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(54) IMPROVED POLYESTER RESINS CONTAINING DICYCLOPENTADIENE

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyester resins containing dicyclopentadiene and molded products or coatings prepared from them.

More specifically, the invention relates to polyester resins and alkyd resins produced by reacting a polyol or an alkylene oxide, and olefinically unsaturated dicarboxylic acid or anhydride or a saturated polycarboxylic acid or anhydride, water, and a C₁₀ hydrocarbon concentrate which comprises at least 60% by weight of dicyclopentadiene.

It has now been found that polyester resins modified with such C₁₀ hydrocarbon concentrates and prepared using water during the reaction sequence are better than those prepared without the use of water in that the resins are more reactive and thus cure or harden faster and have better heat distortion temperatures.

The polyester resins of this invention are prepared by reacting a mixture comprising

(A) (1) an alpha, beta ethylenically unsaturated dicarboxylic acid or the anhydride thereof, or mixtures thereof, or

(2) a saturated polycarboxylic acid or the anhydride thereof, or

(3) mixtures of (1) and (2),

(B) from 0.03 to 10 moles water per mole of (A) (1) and/or (A) (2),

(C) from 0.05 mole to 1.0 mole of a C₁₀ hydrocarbon concentrate, which comprises at least 60% by weight of dicyclopentadiene, per mole of (A) (1) and/or (A) (2), and

(D) a polyol or an alkylene oxide with the proviso that when (D) is an alkylene oxide of 2—4 carbons, (A) is at least 90% by weight of a dicarboxylic acid anhydride, the reaction having been carried out at a temperature within the range of from 180°C to 250°C with the removal of the water of condensation until the acid number of the resin is within the range of from 30 to 35.

When (D) is a polyol and (A) is a polycarboxylic acid or anhydride, the reaction mixture may additionally contain up to 25% by weight based on the total weight of the polycarboxylic acid or anhydride of

a monohydric alcohol having 3—18 carbon atoms,

a fatty acid or oil having up to 22 carbon atoms,

a monocarboxylic aromatic acid, or mixtures thereof.

A related aspect of this invention is the cross-linkable mixture of the above polyester resin with an olefinically unsaturated monomer such as styrene and a fibrous laminate which has been impregnated and cured with the above mixture.

The polyols used to prepare the resins of this invention are those which are reactive with acids and/or anhydrides and include, for example, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butanediol, hexanediol, pentaerythritol, triethylene glycol, trimethylol propane, glycerol, or mixtures

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thereof. Preferably, the polyols used in this invention are glycols such as ethylene glycol, propylene glycol, dipropylene glycol or diethylene glycol.

The unsaturated dicarboxylic acids or anhydrides that can be used include, for example, maleic, fumaric, mesaconic, itaconic, and citraconic.

Conventional saturated polybasic acids useful to prepare these resins include, for example, orthophthalic anhydride or acid, terephthalic acid, isophthalic acid, trimellitic anhydride, adipic acid, sebacic acid, and succinic acid.

The C_{10} hydrocarbon concentrate used in this invention may be a commercial product prepared by dimerizing a crude C_8 stream from the cracking of crude mixtures of hydrocarbons as set forth by Gebhart, et al. in U.S. Patent 3,557,239 issued January 19, 1971.

These commercial products have as the main reactive components about 60 to about 90 percent by weight of dicyclopentadiene, about 5 to about 30 percent by weight of the mixed Diels-Alder dimers of diolefins such as butadiene, cis and trans piperylene, isoprene, cyclopentadiene, and methyl cyclopentadiene. The remainder of these concentrates generally comprise benzene, cyclopentene, 1,5-hexadiene and oligomers of the above diolefins.

Examples of some of the dimers which have been identified in these concentrates are the Diels-Alder adducts of two moles of isoprene (isoprene dimers), the adduct of cyclopentadiene and isoprene, and the adduct of cyclopentadiene and piperylene.

