



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

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| <b>(51) International Patent Classification<sup>3</sup> :</b><br><b>C08G 59/14</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 84/ 00765</b><br><b>(43) International Publication Date:</b> 1 March 1984 (01.03.84)                                                                     |
| <b>(21) International Application Number:</b> PCT/US83/01191<br><b>(22) International Filing Date:</b> 3 August 1983 (03.08.83)<br><br><b>(31) Priority Application Number:</b> 406,816<br><b>(32) Priority Date:</b> 10 August 1982 (10.08.82)<br><b>(33) Priority Country:</b> US<br><br><b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/<br>US]; 2030 Dow Center, Abbott Road, Midland, MI<br>48640 (US).<br><br><b>(72) Inventors:</b> HECK, Henry, G. ; 514 Daffodil, Lake Jack-<br>son, TX 77566 (US). MOORE, Charles, H. ; 207 Mari-<br>gold, Lake Jackson, TX 77566 (US). LINDLEY, Nan-<br>cy, L. ; 2584 Olympia Drive, West Columbia, TX<br>77486 (US).<br><br><b>(74) Agent:</b> RUSSELL, H., David; The Dow Chemical<br>Company, P.O. Box 1967, Midland, MI 48640 (US).                                                                                                                           |           | <b>(81) Designated States:</b> AU, BR, DE (European patent), FR<br>(European patent), GB (European patent), JP, NL<br>(European patent).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> PROCESS FOR CONTROLLING GELATION AND CURE OF UNSATURATED RESINS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |           |                                                                                                                                                                                                              |
| <b>(57) Abstract</b><br><br>A process for controlling the gelation and cure rate of unsaturated resins useful for thermosettable compositions and laminates. A small amount of an enolizable beta-diketone such as 2,4-pentadione added to a vinyl ester of a polyglycidyl ether of a polyhydric compound, an unsaturated polyester or a mixture thereof contributes toward the control of the rates. Admixed with the enolizable beta-diketone and unsaturated resin is a peroxide selected from ketone peroxides, tertiary hydroperoxides or peroxyesters, and a redox reactive metal salt soluble in the curable resin such as cobalt naphthenate. The unsaturated resins have a pH greater than 5.7 measured as a 10 percent methanol solution. The mixture is maintained at a temperature less than 54°C to extend the nongelled state and then raised above 54°C to achieve acceleration of the cure rate. |           |                                                                                                                                                                                                              |

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## PROCESS FOR CONTROLLING GELATION AND CURE OF UNSATURATED RESINS.

A variety of additives are taught by the art as useful in controlling the gelation and/or cure of unsaturated resins, such as vinyl ester resins or unsaturated polyester resin.

5           Generally, the time it takes for a resin to gel decreases as the temperature increases. The tendency to gel is also dependent on the nature of the resin, on the kind and amount of monomer which is generally mixed with the resin, on the catalyst/promoter  
10       system and on other factors.

          In the past, attempts with known materials to retard gelation have also resulted in an undesirable increase in the subsequent cure time of the resins. That can be a problem during fabrication and can lessen  
15       the usefulness of the resin.

Fabrication techniques vary widely. In some instances, it may be desirable to have a very short pot life and a very fast cure. In other instances, such as in hand lay up techniques, it is desirable to have a



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long pot life and a quick cure on demand. Other instances may have different optimum schedules. It would be a great help to the formulator and fabricator if flexibility could be built into a formulation to  
5 avoid the necessity of a special mixture for each schedule.

U.S. Patent No. 3,584,076 teaches that the rate of polymerization initiation of unsaturated polyester resins and other monomers by redox reactions  
10 involving peroxide such as methyl ethyl ketone peroxide and tert-butyl perbenzoate with soluble salts of redox active metals such as cobalt octoate is greatly accelerated in the presence of enolizable ketones such as 2,4-pentanedione.

