



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <p>(51) International Patent Classification <sup>4</sup> :<br/><b>C08G 18/00, 73/06, 59/40</b></p>   | <p><b>A1</b></p> | <p>(11) International Publication Number: <b>WO 85/ 05367</b><br/>(43) International Publication Date: 5 December 1985 (05.12.85)</p>   |
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| <p>(54) Title: THERMOSETTING RESIN COMPOSITIONS</p>  |                  |   |
| <p>(57) Abstract</p> <p>A method of preparing an oxazolidone polymer which comprises reacting a vicinal polyepoxide having a functionality of greater than 1 with an organic polyisocyanate or polyisothiocyanate, in the presence of a catalyst comprising an s-triazine compound or a derivative thereof, at a temperature between 20°C and 250°C. The catalyst is preferably hexamethylene tetramine.</p>   |                  |   |

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THERMOSETTING RESIN COMPOSITIONS

This invention relates to a method of curing a thermosetting resin composition into an oxazolidone polymer.

Oxazolidone polymers are well known in the art. They are usually prepared by reacting an isocyanate or isothiocyanate with a vicinal epoxide in the presence of a catalyst. The catalysts which has been used in the past include alkali metal halides, tertiary amines, and quaternary ammonium halides (eg tetraethyl ammonium bromide) as described in, for example, US Patent No. 3,020,262. More recently, catalysts consisting of phosphonium salts (US Patent No. 3,687,897) and magnesium halide/phosphine oxide complexes (US Patent No. 3,905,945) have been employed.

Many of the catalysts which have previously been employed have not favoured the production of the preferred oxazolidone structure over the production of the isocyanurate/isothiocyanurate structure in the resulting polymer, and in certain cases have catalysed the production of polymers containing hydrophilic groupings which are undesirable in the formation of polymers required to be water resistant.

It has previously been shown that the oxazolidone content of a poly (oxazolidone/isocyanurate) polymer may be increased by increasing the molar proportion of isocyanate in the starting composition used to produce the polymer. However, this leads to an increase in the brittleness of the polymer produced. The molar ratio of epoxy : isocyanate in the starting composition is preferably kept reasonably close to unity in order to avoid an increase in brittleness.

It is an object of the present invention to provide a method of preparing an oxazolidone polymer in the presence of a catalyst which favours the formation of an oxazolidone rather than an isocyanurate structure in the resulting polymer.

Accordingly, the present invention provides a method of preparing an oxazolidone polymer which comprises reacting a vicinal polyepoxide having a functionality greater than 1 with an

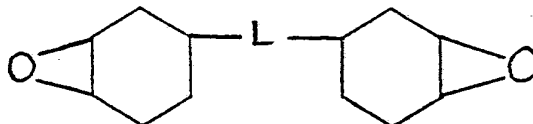
organic polyisocyanate or polyisothiocyanate, in the presence of a catalyst comprising an aliphatic s-triazine compound or an aliphatic derivative thereof, at a temperature between 20°C and 250°C.

The vicinal polyepoxide compound and the polyisocyanate or polyisothiocyanate compound may be any suitable compounds which are known to react together to give an oxazolidone polymeric structure.

Preferred polyepoxides include compounds containing a di- or poly-glycidyl grouping. For example, they include polyglycidyl ethers of polyhydric alcohols, such as Bisphenol A. They may also be polyglycidyl ethers of ethylene glycol, 1,2-propylene glycol, 1,2-butylene glycol, 1,5-pentanediol, 2,4,6-hexanetriol, glycerol and trimethylolpropane.

Polyglycidyl esters of polycarboxylic acids such as oxalic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, phthalic acid, isophthalic acid, terephthalic acid, 2,5-naphthalene dicarboxylic acid and dimerised linolenic acid may be employed as the polyepoxide. Examples include diglycidyl adipate and diglycidyl phthalate.

Other examples include polyepoxides derived from the epoxidation of olefinically unsaturated aliphatic compounds, polyepoxides of organic amines, eg a tetraglycidyl substituted 4,4'-diaminodiphenyl-methane, and dialicyclic compounds of the general formula:



where L is a simple linkage group such as  $\text{CH}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{CO}$ ,  $\text{COO}$ ,  $\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{OCH}_2$ ,  $\text{CH}_2\text{CO}$ ,  $\text{CH}_2\text{OCO}$  and  $\text{CH}_2\text{COO}$ .