If desired, relatively pure dicyclopentadiene (90—100%) can be used herein. The polyesters are prepared by reacting in the substantial absence of oxygen an alpha, beta ethylenically unsaturated dicarboxylic acid or its anhydride or mixtures of both with a polyol. The unsaturated dicarboxylic acid or anhydride can be totally replaced with a saturated polycarboxylic acid or anhydride if saturated esters are desired or can be partially replaced with the saturated polycarboxylic acid or anhydride.

The reaction is carried out in the presence of 0.03 to 10 moles water per mole of dicarboxylic acid and/or anhydride and/or polycarboxylic acid or anhydride used. The preferred range is from 0.05 to 3 moles water.

The reactants such as acid or anhydride, polyol and water can be heated to a temperature range from 25°C to 140°C prior to the addition and reaction of the dicyclopentadiene.

However, this is optional since essentially the same results are obtained if all the reactants are heated initially with water to about the same temperature range for about the same time period.

While the reaction of dicyclopentadiene and a carboxylic acid to form an ester will occur at temperatures as low as 50°C, it is sometimes desirable to heat the reaction mixture to a temperature range from about 100°C to about 140°C after the addition of dicyclopentadiene to ensure the complete reaction thereof.

If desired, the use of a polyol can be eliminated if at least 90% of a dicarboxylic anhydride is used as a component of the reactants. In this instance the reaction of the polycarboxylic acid which may be created by the addition of water, and the dicyclopentadiene is allowed to proceed to near completion before an alkylene oxide having 2—4 carbon atoms such as ethylene oxide, propylene oxide or butylene oxide is added to the reactants in a known manner.

The technique of preparing polyesters from anhydrides and alkylene oxides is generally known from U.S. Patents 3,374,208 and 2,822,350.

If desired the particular polyesters of this invention may be further modified by incorporating into the reaction mixture up to 25% by weight based on the total weight of polycarboxylic acid or anhydride of a monohydric alcohol having 3—18 carbon atoms, a fatty acid or oil having up to 22 carbon atoms, a mono-carboxylic aromatic acid, or mixtures thereof.

Examples of suitable monohydric alcohols are butanol, propanol, allyl alcohol, and stearyl alcohol.

Examples of suitable fatty acids or oils are caproic, lauric, palmitic, and stearic as well as the unsaturated fatty acids such as oleic, linoleic, ricin and oleic.

Examples of fatty oils are linseed oil, soybean oil, tall oil and fish oil. Examples of suitable monocarboxylic aromatic acids are benzoic acid and tertiary butyl benzoic acid.

After the initial reaction, the reaction is heated to between 180°C and 250°C, preferably 190°C to 205°C, with a removal of the water of condensation, preferably by a Dean Stark trap, until the acid number is from 30 to 35.

The resin is then recovered and preferably blended with an ethylenically

unsaturated monomer copolymerizable with the unsaturated polyester polymers to form a blend wherein the weight ratio of polyester to monomer is in the range from about 4:1 to about 1:2. Such ethylenically unsaturated monomers are well known and include, for example, styrene, methyl styrene, chlorostyrene, vinyl toluene, divinyl benzene, vinyl acetate, acrylic acid, methacrylic acid, diallyl phthalate and mixtures thereof. A small amount of an inhibitor such as, for example, tertiary butyl catechol or hydroquinone may be added to this mixture. The final blend is a crosslinkable polyester composition which is useful to make laminates, castings or coatings.

The laminates of this invention are made by mixing into the crosslinkable composition free radical forming catalysts in known amounts and adding this mixture to a suitable fibrous reinforcement such as, for example, asbestos fibers, carbon fibers, fibrous glass, or inorganic fibers.

Examples of these catalysts are benzoyl peroxide, tertiary butyl peroxide, and methylethyl ketone peroxide. It is frequently of value to add accelerators such as, for example, cobalt naphthenate and dimethyl aniline.

The polyester resin is rolled, sprayed or impregnated into the fibrous reinforcement such as fibrous glass and cured in a manner well known in the art. When fibrous glass is used, it can be in any form such as, for example, chopped strands, filaments, glass ribbons, glass yarns, or reinforcing mats.

The alkyd resins may be compounded with solvents pigments or other resinous products and cured to form useful coatings in a known manner.

