

**Reinforced Composites  
from Polyester Resins  
1972**

Dr. M.W. Ranney

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**Thirty-Six Dollars**

**NOYES DATA CORPORATION  
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## FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1965 relating to reinforced composites from polyester resins.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legalistic phraseology, this book presents an advanced commercially oriented review of current technology and uses of polymers in making reinforced composites.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easy access to the information contained in this volume.

# CONTENTS AND SUBJECT INDEX

INTRODUCTION	1
1. SYNTHESIS OF POLYESTER INTERMEDIATES	2
Hydroxy Intermediates	2
Hydroxyneopentyl Hydroxypivalate	2
Cyclohexane Dimethanol Carbonates, Alkali Resistance	4
Hydroxyl Dicyclopentadiene, Low Shrinkage	6
2,2-Di(4-Hydroxyethylphenyl)Propane, Cycloalkanediois	7
3,3,3',3'-Tetramethyl-6,6'-Di(2-Hydroxypropoxy)-1,1'-Spirobiindane	10
Bis(Hydroxyalkyleneoxycarbonyl)Benzenes	12
Diallylidene Pentaerythritol, Air Drying Coatings	15
Neopentyl Glycol, Solvent Resistant Coatings	17
Polyhydric and Unsaturated Ether Alcohols, Coatings	19
Carboxylic Acids, Anhydrides	20
Nitrilotriacetic Acid	20
3,4,3',4'-Benzophenone Tetracarboxylic Acid	21
Cycloaliphatic Dicarboxylic Acid and Glycol Mixtures	23
Dimer Acid, Polymeric Fatty Alcohols	24
Metal Phthalocyanine Octacarboxylic Acid	26
Tetralin Dianhydride, Cyclohexane Dimethanol	28
Tetrahydrophthalic Anhydride, High Temperature Polyesters	30
Esters of cis-1,2,3,4-Cyclopentanetetracarboxylic Acid	34
Dimethyl Muconic Acids	36
Sulfur-Containing Carboxylic Acids, Petroleum Fractions	38
Glycidyl Esters of Monocarboxylic Acids	41
Diels-Alder Adducts	43
1,3-Diene Lactones	43
Fulvene	46
Alpha-Pinene	47
Anthracene	49
Dicyclopentadiene	51
Cross-Linking, 2-Vinyl Butadiene	53
Dicyclopentadiene, Air Drying Coatings	55
Miscellaneous	57
Anhydride-Propylene Oxide	57
Flexible Polyester-Ether Compositions	59
Polyester-Polyether Copolymers	61
Branched Chain Thermoplastic Polyesters	64
Phenol-Aldehyde, Oxirane Compounds, Polycarboxylic Acid	66
Carboxylic Esters of Diphenyl Oxides	67
Methylene Hydroxypropionic Acid	69
Formalized Polyester Resin, Air Drying Coatings	70
Tetrahydrobenzaldehyde Derivatives, Air Drying Systems	71

