preparation of a Vinyl Monomer Containing Oxazolidone Functionality

Into a 50 ml glass jar equipped with a screw-on lid was placed a 5.0 g of 3-isopropenyl(α,α -dimethylbenzyl)isocyanate (m-TMI, 0.05 M) and 8.8 g of a diglycidyl ether of bisphenol A (EPON[™] 825, 0.025 M) and 0.05 g of zinc iodide. The jar was sealed and placed into an oven and heated for 2 hours at 125° C. The material in the jar was semisolid at the end of the period, having a softening point between 30° C and 50° C. An infrared analysis of the reaction mixture indicated the presence of epoxy functionality and oxazolidone functionality with a substantial absence of residual isocyanate. The proposed structure of the resulting reaction product is as follows:

30

35



Example 8

Comparative Example: Preparation of a Linear Oxazolidone Using a Nonhindered Isocyanate

Into a 50 ml glass jar equipped with a screw-on lid was

placed 5.16 g of a diglycidyl ether of bisphenol A (EPON™ 825, 0.03 equivalents), 3.75 g of 4,4'-diphenylmethane diisocyanate (MONDUR™ M available from Mobay Chemicals, 0.03 equivalents), and 0.1 g zinc iodide. The jar was
5 sealed and placed in an oven at 125° C for 2 hours. Upon cooling, the material was a viscous liquid.

Upon inspection of the reaction product by infrared analysis, a small amount of oxazolidone formation was shown by the presence of a weak absorption at 1755 cm⁻¹, a very
10 incomplete reaction due to the presence of a strong absorption at 2274 cm⁻¹ due to the presence of substantial unreacted isocyanate. However, more significantly, substantial amounts of isocyanurate was formed as shown by the strong absorption at 1710 cm⁻¹.

15 Example 9

Comparative Example: Preparation of Linear Oxazolidones Using Various Catalysts

Example 1 was repeated using the catalyst, epoxy, and hindered isocyanate as shown in the Table 1. The results
20 of the reactions are shown in the last column.

The results of the various experiments shown in this example indicate that certain compounds, as for example some tetraalkyl ammonium halide materials, have some activity in promoting the reaction between the hindered
25 isocyanate and an epoxy compound to form an oxazolidone compound. However, these compounds do not catalyze the reaction at an efficient enough rate for commercial feasibility when compared to the zinc halide compounds, particularly ZnI₂.

30 It is also noted that the zinc halide catalysts generally need to be relatively soluble in the reactant mixture for best results. This is illustrated in an example in Table 1 in which ZnBr₂ was used. Although ZnBr₂ is effectively and advantageously used in many systems, it

is believed that it was not soluble enough in the reactant mixture of EPON™ 828 and m-TMXDI to affect curing.

Table 1

Catalyst	Amount	EPON™ 828	m-TMXDI	Results
LiCl	0.20	9.40	6.10	No Curing (NC)
KBr	0.20	9.40	6.10	NC
5 BTEAC ¹	0.20	9.40	6.10	Cured to a
Solid				
Zn(acac) ₂ ²	0.20	9.40	6.10	NC
Fe(acac) ₃	0.20	9.40	6.10	NC
Cu(acac) ₂	0.20	9.40	6.10	NC
10 Ni(acac) ₂	0.20	9.40	6.10	NC
ZnO ₂ ³	0.10	5.00	4.40	NC
15 NiO ₂	0.10	5.00	4.40	NC
Sodium Acetate	0.20	9.40	6.10	NC
KI	0.20	9.40	6.10	NC
20 AlCl ₃	0.20	9.40	6.10	NC
V(acac) ₂	0.20	9.40	6.10	NC
Cr(acac) ₂	0.20	9.40	6.10	NC
Co(acac) ₃	0.20	9.40	6.10	NC
25 Mn(acac) ₂	0.20	9.40	6.10	NC
Triphenyl Phosphine	0.20	9.40	6.10	NC
Co(acac) ₂	0.20	9.40	6.10	NC
Tetra(t-butyl)	0.20	9.40	6.10	NC
phosphonium bromide	0.20	9.40	6.10	Some Thickening
30				