15 It has been found that a small amount of a beta-diketone added to a redox catalyzed vinyl ester resin, an unsaturated polyester resin or a mixture of the two materials having a pH greater than 5.7 when measured as 10 percent methanol solution provides a  
20 means for thermally controlling (retard or accelerate) gelation and cure of those resins.

This invention is directed to a process for controlling the gelation and cure rates of free radical curable resins comprising admixing (1) a vinyl ester of  
25 a polyglycidyl ether of a polyhydric compound, an unsaturated polyester or a mixture thereof, (2) a peroxide selected from ketone peroxides, tertiary hydroperoxides or peroxyesters, (3) a redox reactive metal salt soluble in the curable resin, and (4) an  
30 enolizable beta-diketone characterized in that the vinyl ester, the unsaturated polyester or a mixture

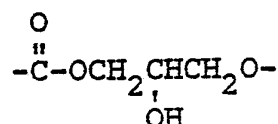


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thereof has a pH greater than 5.7 measured as a 10 percent methanol solution and further characterized by maintaining the mixture at a temperature less than 130°F (54°C) to extend the nongelled state and subsequently raising the temperature above 130°F (54°C) to achieve acceleration of the cure rate.

Vinyl ester resins are described in U.S. Patent No. 3,367,992 wherein dicarboxylic acid half esters of hydroxyalkyl acrylates or methacrylates are reacted with polyepoxide resins. Bowen in U.S. Patent Nos. 3,066,112 and 3,179,623 describes the preparation of vinyl ester resins from monocarboxylic acids such as acrylic and methacrylic acid. Bowen also describes alternate methods of preparation wherein a glycidyl methacrylate or acrylate is reacted with the sodium salt of a dihydric phenol such as bisphenol A. Vinyl ester resins based on epoxy novolac resins are described in U.S. Patent No. 3,301,743 to Fekete et al. Fekete et al. also describe in U.S. Patent No. 3,256,226 vinyl ester resins wherein the molecular weight of the polyepoxide is increased by reacting a dicarboxylic acid with the polyepoxide resin. Other difunctional compounds containing a group which is reactive with an epoxide group, such as, for example, an amine or a mercaptan, may be utilized in place of the dicarboxylic acid. All of the above-described resins, which contain the characteristic linkages

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and terminal, polymerizable vinylidene groups, are classified as vinyl ester resins.

Briefly, any of the known polyepoxides may be employed in the preparation of the vinyl ester resins of this invention. Useful polyepoxides are glycidyl polyethers of both polyhydric alcohols and polyhydric phenols, epoxy novolacs, epoxidized fatty acids or drying oil acids, epoxidized diolefins, epoxidized diunsaturated acid esters as well as epoxides of unsaturated polyesters, as long as they contain more than one oxirane group per molecule.

Preferred polyepoxides are glycidyl polyethers of polyhydric alcohols or polyhydric phenols having weights per epoxide group from 150 to 2000. These polyepoxides are usually made by reacting at least about two moles of an epihalohydrin or glycerol dihalohydrin with one mole of the polyhydric alcohol or polyhydric phenol, and a sufficient amount of a caustic alkali to combine with the halogen of the halohydrin. The products are characterized by the presence of more than one epoxide group per molecule, i.e., a 1,2-epoxy equivalency greater than one.

Unsaturated monocarboxylic acids include, for example, acrylic acid, methacrylic acid, halogenated acrylic or methacrylic acid, cinnamic acid and mixtures thereof. Also included within the term "unsaturated carboxylic acids" are the hydroxyalkyl acrylate or methacrylate half esters of dicarboxyl acids as described in U.S. Patent No. 3,367,992 wherein the hydroxyalkyl group preferably has from 2 to 6 carbon atoms.