The following examples are presented to illustrate the invention.

EXAMPLE 1

To a reaction flask equipped with a stirrer, heating coil with controller, thermowell, nitrogen sparge tube, and a reflux condenser were added:

174.1 gms (1.775 moles) maleic anhydride
262.7 gms (1.775 moles) phthalic anhydride
296.8 gms (3.9 moles) propylene glycol
54.0 gms (3.0 moles) water

The reaction mass was heated to 90°C and held at that temperature for about 45 minutes. 144.6 gms (1.05 moles) of a C₁₀ hydrocarbon concentrate containing 81% dicyclopentadiene and 95.5% total C₁₀ hydrocarbons were added over a 3 minute period. The temperature controller was set at 140°C. The reaction mass refluxed at 130°C. After refluxing for about 2-1/2 hours, the reflux condenser was replaced with a steam condenser, a water cooled condenser and a Dean Stark trap to collect the distillate. The temperature controller was set at 200°C and the reaction was allowed to proceed until an acid number of 32 was attained for the polyester resin.

100 ppm of hydroquinone was added (based on 40% styrene) when the temperature went down to 150°C. At 100°C, 543 gms of styrene were blended with the polyester.

Control A (Polyester resin prepared without water)

To a reaction flask equipped as above as charged:

147 gms (1.5 moles) maleic anhydride
222 gms (1.5 moles) phthalic anhydride
251 gms (3.3 moles) propylene glycol

The reaction mass was heated to 90°C over a 22 minute period at which point 122 gms (0.90 moles) of a C₁₀ hydrocarbon concentrate containing 81% dicyclopentadiene and 95.5% total C₁₀ hydrocarbon were added over a six minute period. The controller was set for 140°C and left in that mode for 2 hours. After an additional hour of heating at 170°C, the reflux condenser was replaced with a steam condenser. The temperature controller was set at 200°C and the polyesterification process was continued until an acid number of 34 was attained.

Styrene and inhibitor were added in a manner similar to Example 1.

The resin had a maximum exotherm of only 309°F (154°C) when catalyzed with 1% benzoyl peroxide and cured at 180°F (82°C) in the SPI gel test.

Control B (Polyester resin prepared with maleic acid)

Using substantially same procedures and equipment as in Control A and substituting the same molar amount of maleic acid for the maleic anhydride, a

polyester resin was prepared having an acid number of 34. Styrene and hydroquinone were added as in Example 1.

Example 2

To a resin flask equipped as described in Example 1 was added:

5 147 gms (1.5 moles) maleic anhydride
 251 gms (3.3 moles) propylene glycol
 27 gms (1.5 moles) water.

10 The reaction mass was heated to 90°C and held at that temperature for 1 hour. 122 gms (0.90 moles) of a C₁₀ hydrocarbon concentrate containing 81% dicyclopentadiene were then added over a 2—3 minute period. 1.5 moles (222 grams) of phthalic anhydride was added when the temperature reached 100°C, 2—5 minutes after setting the temperature controller at 140°C. The controller was then set at 140°C for a 2 hour period and at 170°C for about 1 hour.

15 The reflux condenser was then replaced with apparatus suitable for water removal and the temperature controller set at 200°C. After 9.2 hours total reaction time, an acid number of 30 was attained and the reaction was terminated.

 The resin was blended with hydroquinone and styrene as before. The SPI exotherm of 402°F (206°C) is superior of Example 1 where water was used but phthalic anhydride was not staged.

Example 3

To a reactor equipped as described in Example 1 was added:

20 147 gms (1.5 moles) maleic anhydride
 251 gms (3.3 moles) propylene glycol
 9 gms (0.5 moles) water

25 The reaction mass was heated to 90°C over a 13 minute period. At this point 122 gms (0.90 moles) of a C₁₀ hydrocarbon concentrate containing 81% dicyclopentadiene (DCPD) was added over a 2—3 minute period. A heat up to 140°C was started. 222 gms of phthalic anhydride was added about 5 minutes after the 90°C temperature was attained or 2—3 minutes after the DCPD was added. After 2 hours at 140°C, the controller was set at 170°C and held there for 1 hour.