1 Benzyltriethylammonium chloride

2 Acetylacetonate (CH₃COCH₂CO⁻)

3 Substituted DER™ 332 and m-TMI for EPON™ 828 and m-TMXDI.

<u>Catalyst</u>	<u>Amount</u>	<u>EPON™ 828</u>	<u>m-TMXDI</u>	<u>Results</u>
ZnCl ₂	0.20	9.40	6.10	Very Thick
KIO ₃	0.20	9.40	6.10	NC
5 NiCl ₂	0.20	9.40	6.10	NC
CuCl	0.20	9.40	6.10	NC
FeCl ₂	0.20	9.40	6.10	Thick
ZnSO ₄	0.20	9.40	6.10	NC
CaCl ₂	0.20	9.40	6.10	Slight
10 Thickening				
CuSO ₄	0.20	9.40	6.10	NC
MnO ₂	0.20	9.40	6.10	NC
ALK(SO ₄) ₂	0.20	9.40	6.10	NC
FeCl ₃	0.20	9.40	6.10	Very Thick
15 Fe ₂ (SO ₄) ₃	0.20	9.40	6.10	NC
MgSO ₄	0.20	9.40	6.10	NC
PdCl	0.20	9.40	6.10	NC
20 ZnBr ₂	0.20	9.40	6.10	NC
Zn(OAc) ₂	0.20	9.40	6.10	NC
Tetra Ethyl Ammonium Bromide	0.20	9.40	6.10	NC
25 Tetra Methyl Ammonium Bromide	0.20	9.40	6.10	NC
Tetra Methyl Ammonium Chloride	0.20	9.40	6.10	NC
Tetra Ethyl Ammonium Iodide	0.20	9.40	6.10	NC
Tetra Butyl Ammonium Iodide	0.20	9.40	6.10	Thickening
Tetra Butyl Ammonium Bromide	0.20	9.40	6.10	Thick, No Flow
30 Tetra Butyl Ammonium Chloride	0.20	9.40	6.10	Solid
Tetra Ethyl Ammonium Chloride-hydrate	0.20	9.40	6.10	Solid
35 LiBr	0.15	9.40	6.10	EPON™ & EPON™/ TMXDI Reaction

Example 10Preparation of an Isocyanate-Terminated Prepolymer

Into a 2 liter reaction vessel equipped with a reflux condenser, a nitrogen gas inlet, a mechanical stirrer, and
5 a thermometer was added 1001.8 g of PEG™ 1000 (polyethylene glycol, 2.0 equivalents) and 488.6 g of m-TMXDI (4.0 equivalents). The reaction mixture was heated to 170° C and maintained there until the % NCO reached 5.3% (approximately 2 hours).

10

Example 11Preparation of an Oxazolidone
from an Isocyanate-Terminated Prepolymer

Into a 1 liter reaction vessel equipped with a reflux condenser, a nitrogen gas inlet, a mechanical stirrer, and
15 a thermometer was added 200 g of the prepolymer made in Example 10 (0.253 equivalents) and 200 g of Epon™ 828 (1.064 equivalents). Following this, 1.74 g of a 3:2 (w/w) mixture of KI and Zn(OAc)₂ (0.0032 equivalents) was added. The reaction mixture was heated to 150° C and maintained at
20 that temperature until the epoxy equivalent weight reached 470 (approximately 2 hours).

Example 12Preparation of an Oxazolidone
from an Isocyanate-Terminated Prepolymer

25 Into a 1 liter reaction vessel equipped with a reflux condenser, a nitrogen gas inlet, a mechanical stirrer, and a thermometer was added 200 g of the prepolymer made in Example 10 (0.253 equivalents) and 200 g of Epon™ 828 (1.064 equivalents). To this was added 1.23 g of a 2:3
30 (w/w) mixture of KI and Zn(OAc)₂·2H₂O (0.0016 equivalents of KI and 0.0032 equivalents of Zn(OAc)₂·2H₂O). The reaction mixture was heated to 150° C and maintained there until the epoxy equivalent weight reached 484 (approximately 2 hours).

35

Example 13Preparation and Testing of an Adhesive Formulation
Using an Epoxy-Terminated Oxazolidone

An isocyanate-terminated prepolymer was formed by
5 charging a two liter reaction kettle with 1101.44 g of
Terathane™ 2900 (1470 equivalent weight, 0.75 equivalents,
a polyol available from duPont) and 183.23 g of m-TMXDI
(122.15 equivalent weight, 1.50 equivalents, available from
American Cyanamid). The mixture was stirred under an
10 atmosphere of nitrogen. The temperature was increased to
350° F (177° C) and maintained at that temperature for two
hours. At this time the % NCO was 2.57% (theoretical =
2.45%).