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A wide variety of unsaturated polyesters are readily available or can be prepared by methods well-known to the art. Such polyesters result from the condensation of polybasic carboxylic acids and compounds having two or more hydroxyl groups. Generally, in the preparation of suitable polyesters, an ethylenically unsaturated dicarboxylic acid such as, for example, maleic acid, fumaric acid, or itaconic acid is inter-esterified with an alkylene glycol or polyalkylene glycol having a molecular weight of up to 2000. Frequently, dicarboxylic acids free of ethylenic unsaturation such as, for example, phthalic acid, isophthalic acid, adipic acid, or succinic acid may be employed within a molar range of 0.25 to as much as 15 moles per mole of the unsaturated dicarboxylic acid. It will be understood that the appropriate acid anhydrides when they exist may be used and usually are preferred when available.

The glycol or polyhydric alcohol component of the polyester is usually stoichiometric or in slight excess with respect to the sum of the acids. The excess of polyhydric alcohol seldom will exceed 20 to 25 percent and usually is 10 to 15 percent.

These unsaturated polyesters may be generally prepared by heating a mixture of the polyhydric alcohol with the dicarboxylic acid or anhydride in the proper molar proportions at elevated temperatures, usually 150° to 225°C for a period of time ranging from 1 to 5 hours. For unsaturated polyester resins suitable in the process of this invention, the condensation reaction is contained until the acid content drops to a level such that the resulting polyester has a pH greater than 5.7 measured as a 10 percent methanol solution.



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Polymerization inhibitors, commonly called process inhibitors, such as t-butyl catechol, monomethyl ether of hydroquinone (MEHQ) or hydroquinone, are advantageously added to prevent premature polymerization during the preparation of the vinyl ester resin or the unsaturated polyester.

Vinyl ester/unsaturated polyester resin blends are also effectively stabilized. The blends may be prepared either by physically mixing the two resins in the desired proportions or by preparing said vinyl ester resin in the presence of said unsaturated polyester.

Preferably, as is generally true in the thermosettable resin art, the resin phase is blended with a copolymerizable monomer.

Suitable monomers include vinyl aromatic compounds such as, for example, styrene, vinyl toluene, or divinyl benzene. Other useful monomers include the esters of saturated alcohols such as, for example, methyl, ethyl, isopropyl, and octyl, with acrylic acid or methacrylic acid; vinyl acetate, diallyl maleate, dimethallyl fumarate; mixtures of the same and all other monomers which are capable of copolymerizing with the vinyl ester resin.

Catalysts that may be used for the curing or polymerization are ketone peroxides, such as methyl ethyl ketone peroxide, tertiary peroxides such as cumene hydroperoxide, or peroxyesters such as 2,5-dimethyl-2,5-bis(2-ethylhexoylperoxy)hexane. The amount of the catalyst added will vary preferably from 0.5 percent to 3.0 percent by weight of the resin phase.



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The cure system also includes known redox reactive metal salts accelerating agents in an amount to provide from 0.0001 to 0.1 parts metal per 100 parts resin. Such salts include, for example, the naphthenate  
5 or octoate salts of cobalt, manganese, nickel, vanadium and molybdenum.

Other accelerators and promoters, such as, for example, dimethylaniline or N,N-dimethyltoluidine, may be employed in addition to the metal salts. The  
10 amount of these amines will vary, preferably from 0.0 to 0.5 percent by weight of the resin phase.

The final essential part of the cure system is an enolizable beta-diketone. A preferred species is 2,4-pentadione. The amount of the beta-diketone will  
15 vary preferably from 0.001 to 2.0 percent by weight of the resin phase.

Optimum ratios of the resin and cure system ingredients can be easily determined by preliminary tests.

20 The cure system varies the gel and cure times depending upon temperature. When using 2,4-pentanedione with the resins having pH greater than 5.7, it is found that below 130°F (54°C) the gel time is retarded to provide up to several hours pot life. Above 130°F  
25 (54°C), the cure is accelerated. The inventive concept, therefore, provides a choice of gel and cure times. The resin can be formulated to remain an ungelled liquid for several hours at less than 130°F (54°C). When gelation begins, the exotherm of the reaction  
30 raises the temperature of the resin above 130°F (54°C)



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resulting in an acceleration of the cure rate. As an alternative at any time prior to gelation, the temperature of the resin can be raised above 130°F (54°C) by the application of heat to achieve rapid gel and cure.