30 The reflux condenser was removed, replaced with water removal equipment as in the above examples, and the reaction continued until an acid number of 35 was reached for the resin. After blending the resin with hydroquinone and styrene as before, the resin had a maximum exotherm of 378°F (192°C) pointing out the beneficial effect of a minimal hydrolysis period and low levels of water.

Example 4

To a reactor equipped as described in previous examples was added:

40 147 gms (1.5 moles) maleic anhydride
 251.1 gms (3.3 moles) propylene glycol
 18 gms (1.0 moles) water.

45 The above mass was heated to 55°C over a one-half hour period (The controller was set at 50°C so there was a 5°C exotherm). At the 1/2 hour point, 122 gms of 81% dicyclopentadiene were added over a 1-1/2 minute period. The controller was set at 140°C. When the temperature reached 100°C 222 gms (1.5 moles) of phthalic anhydride were added. This reduced the mass temperature to 85°C but the 140°C temperature was attained fifteen minutes later. After 37 minutes at 140°C, the reflux condenser was replaced with a Dean Stark trap, the steam condenser was engaged and normal polyesterification techniques employed.

50 The reaction temperature was set at 200°C and the resin was cooked to an acid number of 34.

 Hydroquinone and styrene were added in the manner described in previous examples to a 40% monomer level.

Example 5

To a reactor equipped in a manner described in previous examples was charged:

147 gms (1.5 moles) maleic anhydride
222 gms (1.5 moles) phthalic anhydride
251.1 gms (3.3 moles) propylene glycol
54 gms (3.0 moles) water
122.2 gms (0.90 moles) of 95.5% C₁₀ hydrocarbon concentrate.

After 35 minutes of agitation at room temperature, the temperature controller was set at 140°C. The reaction mass was allowed to reflux in the range of 130°C to 136°C for 3 hours. A steam condenser and Dean Stark trap was installed, the temperature controller set at 200°C and a normal polyesterification procedure was allowed to continue to an acid number of 33.

The resin was cooled to 150°C where 0.046 grams of hydroquinone (100 ppm based on 40% styrene) was added. The reactor mass was further cooled to 100°C, at which point 461 gms of styrene was added.

Example 6

To a reactor equipped as described in the previous examples was charged:

1.5 moles (147 gms) maleic anhydride
3.3 moles (251.1 gms) propylene glycol
0.1 moles (1.8 gms) water

The reactants were heated to 90°C over a 15 minute period. Over a 2 minute period, 0.9 moles (121.9 gms) of 97.46% C₁₀ hydrocarbon concentrate were added. The temperature controller was set at 140°C. At 100°C, 1.5 moles (222 gms) phthalic anhydride were added to the reactor. Once 140°C was reached, the reaction mass exothermed to 160°C. After 2 hours at 140°C, the temperature controller was set at 170°C for 1 hour. A steam condenser and Dean Stark trap were set in place and the polyesterification process continued at a temperature of 200°C to an acid number of 33. During the cooling phase, 0.045 gms hydroquinone were added.

Example 7

To a reactor equipped as described in the previous examples was charged:

1.5 moles (147 gms) maleic anhydride
3.3 moles (251.1 gms) propylene glycol
0.3 moles (5.4 gms) water

The reactants were heated to 90°C over a 15 minute period. Over a 2 minute period, 0.9 moles (121.9 gms) of 97.46% C₁₀ hydrocarbon concentrate were added. The temperature controller was set at 140°C for 2 hours. At 100°C, 1.5 moles (222 gms) phthalic anhydride were added to the reactor. The temperature controller was set at 170°C for 1 hour. A steam condenser and Dean Stark trap were set in place and the polyesterification process continued at a temperature of 200°C until an acid number of 35 was reached.

The resins prepared in the foregoing examples and their physical properties are summarized in Tables I—V.