An epoxy-terminated oxazolidone was formed using 850 g
15 of this prepolymer (0.50 equivalents), 850 g of EPON™ 828
(188 equivalent weight, 4.52 equivalents), and 2.04 g ZnI₂
(319.18 equivalent weight, 0.0064 equivalents). These
components were charged into a two liter reaction kettle
and stirred under nitrogen. The material was heated to
20 150° C and held at that temperature for 4 hours. At that
time an IR scan showed no residual -NCO.

The following adhesive formulations were prepared using
this epoxy-terminated oxazolidone and using standard curing
procedures. All amounts are in grams. Cab-O-Sil™ M-5 is a
25 fumed silica, which is used as a thickener, and is
available from Cabot Corporation. The adhesive
formulations were used to bond chromic acid etched 2024-T3
aluminum by curing at 350° F (177° C) for 2 hours. Single
lap shear results at room temperature (performed according
30 to ASTM D-1002 procedure) are also provided in Table 3.

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Table 2

<u>Material</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Epoxy Oxazolidone	2.98	1.75	4.65	2.92
EPON™ 828	7.08	8.25	5.35	6.87
5 Dicyandiamide	0.64	0.46	0.38	0.46
Cab-O-Sil™ M-5	0.30	0.30	0.30	0.30

Table 3

<u>Formulation</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
10 Lap Shear (p.s.i.)	3390	3300	1620	2990

The above specification, Examples, and data provide a description of the invention as it is currently understood.

15 However, since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention is embodied in the claims hereafter appended.

WE CLAIM:

1. A linear polymer comprising a polymer sequence having alternating residues derived from a reaction between a hindered diisocyanate compound and a diepoxy compound, wherein the linear polymer is substantially free of an isocyanurate, a biuret or an allophanate reaction by-product.

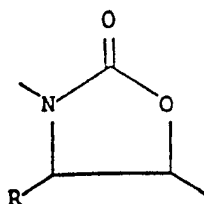
2. The linear polymer of claim 1 wherein for each -NCO equivalent of the hindered diisocyanate compound there is about 0.2 to 5 epoxy equivalents of the diepoxy compound.

3. The linear polymer of claim 1 wherein there are approximately equimolar proportions of hindered diisocyanate compound and diepoxy compound.

4. The linear polymer of claim 3 wherein the diepoxy compound comprises a diglycidyl ether of (i) bisphenol A, (ii) bisphenol F, (iii) hydrogenated bisphenol A, (iv) butanediol, (v) neopentylglycol, or (vi) mixtures thereof.

5. The linear polymer of claim 4 wherein the hindered diisocyanate compound comprises 1,3-bis-($\dot{A}$ -isocyanatoisopropyl)benzene or 1,4-bis-($\dot{A}$ -isocyanatoisopropyl)benzene.

6. The linear polymer of claim 4 comprising a polymer sequence of the formula: $(-A - R' - A - R'')_n$, wherein A is an oxazolidone residue having the formula:



wherein R' comprises a residue derived from a hindered diisocyanate compound used in the formation of the oxazolidone and R'' comprises a residue derived from a

diepoxy compound used in forming the oxazolidone; and wherein n is an integer of 1 to 1,000.

7. The linear polymer of claim 3 having a molecular weight of about 400 to 500,000.

5 8. The linear polymer of claim 1 wherein the reaction by-product comprises isocyanate and there is less than about 1 wt-% of the isocyanurate compound.

9. The linear polymer of claim 1 wherein the reaction product contains less than about 2 wt-% of a zinc halide catalyst residue.

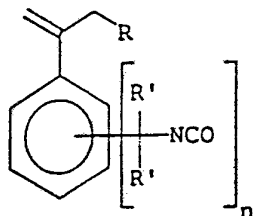
10. The linear polymer of claim 1 wherein the hindered diisocyanate compound comprises an aromatic diisocyanate.

11. The linear polymer of claim 10 wherein the hindered diisocyanate compound comprises 1,3-bis-($\bar{A}$ -isocyanatoisopropyl)benzene.