Although the polyepoxide preferably does not contain high concentrations of secondary groups which react with isocyanates or isothiocyanates, (eg hydroxy groups), the polyepoxide may be

selected from prepolymers which contain terminal epoxy and secondary, non-terminal hydroxy groups, as described in US Patent No. 4,386,191, for example.

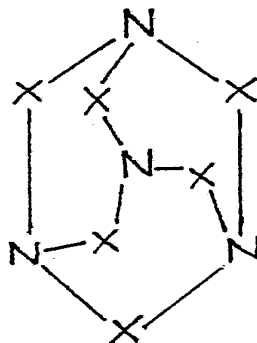
Suitable organic poly-isocyanate or poly-isothiocyanate compounds are the aliphatic and aromatic isocyanates including, for example, 5  
toluene-2,4-diiso-cyanate; 1,5-naphthalenediisocyanate; cumene-2,4-diisocyanate; 4-methoxy-1,3-phenylenediisocyanate; 4-chloro-1,3-phenylenediisocyanate; 4-bromo-1,3-phenylenediisocyanate; 4-ethoxy-1,3-phenylenediisocyanate; 5-6-dimethyl-1,3-phenylene-  
10 diisocyanate; 2,4-dimethyl-1,3-phenylenediisocyanate; 4,4'-diisocyanatodiphenylether; benzidinediisocyanate; hexamethylene diisocyanate; 4,6-dimethyl-1,3-phenylenediisocyanate; 9-10-anthracenediisocyanate; 4,4'-diisocyanatodibenzyl; 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane; 2,6'-dimethyl-4,4'-diisocyanatodiphenyl;  
15 2,4-di so-cyanatostilbene; 3,3'-dimethyl-4,4'-diisocyanatodiphenyl; 3,3'-dimethoxy-4,4"-diisocyanatodiphenyl; 1,4-anthracenediisocyanate; 2,5-fluorene-diisocyanate; 1,8-naphthalenediisocyanate; 2,6-diisocyanatobenzfuran; 2,4,6-toluenetriisocyanate; and 2,3,4'-triisocyanatodiphenylether.

20 Other organic polyisocyanates are the polyiso-cyanates described in Canadian Pat No. 700,026 and in US Pat No.2,688,730; the phenyl indane diisocyanates which are described in US Pat No. 2,855,385, the organic diisocyanates and the organic triisocyanates which are described in US Pat No. 2,292,443; and the organic  
25 triisocyanates which are described in US Pat No. 2,929,794.

When polyisocyanates having a functionality above about 2 are employed, they are employed in small quantities in admixture with a diisocyanate.

Also included as useful isothiocyanates are the sulphur  
30 analogues of the above mentioned isocyanates.

The catalyst preferably comprises hexamethylene tetramine, an aliphatic s-triazazine (1,3,5-triazazine) having the following structure:



5  
10 where X is  $\text{CH}_2$ .

Hexamethylene tetramine advantageously breaks down during the thermosetting reaction and does not therefore degrade the oxazolidone polymer produced.

15 The amount of s-triazazine catalyst used in the present method will usually be in the range 1 part of catalyst per 10,000 parts of polyisocyanate or polyisothiocyanate by weight to 1 part of catalyst per 20 parts of polyisocyanate or polyisothiocyanate by weight. The ratio by weight of polyisocyanate or polyisothiocyanate to catalyst is preferably more than 50:1, most preferably more  
20 than 100:1.

The reaction between the polyepoxide and the polyisocyanate or polyisothiocyanate in accordance with the present invention is carried out at a temperature between  $20^\circ\text{C}$  and  $250^\circ\text{C}$ , preferably between  $50^\circ\text{C}$  and  $180^\circ\text{C}$ .

25 Although the molar ratio of the epoxy groups to CNO or CNS groups in the reaction mixture is preferably 1:1 it may be any ratio in the range from 1:5 to 5:1, but is desirably within the range of epoxy: CNO or CNS molar ratios from 1:2 to 2:1 especially from 1:1.2 to 1.2:1.

30 By forming an oxazolidone polymer in accordance with the present invention, it is possible to obtain a relatively high oxazolidone content in the polymer because the catalyst incorporated in the reaction mixture unexpectedly favours the

production of the oxazolidone structure rather than that of the isocyanurate or isothiocyanate.