TABLE I
Reaction Conditions

Examples	Water to Maleic Anhydride mole ratio	Temp. of Hydrocarbon Add'n	Addition Temp. of Phthalic Anhydride
Control A	none	90°C	ambient
Control B	None	90°C	ambient
Example 1	1.7:1	90°C	ambient
Example 2	1:1	90°C	ambient
Example 3	0.33:1	90°C	100°C
Example 4	0.66:1	50°C	100°C
Example 5	2:1	ambient	ambient
Example 6	0.066:1	90°C	100°C
Example 7	0.2:1	90°C	100°C

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TABLE II
Reaction Results

	Example	Total Reaction Time (Hours)	Acid Number	Hydrocarbon Efficiency (%)	
5	Control A	9.2	34	92.8	5
	Control B	10.5	34	96.7	
	1	10.0	32	92.3	
	2	9.2	30	98.7	
	3	9.9	34	96.3	
10	4	6.2	34	90.3	10
	5	9.0	33	93.2	
	6	8.4	33	89.1	
	7	9.2	35	97.5	

TABLE III
Resin Properties/SPI Cure*

	Example	Viscosity (cps) 40% Styrene	Gardner Color	Gel time (minutes)	Cure Time (minutes)	Maximum Exotherm	
	Control A	94	>1, <2	5.0	9.6	309°F (154°C)	
	Control B	92.5	2	4.3	8.7	352°F (178°C)	
20	1	82.5	1	3.8	8.2	368°F (187°C)	20
	2	78.8	>1, <2	2.3	8.0	402°F (206°C)	
	3	81.6	>1, <2	3.3	8.1	378°F (192°C)	
	4	89.0	>1, <2	4.9	9.2	367°F (186°C)	
	5	82.5	1	3.6	8.3	343°F (173°C)	
25	6	77.5	N.A.	4	9.54	345°F (174°C)	25
	7	80	N.A.	3.8	8.3	359°F (182°C)	

*Using 1% benzoyl peroxide as the catalyst.

TABLE IV
Room Temperature Cure Properties*

	Example	Gel Time (minutes)	Cure Time (minutes)	10 Min. Temp. (°F)	Max. Exotherm (°F)	
30	Control A	8.6	22.2	91°F (33°C)	241°F (116°C)	30
	Control B	7.8	20.6	91°F (33°C)	270°F (132°C)	
	1	4.1	14.2	160°F (71°C)	284°F (140°C)	
35	2	6.0	15.5	150°F (66°C)	288°F (142°C)	35
	3	5.1	14.5	163°F (73°C)	291°F (144°C)	
	4	5.2	14.5	153°F (67°C)	291°F (144°C)	
	5	4.6	14.2	171°F (77°C)	279°F (137°C)	
	6	N.A.	N.A.	N.A.	N.A.	
40	7	N.A.	N.A.	N.A.	N.A.	40

*Using 1% methyl ethyl ketone peroxide, 0.1% cobalt naphthenate 6%, 0.1% dimethyl aniline as the catalyst

TABLE V
Physical Properties

	Example	2 hrs.	4 hrs.	1 day	10 days	Heat Distortion Temp. (°C)	
45	Control A	0	0	33	43	54	
	Control B	0	0	28	—	62.5	
	1	0	12	41	54	59	
	2	0	12	41	51	63	
50	3	0	7	33	41	61.5	50
	4	0	7	38	45	61.5	
	5	0	5	33	42	63	
	6	N.A.	N.A.	N.A.	N.A.	58	
55	7	N.A.	N.A.	N.A.	N.A.	60	55

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Examples 8—12

Glass laminates, containing 25% random fiber glass matt, were prepared using the styrene-resin blends of Examples 1—6. Two fiber glass plys and a normal hand-roller technique were used to make a part about 1/8-inch thick and 12" by 14" in dimensions from each resin blend.

The catalyst used in each case consisted of 1% methyl ethyl ketone peroxide, 0.1% cobalt naphthenate and 0.02% dimethyl aniline.

The catalyst-resin blends were modified with p-benzoquinone in each instance to give a room temperature gel time in the range from about 15—20 minutes.

The glass laminates were cured at 22—24°C and tested after at least 10 days. The properties set forth in Table VI were found.