12. A vinyl monomer composition comprising a reaction product of:

(a) a hindered isocyanate compound of the formula:

20



25 wherein each R' is independently a C₁₋₆ alkyl, R is H or R', and n = 1-3; and

(b) an epoxy compound;

wherein the reaction product is substantially free of an isocyanurate, a biuret or an allophanate reaction by-

30 product.

13. The vinyl monomer of claim 12 wherein the reaction product is formed at a ratio of about 0.8 to 1.2 equivalents of epoxy group per equivalent of isocyanate.

14. The vinyl monomer of claim 12 wherein the reaction product is formed using a mono-isocyanato compound and a

35

diepoxy compound and the reaction product is formed at a ratio of about 1 equivalent of epoxy functionality per equivalent of isocyanate functionality.

15 15. The vinyl monomer of claim 14 wherein the epoxy compound is selected from the group consisting of a diglycidyl ether of (i) bisphenol A, (ii) bisphenol F, (iii) hydrogenated bisphenol A, (iv) butanediol, (v) neopentylglycol, and (vi) mixtures thereof.

10 16. The vinyl monomer of claim 12 wherein the reaction by-product is isocyanate and there is less than about 1 wt-% of isocyanurate compound.

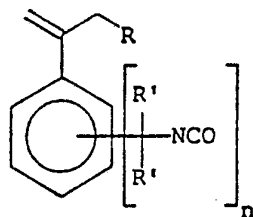
17. The vinyl monomer of claim 12 wherein the reaction product is formed in the presence of less than about 4 wt-% zinc halide.

15 18. The vinyl monomer of claim 12 wherein the reaction product is formed in the presence of less than about 2 wt-% zinc iodide.

19. The vinyl monomer of claim 12 wherein the vinyl monomer having hindered isocyanate functionality comprises
20 a vinyl monomer having a single pendant hindered isocyanate group.

20. A vinyl polymer composition comprising a reaction product of:

25 (a) a hindered isocyanate compound of the formula:



30 wherein each R' is independently a C₁₋₆ alkyl, R is H or R', and n = 1-3;

(b) an epoxy compound, wherein the reaction product is substantially free of an isocyanurate, a
35 biuret or an allophanate reaction by-product; and

(c) a vinyl monomer.

21. The vinyl polymer composition of claim 20 wherein the vinyl monomer is of the formula:



wherein R may be H, CH₃, C₂H₅; R' may be H or an alkyl group ranging from CH₃ to C₄H₉; and R'' may be derived from:

- 10 (a) H, CH₃- to C₄H₉-;
- (b) saturated or unsaturated cyclic alcohols containing up to 20 carbon atoms;
- (c) C₃H₇ to C₁₆H₃₇ branched alkyl or C₅H₁₁ to C₂₂H₄₅ straight chain alkyl alcohols; and
- 15 (d) alkoxy or aryloxy alkyl alcohols.

22. The vinyl polymer of claim 20 wherein the vinyl monomer having hindered isocyanate functionality comprises a vinyl monomer having a single pendant hindered isocyanate group.

20 23. An epoxy-terminated oxazolidone prepolymer comprising the reaction product of:

- (a) an isocyanate-terminated prepolymer comprising the reaction product of:
- (i) a hindered polyisocyanate compound; and
- 25 (ii) a polymeric polyol compound having at least two hydroxy groups; and
- (b) a polyepoxy compound.

24. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein the hindered polyisocyanate compound is a

30 hindered diisocyanate compound.

25. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein the polyol comprises a polyoxyalkylene compound.

26. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein the polyepoxy compound comprises a diepoxy compound.

27. The epoxy-terminated oxazolidone prepolymer of
5 claim 26 wherein the diepoxy compound comprises a diglycidyl ether of (i) bisphenol A, (ii) bisphenol F, (iii) hydrogenated bisphenol A, iv) butanediol, (v) neopentylglycol, or (vi) mixtures thereof.

28. The epoxy-terminated oxazolidone prepolymer of
10 claim 26 wherein in the reaction forming the isocyanate-terminated prepolymer there is about 1.1 to 5 equivalents of -NCO per equivalent of hydroxy group in the polymeric polyol.

29. The epoxy-terminated oxazolidone prepolymer of
15 claim 26 wherein in the reaction between the polyepoxy compound and the isocyanate-terminated prepolymer there is about 1.1 to 10 equivalents of epoxy functionality per equivalent of -NCO functionality.