5 Finally, just after gelation, heat can be added to that being generated by the exotherm to raise the temperature above 130°F (54°C) and achieve fast cure.

The procedure finds particular use where a variety of procedures are to be used. It is especially adapted for the hand lay up of thermosettable resin compositions and laminates.

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The benefits and advantages of the invention and the best mode for carrying out the same are illustrated in the following examples wherein all parts and percents are by weight unless otherwise specified.

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The following free radical curable resins were utilized:

Resin A was a vinyl ester resin prepared by catalytically reacting 1 equivalent of bisphenol A with 2.2 equivalents of a diglycidyl ether of bisphenol A having an epoxy equivalent weight (EEW) between 172 and 176 at 150°C under a nitrogen atmosphere for one hour to form a polyepoxide having an EEW of 535. After cooling to 110°C, an additional equivalent of the diglycidyl ether of bisphenol A was added with 1.6 equivalents of methacrylic acid and hydroquinone and reacted to a carboxylic acid (COOH) content of 3 percent. Then, 0.4 equivalent of maleic anhydride was added to the reaction mixture and reacted therewith to an acid content of 1 percent. The final resin, diluted with styrene containing 50 ppm of t-butyl catechol to a styrene content of 45 percent, had a pH of 7.7.

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Resin B was a vinyl ester resin prepared by reacting 1 equivalent of methacrylic acid with 0.75 equivalent of an epoxy novolac having an epoxide equivalent weight between 175 and 182 and 0.25 equivalent of a diglycidyl ether of bisphenol A having an EEW between 186 and 192. The above reactants were heated to 115°C with catalyst and hydroquinone present until the carboxylic acid content reached 1 percent. The reactants were cooled and then styrene containing 50 ppm of t-butyl catechol was added until the styrene content was 36 percent. The final resin diluted with styrene had a pH of 7.3.

Resin C was a vinyl ester resin prepared by catalytically reacting 0.05 equivalent of bisphenol A with 0.25 equivalent of the diglycidyl ether of bisphenol A having an EEW between 186 and 192 to form a polyepoxide having an EEW of 275. After cooling 1 equivalent of an epoxy novolac having an EEW between 172 and 182 and 1.05 equivalent of methacrylic acid are added and reacted to an acid content of 1 percent. Then, 0.75 equivalent of maleic anhydride is added and reacted to an acid content of 5 percent. The final resin, diluted with styrene containing 50 ppm of t-butyl catechol to a styrene content of 33 percent, had a pH of 4.5.

Resin D was a vinyl ester resin prepared by catalytically reacting 1 equivalent of bisphenol A and 100 parts of a carboxy terminated butadiene-acrylonitrile rubber with 2.25 equivalents of the diglycidyl ether of bisphenol A having an EEW between 180 and 185 to form a polyepoxide having an EEW of 550. Then, 1.2 equivalents of methacrylic acid are added and reacted to an acid



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content of 1 percent. The final resin, diluted with styrene containing 50 ppm of t-butyl catechol to a styrene content of 45 percent, had a pH of 7.3

Resin E was a vinyl ester resin prepared by  
5 catalytically reacting 1 equivalent of tetrabromobisphenol A with 0.9 equivalent of the diglycidyl ether of tetrabromobisphenol A advanced with tetrabromobisphenol A to an EEW of 460 and 1.5 equivalents of the diglycidyl ether of bisphenol A having an EEW between 182 and 192,  
10 the reaction product having an EEW of 700. This reaction product was then reacted with 1.4 equivalents of methacrylic acid to an acid content of 1 percent and an epoxide content of 0.4 percent. The final resin, diluted with styrene containing 50 ppm of t-butyl  
15 catechol to a styrene content of 37.5 percent, had a pH of 7.7.