TABLE VI
Physical Properties
75% Resin, 25% Glass Mat

Examples	Flex Strength kg/cm ²	Flex Modulus kg/cm ²	Tensile Strength kg/cm ²	Tensile Modulus kg/cm ² × 10 ³	Percent Elongation
Control X (with resin of Control A)	1273	56.7	678	51.7	1.5
Control Y (with resin of Control B)	1273	56.7	678	51.7	1.5
8 (with resin of Example 1)	1136	54.0	752	50.4	1.7
9 (with resin of Example 2)	1176	50.5	925	57.6	1.9
10 (with resin of Example 3)	1221	55.8	745	42.5	2.0
11 (with resin of Example 4)	1387	70.7	731	69.0	1.3
12 (with resin of Example 5)	1289	63.4	728	65.6	1.3

Example 13

To a reaction flask equipped with a stirrer, thermowell, nitrogen sparge tube and a reflux condenser were added:

174.1 gms (1.5 moles) maleic acid
249.2 gms (1.5 moles) o-phthalic acid
251.1 gms (3.3 moles) propylene glycol
36.0 gms (2.0 moles) water

The reaction mass was heated rapidly to 90°C under agitation. 123.75 gms (0.9 moles, of a C₁₀ hydrocarbon concentrate (96% reactive) were added over a 3 minute period. The temperature controller was set at 140°C. The reaction mass refluxed at 127°C. After about 2 hours of refluxing the temperature controller was set at 170°C for 3/4 hour. The reflux condenser was replaced with a steam condenser, a water cooled condenser and a Dean Stark trap to collect the distillate. The reaction temperature was set at 200°C and the resin was allowed to proceed until an acid number of 34.6 was attained.

100 ppm of hydroquinone was added (based on 40% styrene) when the temperature went down to 150°C. At 100°C, 447 gms of styrene were blended with the polyester.

Reaction Results

1. Reaction Time 10.73 hours.
2. Acid Number 34.6
3. Hydrocarbon Effic. 87.95%
4. Viscosity 68 cps.

Reaction Results (cont.)

	*5. Room Temp. Gel.	6 min.	
	*6. Room Temp. Cure—		
	—cure time	13.66 min.	
5	—10 min. temp.	180.5°F (82.5°C)	5
	—max. exotherm	294.8°F (146°C)	
	**7. SPI 180°F Test		
	—gel time	3.46 min.	
	—cure time	7.84 min.	
10	—max. exotherm	363.2°F (184°C)	10
	8. Gardner Color	1	
	9. Heat Distortion Temp.	71°C	
	*Room Temp. cure system:		
	0.1% cobalt naphthenate		
15	0.1% dimethyl aniline		15
	1% methyl ethyl ketone peroxide		
	**SPI 180°F (82°C) cure system.		
	1% benzoyl peroxide.		

20 The foregoing example illustrates the beneficial results of adding water to a system wherein the dicarboxylic acid anhydrides are replaced with dicarboxylic acids. It is to be noted that the maximum exotherm of the room temperature cure and the S.P.I. cure, and the heat distortion temperature are improved over example 2 and control B.