30. A process for the manufacture of oxazolidone
20 compounds comprising the reaction of an epoxy compound and a hindered isocyanate compound wherein the reaction is conducted at a ratio of about 0.2 to 20 equivalents of epoxy functionality per equivalent to -NCO functionality and in the presence of an effective catalytic amount of a
25 zinc halide or in situ generated zinc halide compound.

31. The process according to claim 30 wherein the zinc halide is preferably zinc iodide.

32. The process according to claim 30 wherein the reaction is carried out in the melt.

30 33. The process according to claim 32 wherein the reaction is carried out at a temperature of about 80½ C to about 250½ C.

AMENDED CLAIMS

[received by the International Bureau on 15 June (15.06.92);
original claims 6 and 13 deleted; original claims 8,12,
14,16,19-22,28 and 29 amended; remaining claims unchanged (6 pages)]

1. A linear polymer comprising a polymer sequence
5 having alternating residues derived from a reaction between
a hindered diisocyanate compound and a diepoxy compound,
wherein the linear polymer is substantially free of an
isocyanurate, a biuret or an allophanate reaction by-
product.
- 10 2. The linear polymer of claim 1 wherein for each -
NCO equivalent of the hindered diisocyanate compound there
is about 0.2 to 5 epoxy equivalents of the diepoxy
compound.
3. The linear polymer of claim 1 wherein there are
15 approximately equimolar proportions of hindered
diisocyanate compound and diepoxy compound.
4. The linear polymer of claim 3 wherein the diepoxy
compound comprises a diglycidyl ether of (i) bisphenol A,
(ii) bisphenol F, (iii) hydrogenated bisphenol A, (iv)
20 butanediol, (v) neopentylglycol, or (vi) mixtures thereof.
5. The linear polymer of claim 4 wherein the hindered
diisocyanate compound comprises 1,3-bis-(α -
isocyanatoisopropyl)benzene or 1,4-bis-(α -
isocyanatoisopropyl)benzene.
- 25 7. The linear polymer of claim 3 having a molecular
weight of about 400 to 500,000.
8. The linear polymer of claim 1 which comprises less
than about 1 wt-% of an isocyanurate compound.

9. The linear polymer of claim 1 wherein the reaction product contains less than about 2 wt-% of a zinc halide catalyst residue.

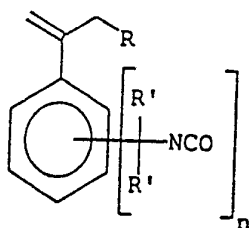
5 10. The linear polymer of claim 1 wherein the hindered diisocyanate compound comprises an aromatic diisocyanate.

11. The linear polymer of claim 10 wherein the hindered diisocyanate compound comprises 1,3-bis-(α -isocyanatoisopropyl)benzene.

10 12. A vinyl monomer composition comprising a reaction product of:

(a) a hindered isocyanate compound of the formula:

15



wherein each R' is independently a C₁₋₆ alkyl, R is H or
20 R', and n = 1-3; and

(b) a polyepoxy compound;

wherein the reaction product has epoxy functionality and is substantially free of an isocyanurate, a biuret or an allophanate reaction by-product.

25 14. The vinyl monomer of claim 12 wherein the reaction product is formed using a mono-isocyanato compound and a diepoxy compound.

15. The vinyl monomer of claim 14 wherein the epoxy compound is selected from the group consisting of a diglycidyl ether of (i) bisphenol A, (ii) bisphenol F,
5 (iii) hydrogenated bisphenol A, (iv) butanediol, (v) neopentylglycol, and (vi) mixtures thereof.

16. The vinyl monomer of claim 12 which comprises less than about 1 wt-% of an isocyanurate compound.

17. The vinyl monomer of claim 12 wherein the reaction
10 product is formed in the presence of less than about 4 wt-% zinc halide.

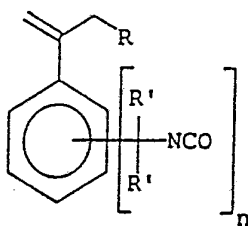
18. The vinyl monomer of claim 12 wherein the reaction product is formed in the presence of less than about 2 wt-% zinc iodide.