Resin F was a commercially available isophthalic unsaturated polyester having a pH of 4.8.

20 In the following examples and comparative runs, the following tests were conducted.

One hundred grams of resin are placed into a 4 ounce (108.2 ml) wide mouth glass jar and held in a constant temperature bath at 77°F (25°C) for 45 minutes. 0.5 ml of 6 percent cobalt naphthenate in petroleum  
25 spirits is then mixed in thoroughly. To that is added 1.5 ml of 60 percent methyl ethyl ketone peroxide (MEKP) in dimethyl phthalate. The jar is placed on the gelometer stand with the probe extending into the resin. The timer is started and the time recorded when  
30 the timer stops and alarm is sounded. That time is the



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Gel Time. The jar is removed from the gelometer and a thermocouple placed about 3/4 inch (19 mm) from the bottom of the jar. The temperature at which the sample breaks away from the side of the jar is the Peak Exotherm.

- 5 The total elapsed time is the Peak Time. Similar tests were performed using other catalysts and accelerators.

Examples 1 and 2 and Comparative Runs A to F

- 10 Gel Times, Peak Times and Peak Exotherm were measured for 100 parts of compositions of different ratios of Resin B and Resin C containing 0.2 percent of 2,4-pentanedione (2,4-P) or none and each sample catalyzed with 1.0 part methyl ethyl ketone peroxide and 0.3 part of 6 percent cobalt naphthenate.

The results are listed in Table I.



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TABLE I

|                      | Comp.<br>Run A | Ex.<br>No. 1 | Comp.<br>Run B | Ex.<br>No. 2 | Comp.<br>Run C | Comp.<br>Run D | Comp.<br>Run E | Comp.<br>Run F |
|----------------------|----------------|--------------|----------------|--------------|----------------|----------------|----------------|----------------|
| Resin B,<br>parts    | 100            | 100          | 96             | 96           | 94             | 94             | 0              | 0              |
| Resin C,<br>parts    | 0              | 0            | 4              | 4            | 6              | 6              | 100            | 100            |
| 2,4-P, phr           | 0              | 0.2          | 0              | 0.2          | 0              | 0.2            | 0              | 0.2            |
| pH                   | 7.3            | 7.3          | 6.0            | 6.0          | 5.0            | 5.7            | 4.5            | 4.5            |
| Gel time,<br>min.    | 42             | 380          | 80             | 91           | 83             | 63             | 180            | 39             |
| Peak Time,<br>min.   | 65             | 420          | 95             | 109          | 100            | 75             | 203            | 49             |
| Peak Exotherm,<br>°C | 168            | 169          | 169            | 171          | 170            | 179            | 159            | 177            |



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Examples 3 and 4 and Comparative Runs G to L

Eight compositions were prepared according to the previous examples and comparative runs using Resins A, C, D, and F. The same curing system and test procedure  
5 were followed. The results are shown in Table II.



TABLE II

|                   | <u>Ex. No. 3</u> | <u>Comp. Run G</u> | <u>Comp. Run H</u> | <u>Comp. Run I</u> | <u>Comp. Run J</u> | <u>Ex. No. 4</u> | <u>Comp. Run K</u> | <u>Comp. Run L</u> |
|-------------------|------------------|--------------------|--------------------|--------------------|--------------------|------------------|--------------------|--------------------|
| Resin, 100 parts  | A                | A                  | C                  | C                  | D                  | D                | F                  | F                  |
| 2,4-P, phr        | 0.2              | 0                  | 0                  | 0.2                | 0                  | 0.2              | 0                  | 0.2                |
| Gel time, min.    | 260              | 24                 | 108                | 41                 | 216                | 276              | 15                 | 8                  |
| Peak Time, min.   | 317              | 53                 | 122                | 51                 | 265                | 360              | 34                 | 18                 |
| Peak Exotherm, °C | 144              | 148                | 145                | 150                | 92                 | 96               | 156                | 153                |

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Examples 5 and 6 and Comparative Runs M and N

Compositions were made and tested as in the previous examples and comparative runs using Resin E.