- 25 WHAT WE CLAIM IS:—
1. A resin produced by the reaction of a mixture comprising
 - (A) (1) an alpha, beta ethylenically unsaturated dicarboxylic acid or the anhydride thereof, or mixtures thereof, or
 - (2) a saturated polycarboxylic acid or the anhydride thereof, or
 - (3) mixtures of (1) and (2),
 - (B) from 0.03 to 10 moles water per mole of (A) (1) and/or (A) (2),
 - (C) from 0.05 mole to 1.0 mole of a C₁₀ hydrocarbon concentrate, which comprises at least 60% by weight of dicyclopentadiene, per mole of (A) (1) and/or (A) (2), and
 - (D) a polyol or an alkylene oxide with the proviso that when (D) is an alkylene oxide of 2—4 carbons, (A) is at least 90% by weight of a dicarboxylic acid anhydride, the reaction having been carried out at a temperature within the range of from 180°C to 250°C with the removal of the water of condensation until the acid number of the resin is within the range of from 30 to 35.
 2. A resin as claimed in Claim 1 in which the unsaturated dicarboxylic acid is selected from maleic, fumaric, mesaconic, itaconic, and citraconic acids.
 3. A resin as claimed in Claim 1 or Claim 2 in which the saturated polycarboxylic acid is selected from orthophthalic, terephthalic, isophthalic, trimellitic, adipic, sebacic, and succinic acids.
 4. A resin as claimed in any one of the preceding claims in which the C₁₀ hydrocarbon concentrate comprises 60 to 90% by weight of dicyclopentadiene.
 5. A resin as claimed in any one of Claims 1 to 3 in which the C₁₀ hydrocarbon concentrate comprises 90 to 100% by weight of dicyclopentadiene.
 6. A resin as claimed in any one of the preceding claims in which the polyol is a glycol selected from ethylene, propylene, diethylene, and dipropylene glycols.
 7. A resin as claimed in any one of Claims 1 to 5 in which the alkylene oxide is ethylene oxide, propylene oxide or butylene oxide.
 8. A resin as claimed in Claim 1 wherein (D) is a polyol and (A) is a polycarboxylic acid or anhydride, and reaction mixture additionally contains up to 25% by weight, based upon the total weight of the polycarboxylic acid or anhydride, of a monohydric alcohol having 3—18 carbon atoms, a fatty acid or oil having up to 22 carbon atoms, a monocarboxylic aromatic acid, or a mixture of two or more thereof.
 9. A resin as claimed in Claim 8 in which the monohydric alcohol is butanol, propanol, allyl alcohol, or stearyl alcohol.
 10. A resin as claimed in Claim 8 in which the fatty acid is selected from caproic, lauric, palmitic, stearic, oleic, and linoleic acids.



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Reaction Results (cont.)

	*5. Room Temp. Gel.	6 min.	
	*6. Room Temp. Cure—		
	—cure time	13.66 min.	
5	—10 min. temp.	180.5°F (82.5°C)	5
	—max. exotherm	294.8°F (146°C)	
	**7. SPI 180°F Test		
	—gel time	3.46 min.	
	—cure time	7.84 min.	
10	—max. exotherm	363.2°F (184°C)	10
	8. Gardner Color	1	
	9. Heat Distortion Temp.	71°C	
	*Room Temp. cure system:		
	0.1% cobalt naphthenate		
15	0.1% dimethyl aniline		15
	1% methyl ethyl ketone peroxide		
	**SPI 180°F (82°C) cure system		
	1% benzoyl peroxide.		

20 The foregoing example illustrates the beneficial results of adding water to a system wherein the dicarboxylic acid anhydrides are replaced with dicarboxylic acids. It is to be noted that the maximum exotherm of the room temperature cure and the S.P.I. cure, and the heat distortion temperature are improved over example 2 and control B.. 20