15 19. The vinyl monomer of claim 12 wherein n is 1.

20. A vinyl polymer composition comprising a reaction product of:

(a) a hindered isocyanate compound of the formula:

20



25 wherein each R' is independently a C₁₋₆ alkyl, R is H or R', and n = 1-3;

(b) a polyepoxy compound; and

(c) a vinyl monomer; wherein the reaction product has epoxy functionality and is substantially free of an isocyanurate, a biuret or a allophanate reaction by-product.

21. The vinyl polymer composition of claim 20 wherein the vinyl monomer is of the formula:



wherein R may be H, CH₃, or C₂H₅; R' may be H or an alkyl group ranging from CH₃ to C₄H₉; and R'' may be derived from:

- (a) H, CH₃- to C₄H₉-;
- (b) saturated or unsaturated cyclic alcohols containing up to 20 carbon atoms;
- (c) C₃H₇ to C₁₆H₃₇ branched alkyl or C₅H₁₁ to C₂₂H₄₅ straight chain alkyl alcohols; or
- (d) alkoxy or aryloxy alkyl alcohols.

22. The vinyl polymer composition of claim 20 wherein n is 1.

23. An epoxy-terminated oxazolidone prepolymer comprising the reaction product of:

- (a) an isocyanate-terminated prepolymer comprising the reaction product of:
 - (i) a hindered polyisocyanate compound; and
 - (ii) a polymeric polyol compound having at least two hydroxy groups; and

(b) a polyepoxy compound.

24. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein the hindered polyisocyanate compound is a
5 hindered diisocyanate compound.

25. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein the polyol comprises a polyoxyalkylene compound.

26. The epoxy-terminated oxazolidone prepolymer of
10 claim 23 wherein the polyepoxy compound comprises a diepoxy compound.

27. The epoxy-terminated oxazolidone prepolymer of claim 26 wherein the diepoxy compound comprises a diglycidyl ether of (i) bisphenol A, (ii) bisphenol F,
15 (iii) hydrogenated bisphenol A, iv) butanediol, (v) neopentylglycol, or (vi) mixtures thereof.

28. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein in the reaction forming the isocyanate-terminated prepolymer there is about 1.1 to 5 equivalents
20 of -NCO per equivalent of hydroxy group in the polymeric polyol.

29. The epoxy-terminated oxazolidone prepolymer of claim 23 wherein in the reaction between the polyepoxy compound and the isocyanate-terminated prepolymer there is
25 about 1.1 to 10 equivalents of epoxy functionality per equivalent of -NCO functionality.

30. A process for the manufacture of oxazolidone compounds comprising the reaction of an epoxy compound and a hindered isocyanate compound wherein the reaction is
5 conducted at a ratio of about 0.2 to 20 equivalents of epoxy functionality per equivalent to -NCO functionality and in the presence of an effective catalytic amount of a zinc halide or in situ generated zinc halide compound.

31. The process according to claim 30 wherein the zinc
10 halide is preferably zinc iodide.

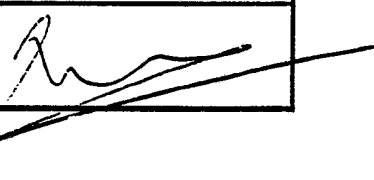
32. The process according to claim 30 wherein the reaction is carried out in the melt.

33. The process according to claim 32 wherein the reaction is carried out at a temperature of about 80° C to
15 about 250° C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/09436

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08G18/00; C08G18/76; C08G18/81; C08G18/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,4 879 365 (PETSCHKE ET AL) 7 November 1989 see column 3, line 1 - column 6, line 47; claims 1-3 ---	1-11, 23-29
A	EP,A,0 237 997 (TAKEDA) 23 September 1987 see page 5, line 30 - page 6, line 52; claim 2; example 1 ---	1-5
A	US,A,3 960 813 (RUSSELL ET AL) 1 June 1976 see claims 1-6 ---	9,17,30
A	EP,A,0 269 853 (AMERICAN CYANAMID) 8 June 1988 & US,A,4 731 428 15 March 1988 cited in the application ---	1-33
¹⁰ 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 document 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 "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. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 APRIL 1992	27. 04, 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BOURGONJE A. F. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9109436
SA 55979

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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US-A-4731428	15-03-88	EP-A, B 0269853	08-06-88
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