The curing system, based upon 100 parts of resin, was

- 5 1.0 part methyl ethyl ketone peroxide, 0.1 part dimethyl-aniline, and in Comparative Run K and Example 7, 0.25 part cobalt naphthenate; in Comparative Run L and Example 8, 0.125 part cobalt octoate. Comparisons were made with
- 10 0.2 part 2,4-pentadione in Examples 7 and 8 and without that compound in Comparative Runs K and L. The results are shown in Table III.



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TABLE III

| <u>Accelerator</u> | <u>Comp. Run M</u><br><u>Co Naphthenate</u> | <u>Ex. No. 5</u><br><u>Co Naphthenate</u> | <u>Comp. Run N</u><br><u>Co Octoate</u> | <u>Ex. No. 6</u><br><u>Co Octoate</u> |
|--------------------|---------------------------------------------|-------------------------------------------|-----------------------------------------|---------------------------------------|
|                    |                                             |                                           |                                         |                                       |
| 2,4-P, phr         | 0                                           | 0.2                                       | 0                                       | 0.2                                   |
| Gel Time, min.     | 21                                          | 180                                       | 16                                      | 275                                   |
| Peak Time, min.    | 37                                          | 191                                       | 34                                      | 315                                   |
| Peak Exotherm, °C  | 108                                         | 153                                       | 153                                     | 143                                   |



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Example 7 and Comparative Runs O Through U

Compositions were prepared from Resins A and F using the procedures of the preceding examples and comparative runs. In Example 9 and Comparative Runs M, N, and O, reported in the following Table IV(a), the cure system, based upon 100 parts of resin, is 1 part cumene hydroperoxide, 0.03 part cobalt naphthenate and with or without 2,4-pentanedione. In Comparative Runs P, Q, R and S, reported in Table IV(b), the cure systems, based upon 100 parts of resin, is 1 part benzoyl peroxide, 0.1 part dimethylaniline and with or without 2,4-pentanedione.



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TABLE IV(a)

|                   | <u>Comp. Run O</u> | <u>Comp. Run P</u> | <u>Comp. Run Q</u> | <u>Ex. No. 7</u> |
|-------------------|--------------------|--------------------|--------------------|------------------|
| Resin             | F                  | F                  | A                  | A                |
| 2,4-P, phr        | 0                  | 0.1                | 0                  | 0.1              |
| Gel Time, min.    | 840                | 1010               | 260                | 510              |
| Peak Time, min.   | >1440              | 1203               | 382                | 664              |
| Peak Exotherm, °C | --                 | 146                | 134                | 124              |

TABLE IV(b)

|                   | <u>Comp. Run R</u> | <u>Comp. Run S</u> | <u>Comp. Run T</u> | <u>Comp. Run U</u> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
| Resin             | F                  | F                  | A                  | A                  |
| 2,4-P, phr        | 0                  | 0.2                | 0                  | 0.2                |
| Gel Time, min.    | 72                 | 78                 | 22                 | 22                 |
| Peak Time, min.   | 88                 | 93                 | 34                 | 37                 |
| Peak Exotherm, °C | 173                | 187                | 167                | 144                |



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## CLAIMS

1. A process for controlling the gelation and cure rates of free radical curable resins, comprising admixing (1) a vinyl ester of a polyglycidyl ether of a polyhydric compound, an unsaturated polyester or a mixture thereof, (2) a peroxide selected from ketone peroxides, tertiary peroxides or peroxyesters; (3) a redox reactive metal salt soluble in said curable resin and (4) an enolizable beta-diketone characterized in that the vinyl ester unsaturated polyester or mixture thereof has a pH greater than 5.7 measured as a 10 percent methanol solution and further characterized by maintaining the mixture at a temperature less than 130°F (54°C) to extend the nongelled state and subsequently raising the temperature above 130°F (54°C) to achieve acceleration of the cure rate.