WHAT WE CLAIM IS:—

- 25 1. A resin produced by the reaction of a mixture comprising 25
- (A) (1) an alpha, beta ethylenically unsaturated dicarboxylic acid or the anhydride thereof, or mixtures thereof, or
- (2) a saturated polycarboxylic acid or the anhydride thereof, or
- (3) mixtures of (1) and (2),
- 30 (B) from 0.03 to 10 moles water per mole of (A) (1) and/or (A) (2), 30
- (C) from 0.05 mole to 1.0 mole of a C₁₀ hydrocarbon concentrate, which comprises at least 60% by weight of dicyclopentadiene, per mole of (A) (1) and/or (A) (2), and
- 35 (D) a polyol or an alkylene oxide with the proviso that when (D) is an alkylene oxide of 2—4 carbons, (A) is at least 90% by weight of a dicarboxylic acid anhydride, the reaction having been carried out at a temperature within the range of from 180°C to 250°C with the removal of the water of condensation until the acid number of the resin is within the range of from 30 to 35. 35
- 40 2. A resin as claimed in Claim 1 in which the unsaturated dicarboxylic acid is selected from maleic, fumaric, mesaconic, itaconic, and citraconic acids. 40
3. A resin as claimed in Claim 1 or Claim 2 in which the saturated polycarboxylic acid is selected from orthophthalic, terephthalic, isophthalic, trimellitic, adipic, sebacic, and succinic acids.
- 45 4. A resin as claimed in any one of the preceding claims in which the C₁₀ hydrocarbon concentrate comprises 60 to 90% by weight of dicyclopentadiene. 45
5. A resin as claimed in any one of Claims 1 to 3 in which the C₁₀ hydrocarbon concentrate comprises 90 to 100% by weight of dicyclopentadiene.
- 50 6. A resin as claimed in any one of the preceding claims in which the polyol is a glycol selected from ethylene, propylene, diethylene, and dipropylene glycols. 50
7. A resin as claimed in any one of Claims 1 to 5 in which the alkylene oxide is ethylene oxide, propylene oxide or butylene oxide.
- 55 8. A resin as claimed in Claim 1 wherein (D) is a polyol and (A) is a polycarboxylic acid or anhydride, and reaction mixture additionally contains up to 25% by weight, based upon the total weight of the polycarboxylic acid or anhydride, of a monohydric alcohol having 3—18 carbon atoms, a fatty acid or oil having up to 22 carbon atoms, a monocarboxylic aromatic acid, or a mixture of two or more thereof. 55
- 60 9. A resin as claimed in Claim 8 in which the monohydric alcohol is butanol, propanol, allyl alcohol, or stearyl alcohol. 60
10. A resin as claimed in Claim 8 in which the fatty acid is selected from caproic, lauric, palmitic, stearic, oleic, and linoleic acids.



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11. A resin as claimed in Claim 8 in which the fatty oil is linseed oil, soybean oil, tall oil, or fish oil.
12. A resin as claimed in Claim 8 in which the monocarboxylic aromatic acid is benzoic acid or tertiary butyl benzoic acid.
13. A resin as claimed in any one of the preceding claims wherein the mole ratio of water to carboxylic acid or anhydride is from 0.05:1 to 3:1.
14. A resin as claimed in any one of the preceding claims in which the reactants have been heated initially to a temperature of at least 50°C.
15. A resin as claimed in any one of the preceding claims in which the reaction has been carried out at a temperature within the range of from 190°C to 205°C.
16. A resin as claimed in Claim 1 substantially as hereinbefore described in any of Examples 1 to 7 and 13.
17. A blend of a resin as claimed in any one of the preceding claims and an ethylenically unsaturated monomer.
18. A blend as claimed in Claim 17 in which the monomer is styrene, methyl styrene, chlorostyrene, vinyl toluene, divinyl benzene, vinyl acetate, acrylic acid, methacrylic acid, diallyl phthalate or a mixture of two or more thereof.
19. A blend as claimed in Claim 17 or Claim 18 in which the weight ratio of resin to monomer is from 4:1 to 1:2.
20. A blend as claimed in Claim 17 substantially as hereinbefore described in any one of Examples 1 to 7 and 13.
21. A fibre-reinforced laminate which has been made using a blend as claimed in any one of Claims 17 to 20 in which the resin is a polyester resin.
22. A laminate as claimed in Claim 21 in which the fibrous reinforcement comprises asbestos fibres, carbon fibres, glass fibres or other inorganic fibres.
23. A laminate as claimed in Claim 21 substantially as hereinbefore described in any one of Examples 8 to 12.
24. A laminate as claimed in any one of Claims 21 to 23 which is in a cured state.
25. A laminate as claimed in Claim 24 substantially as hereinbefore described in any one of Examples 8 to 12.
26. A coating mixture which has been made using a blend as claimed in any one of Claims 17 to 20 in which the resin is an alkyd resin.
27. A coating mixture as claimed in Claim 26 which is in a cured state.
28. An enamel paint comprising a coating mixture as claimed in Claim 27.
29. A method of making a laminate as claimed in Claim 21 which comprises mixing into the blend free radical forming catalysts and mixing the resultant mixture with fibrous reinforcement.
30. A laminate which has been made by a method as claimed in Claim 29.
31. A method of making a coating mixture as claimed in Claim 26 which comprises compounding the resin with one or more solvents, pigments, or other resinous products.
32. A coating mixture which has been made by a method as claimed in Claim 31.

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