## Contents and Subject Index

2. ADDITIVES	75
Catalysts	75
Tertiary Butyl Percrotonate	75
Acetylenic Dipperesters	76
1-Hydroxy-1'-Hydroperoxy-Bis(3,3,5-Trimethylcyclohexylperoxide)	78
Rosin Acid Peroxides	80
Ketone Peroxides from 3,3,5-Trimethylcyclohexanone	81
3,5-Dimethyl-3,5-Dihydroxy-1,2-Peroxycyclopentane	83
1,2-Substituted Ethanes	83
Formyl Phenyl Acetic Acid Derivatives	85
Accelerators, Promoters	87
Aryl Dialkanolamines	87
Adducts of Phosphorus Esters with Diketones	90
N-Ethyl-N-Hydroxyethyl-m-Methylaniline	92
Dimethylaniline, Triethanolamine, Diphenylamine	96
Phenyl Acetaldehyde Compounds	98
Copper, Cobalt, Calcium Salts, Synergistic Accelerator System	99
Antimony Trichloride	102
Cumene Hydroperoxide, MEK Peroxide and Thioglycolic Acid	103
Hydroperoxide, Vanadium Compound, Acid Phosphate Esters	103
Lithium Salts	106
Inhibitors, Storage Stability	106
Allyl t-Butyl-Methylphenyl Ether	106
Boric Acid Esters of Phenols	108
Metal Salts of Phenols, Copper Salts	109
Quinones	111
Dihydroxynaphthaquinones, Dihydroxynaphthalenes	114
Substituted Pyridines, Phenazine	114
Secondary Aromatic Amines	117
Thickening, Gelation	118
Cyclic Anhydrides, Magnesium Oxide	118
Monocarboxylic Acids, Magnesium Oxide	119
Calcined Basic Magnesium Carbonate	121
Calcium Oxide, Lithium Chloride	123
Magnesium-Containing Polyesters	123
Alkaline Oxides, Polyhydric Alcohols	125
Aluminum Octoate	126
Anhydrous Carboxylic Acid Metal Salts	131
Bis(Hydroxymethyl) Phosphinic Acid, Furfuryl Alcohol	132
Polystyrene Fiber-Silica	134
Boron Trifluoride, Metal Alcoholates	136
Substituted Pyrazolones	137
Stannous Chloride, 4-Methyl-2,6-Di-tertiary-Butylphenol	139
Color Control	142
Phosphoric Acid	142
Phosphorus Compounds	143
Copper-Phosphorus Complexes	145
Arsines, Stibenes and Phosphines	146
Tertiary Amine Cure, Triaryl Phosphines	150
Cobalt Salts, 1,10-Phenanthroline	152
Barbituric Acids, Alpha Acyl Nitriles	154
Peroxide, Vanadium Compounds, Reducing Sulfur Component	155
Tin Catalysts	160
Color Indicators - Degree of Cure	162
Miscellaneous	165
Piperidine, Isomerization of Maleic Acid	165
2,4-Dihydroxy-2'-Methylbenzophenone, UV Stabilizer	165
Fatty Acid Cyclohexamides as Flow Control Agents	166

## Contents and Subject Index

3.	<b>FLAME RETARDANT POLYESTERS</b>	168
	Acid, Anhydride Intermediates	168
	Tetrabromophthalic Acid	168
	Tetrabromophthalic Anhydride	170
	Dibromosuccinic Acid	174
	2,3-Dibromoalkyl Succinic Anhydride	177
	Chlorendic Acid, Phosphonated Polyesters	180
	Chlorendic Acid, Unsaturated Phosphorus Compounds	183
	Acyldiphosphonic Acids, Chlorendic Acid	188
	Pentachlorophenoxy Acetic Acid	190
	Hydroxy Intermediates	191
	2,2,4,4-Tetrachloro-1,5-Dihydroxy-3-Pentanone	191
	Alkalene Oxides, Halogenated Alcohols	193
	2,2-Bis(Bromomethyl)-1,3-Propanediol	196
	2-Methyl-3,3,3-Trichloro-1,2-Propanediol	198
	Polyols of Perchlorinated Diaminophenyls	200
	Other Reactants	201
	Polyhalogenous Epoxides	201
	2-Methyl-3,3,3-Trichloro-1,2-Epoxypropane	204
	Allyl Functional Halogenated Agents	206
	Halogenated Bicyclo Vinyl Ethers, Styrene Replacement	207
	Vinyl Ethers of Brominated Phenols	209
	Hexachlorocyclopentadiene	211
	Vinyl Diphenylphosphine Oxide	213
	Diallyl Chlorendate	214
	Additives	218
	Antimony Trihalides	218
	Halogenated Esters of Boron, Silicon, Antimony	219
	Halogenated Triazine Derivatives	222
	Di-(3-Hydroxy-4-Benzoylphenyl)Phenylphosphinate	226
	Phosphoric Acid, Halogenated Resins	227
	Miscellaneous	228
	Blends with Acrylic Resins to Improve Weathering	228
	Aluminum Isopropoxide-Carboxylic Acid Catalyst	230
	Phosphoric Acid-Alkylene Oxide Reaction Products	232
	Post-Halogenation	234
4.	<b>MODIFIED POLYESTER FORMULATIONS</b>	239
	Acrylics	239
	Ethyl Acrylate, Allyl Methacrylate, Triallyl Cyanurate	239
	Methyl Methacrylate, Methyl Methacrylate-Styrene Copolymer	240
	Methacrylate-Styrene Copolymer, Monomer Systems	242
	Amides, Nitrogen Compounds	245
	Soluble Polyester Amide Resins	245
	Polyamides	247
	Imides	250
	Melamine, Dicyandiamide	253
	Other Thermoplastic Polymers	255
	Polyolefin-Polyester Extrusion	255
	Liquid Polyester, PVC	256
	PVC Blow Molding Compositions	259
	Thermoplastic-Polyester Graft Copolymers	260
	Styrene-Butadiene Copolymers	262
	Oxidized Copolymers of Styrene-Butadiene	265
	Reactive Solvents	267
	Bicyclo[2.2.1] Hept-2-yl Acrylate	267
	3-Methyl-1,4,6-Heptatriene	270
	1,5,9-Cyclododecatriene, 1,2,4-Trivinyl Cyclohexane	271
	Toluene Diallyl Diurethane	273