The resulting polymers advantageously show a higher softening point and a glass transition temperature compared with those containing a lower oxazolidone content produced using catalysts previously reported for the reaction.

Furthermore, the strength of bond, if the polymer is bonded to aluminium or other metals used in engineering structures, is also unexpectedly improved by increasing the oxazolidone content of the polymer produced by the present method. There are in addition indications that the present method reduces or avoids the number of hydrophilic groups in the polymeric products, so that the product has a generally improved water resistance.

Conventional additives such as pigments, eg titanium dioxide or carbon black, fillers and flexibilizing agents may also be added to the reaction mixture. Additives forming a copolymer system such as butadiene-acrylonitrile may also be added to the composition to vary its properties in a known way.

The reaction mixture prior to curing may be used in conjunction with reinforcing fibres, which may be woven or unwoven, such as fibres of carbon, glass, aramid, polyolefin, boron or various metals to form fibre-reinforced composites and structural articles formed therefrom as will be familiar to those skilled in the composites art.

Embodiments of the present invention will now be described by way of example.

#### Example 1

The preparation and properties of a cured oxazolidone polymer.

5.1g of the resin MY750 (Trade Mark), a conventional bisphenol A diglycidyl ether epoxy resin marketed by Ciba Geigy and derived from

the reaction of epichlorhydrin with bisphenol A, were mixed with 3.75g of 4,4'-diisocyanatodiphenylene methane (MDI) (equimolar proportions) and 0.008g of hexamethylene tetramine (herein referred to as 'hexa') (0.2% by weight of MDI) as catalyst.

5 After stirring at 50°C for 15 minutes the mixture was cast in a suitable mould and heated at 50°C for 3h, 100°C for 1h and finally cured at 150°C for 18h.

The dark amber resinous product had a softening point of 188°C as determined by thermomechanical analysis. Its ir (infra-red) 10 spectrum exhibited strong absorption at 1750 and 1710 cm<sup>-1</sup>, respectively indicating oxalidone and isocyanurate, but none at 2250 cm<sup>-1</sup>, ie complete reaction of the MDI. The softening point of this resin was significantly above that of MY750 resin cured with a conventional diamine, the latter resin 15 being herein referred to as MY750 DDM which consists of 4,4'-diaminodiphenylene methane 27 parts by weight and 100 parts by weight MY750. A comparison of softening points is given in Table 1 as follows.

Table 1 Softening points of cured MY750.

| 20 | <u>Resin formulation</u> | <u>TMA</u> a°C | <u>DMTA</u> b°C |
|----|--------------------------|----------------|-----------------|
|    | MY 750 DDM               | 143            | 165             |
|    | MY 750 MDI/hexa          | 188            | 205             |

(produced by the above method)

- a) Thermomechanical analysis (TMA) in the penetration mode.  
 25 b) Tan  $\delta$  peak at 3 Hz by dynamic mechanical thermal analysis (DMTA)

Example 2

5.1g MY750 and 3.75g MDI together with 0.08g hexa were mixed together at 50°C for 15 minutes followed by curing at 30 220°C for 10 minutes. The hard resinous product had an ir spectrum which exhibited strong absorption at 1750 cm<sup>-1</sup> but no absorption at 1700 cm<sup>-1</sup>. This is indicative of a complete conversion of MDI to oxazolidone.

Examples 3-11

The method of Example 1 was repeated in 9 further Examples.

In each further Example, one or more of the following parameters were changed over those given in the method of Example 1 :-

MY 750 : MDI molar ratio, concentration of hexa, and cure duration

5 and temperature during the final curing stage (given as 150°C for 18 hours in Example 1). The results are given in Table 2 below.