2. The process of Claim 1 characterized in that the heat necessary for the temperature to rise above 130°F (54°C) is provided by the exotherm from the onset of gelation and cure of the resin.

3. The process of Claim 1 characterized in that the heat needed to raise the temperature above 130°F (54°C) is added externally to obtain rapid gel and cure upon demand.



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4. The process of Claim 1 characterized in that the heat is generated internally by the exotherm until the onset of gelation is then reinforced by external heating to accelerate cure.



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/01191

| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup><br>According to International Patent Classification (IPC) or to both National Classification and IPC<br><div style="text-align: center; padding: 10px;">           INT. CL<sup>3</sup> C08G 59/14         </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                           |                                     |                       |                        |      |         |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-----------------------|------------------------|------|---------|
| <b>II. FIELDS SEARCHED</b><br><div style="text-align: center; padding: 5px;">             Minimum Documentation Searched <sup>4</sup> </div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%;">Classification System</th> <th style="width: 70%;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; padding: 10px;">U.S.</td> <td style="text-align: center; padding: 10px;">525/531</td> </tr> </table> <div style="text-align: center; padding: 5px;">             Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                           |                                     | Classification System | Classification Symbols | U.S. | 525/531 |
| Classification System                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Classification Symbols                                                                                                                                    |                                     |                       |                        |      |         |
| U.S.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 525/531                                                                                                                                                   |                                     |                       |                        |      |         |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                           |                                     |                       |                        |      |         |
| Category *                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>                                            | Relevant to Claim No. <sup>18</sup> |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 3,584,076 (CHETAKIAN) 8 JUNE 1971                                                                                                                  | 1-4                                 |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 3,630,960 (CHETAKIAN) 28 DECEMBER 1971                                                                                                             | 1-4                                 |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 4,083,890 (DRAKE ET AL) 11 APRIL 1978                                                                                                              | 1-4                                 |                       |                        |      |         |
| P, Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | US, A, 4,348,506 (GANGULI ET AL) 7 SEPTEMBER 1982                                                                                                         | 1-4                                 |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 3,669,911 (NAJVAR) 13 JUNE 1972                                                                                                                    | 1-4                                 |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 4,085,018 (ARIGA ET AL) 18 APRIL 1978                                                                                                              | 1-4                                 |                       |                        |      |         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | LEE, HENRY AND NEVILLE, KRIS, <u>HANDBOOK OF RESINS</u> , 1967, MCGRAW-HILL BOOK CO., NEW YORK, N.Y., P. 4-66                                             | 1-4                                 |                       |                        |      |         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 3,651,649 (NAJVAR ET AL) 28 MARCH 1972                                                                                                             | 1-4                                 |                       |                        |      |         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | US, A, 3,792,006 (NAJVAR) 12 FEBRUARY 1974                                                                                                                | 1-4                                 |                       |                        |      |         |
| A, P                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | US, A, 4,343,921 (PIESTERT) 10 AUGUST 1982                                                                                                                | 1-4                                 |                       |                        |      |         |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>15</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> </div> <div style="width: 45%;"> <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> </div> </div> |                                                                                                                                                           |                                     |                       |                        |      |         |
| <b>IV. CERTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                           |                                     |                       |                        |      |         |
| Date of the Actual Completion of the International Search <sup>2</sup><br><div style="text-align: center; padding: 10px;">           16 SEPTEMBER 1983         </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Date of Mailing of this International Search Report <sup>2</sup><br><div style="text-align: center; padding: 10px;">           03 OCT 1983         </div> |                                     |                       |                        |      |         |
| International Searching Authority <sup>1</sup><br><div style="text-align: center; padding: 10px;">           ISA/US         </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | Signature of Authorized Officer <sup>19</sup><br><div style="text-align: center; padding: 10px;">            ROBERT SELLERS         </div>                |                                     |                       |                        |      |         |