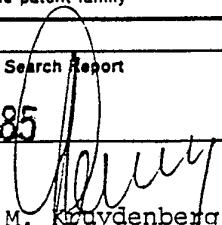
| Example | MY 750 : MDI<br>molar ratio | 'hexa'<br>(% by weight<br>of MDI) | Final stage<br>cure conditions |    | Softening<br>point and Tg |               |
|---------|-----------------------------|-----------------------------------|--------------------------------|----|---------------------------|---------------|
|         |                             |                                   | °C                             | h  | by TMA<br>°C              | by DMTA<br>°C |
| 10 3    | 1 : 1                       | 0.2                               | 130                            | 18 | 147                       | 160           |
| 4       | 1 : 1                       | 0.2                               | 160                            | 18 | 177                       | -             |
| 5       | 1 : 1                       | 0.2                               | 150                            | 6  | 148                       | 162           |
| 15 6    | 1 : 1                       | 0.2                               | 150                            | 7  | 170                       | -             |
| 7       | 1 : 1                       | 1.5                               | 150                            | 7  | 170                       | -             |
| 8       | 1 : 1                       | 0.4                               | 150                            | 21 | 190                       | -             |
| 9       | 100 : 97                    | 0.2                               | 150                            | 21 | 190                       | -             |
| 20 10   | 100 : 182                   | 0.2                               | 150                            | 18 | 207                       | -             |
| 11      | 100 : 202                   | 0.2                               | 130                            | 20 | 215                       | 218           |

Claims

1. A method of preparing an oxazolidone polymer which comprises reacting a vicinal polyepoxide having a functionality greater than 1 with an organic polyisocyanate or polyisothiocyanate, in the presence of a catalyst comprising an aliphatic s-triazine compound or an aliphatic derivative thereof, at a temperature between 20° and 250°C.
2. A method according to claim 1 wherein the molar ratio of NCO groups or NCS groups to epoxide groups is from 1:5 to 5:1.
3. A method according to claim 2 wherein the molar ratio of NCO groups or NCS groups to epoxide groups is from 1:1.2 to 1.2:1.
4. A method according to claim 1 wherein the polyisocyanate or polyisothiocyanate is a diisocyanate or a diisothiocyanate.
5. A method according to claim 5 wherein the ratio by weight of polyisocyanate or polyisothiocyanate to catalyst is from 10,000:1 to 20:1 by weight.
6. A method according to claim 5 wherein the ratio by weight of polyisocyanate or polyisothiocyanate to catalyst is from 10,000:1 to 100:1 by weight.
7. A method according to claim 1 wherein the catalyst comprises hexamethylene tetramine.
8. A method according to claim 1 wherein the temperature of the reaction is between 50°C and 180°C.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00215

|   |   |                                     |
|---|---|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>   |   |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC   |   |                                     |
| IPC <sup>4</sup> : C 08 G 18/00; C 08 G 73/06; C 08 G 59/40   |   |                                     |
| <b>II. FIELDS SEARCHED</b>  |   |                                     |
| Minimum Documentation Searched <sup>7</sup>   |   |                                     |
| Classification System   | Classification Symbols  |                                     |
| IPC <sup>4</sup>  | C 08 G<br>C 07 D  |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>   |   |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>  |   |                                     |
| Category <sup>9</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
| X   | DE, A, 1915766 (THE UPJOHN CO.) 6 November 1969, see claims 1 and 5; page 6, paragraph 2; page 6, last paragraph- page 7, paragraph 1; page 17, paragraph 2; page 21, last paragraph- page 22, paragraph 2<br>--                                  | 1-5                                 |
| X   | GB, A, 1212663 (THE UPJOHN CO.) 18 November 1970, see claims 1 and 4; page 6, lines 19-26 and 74-82<br>--   | 1,2,5                               |
| X   | FR, A, 2207952 (HITACHI) 21 June 1974, see claims 1-6,19,21-24,26-29; page 8, lines 11-24<br>--   | 1,2,4-6,8                           |
| P,X   | Chemical Abstracts, volume 101, nr. 20, 12 November 1984, (Columbus, Ohio, US) Uribe M. et al.: "Isocyanate-oxirane reactions in the formation of resins" page 30, abstract nr. 172.185J & Polymer-Prepr. 1984, volume 25(2) pages 43-44<br>----- | 1,7                                 |
| <p><sup>9</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&amp;" document member of the same patent family</p> |   |                                     |
| <b>IV. CERTIFICATION</b>  |   |                                     |
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report   |                                     |
| 7th August 1985   | 30 AOUT 1985  |                                     |
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| EUROPEAN PATENT OFFICE  | <br>G.L.M. Kruidenberg   |                                     |

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 85/00215 (SA 9647)

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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|  |                  | GB-A- 1259199           | 05/01/72         |
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