## Contents and Subject Index

Miscellaneous	275
Polyethylene Addition to Improve Abrasion Resistance	275
Polycaprolactones as Low Profile Additives	276
Bituminous Compositions	279
5. GENERAL PROCESSING	281
Glass Fiber Treating	281
Glass Fiber Strand Process	281
Transparent Moldings, Silane Coupling Agents	290
Epoxy-Polyester Coatings for Glass Fiber	293
Silane Coupling Agent, Epoxides	298
Other Processes	301
Two-Step Process, Delayed Addition of Acid Component	301
One-Step Process	303
Granular Polyester	305
Powder Composition Containing Diallyl Phthalate	307
Cellular Product	309
Crystallization Promoters	311
Coating for Foamed Polystyrene	312
N,N-Diallylmelamine Coated Clay	313
COMPANY INDEX	317
INVENTOR INDEX	319
U.S. PATENT NUMBER INDEX	322

## INTRODUCTION

Volume of reinforced thermosets was approximately 900 million pounds in the United States in 1970, showing a slight downturn from 1969 but substantial growth over the 1967 volume of 750 million pounds. Future growth, of a predicted minimum of 10 to 15% per year through the seventies is closely related to the high commitment to research and development by the plastics industry during the past few years. This effort has provided improved and strengthened materials, speedier and more automated production techniques and improved surface finishing.

Polyesters which first became available during World War II constitute, by far, the largest volume of the reinforced plastics market. U.S. consumption of reinforced polyesters in 1970 was 450 million pounds, with total consumption for all uses being 600 million pounds. New developments introduced during 1970 included noncombustible, heat resistant resins, and two new low profile resins.

The major research efforts over the past few years have been in the areas of inhibitors, viscosity-thickening additives, thermoplastic modified polyester formulations generally referred to as "low shrink" or "low profile" and flame retardant systems.

This review summarizes the processes relating to unsaturated polyester-based technology, with particular emphasis on new polyester raw materials, catalysts, accelerators, inhibitors and the very considerable activity in flame retardant resin systems.

# SYNTHESIS OF POLYESTER INTERMEDIATES

## HYDROXY INTERMEDIATES

### Hydroxyneopentyl Hydroxypivalate

R.B. Duke, Jr. and M.A. Perry; U.S. Patent 3,320,336; May 16, 1967; assigned to Eastman Kodak Company have found that unsaturated polyesters of desirably improved properties are obtained from bifunctional dihydroxy compounds represented by Formula (1) and certain bifunctional unsaturated dicarboxylic acids. These unsaturated polyesters show marked advantages over conventional polyesters prepared from the more common diols, e.g., ethylene glycol, propylene glycol, diethylene glycol, and the like, both in terms of processability and in the characteristics of the resulting thermoset resins. In terms of processability, the unsaturated polyesters can be prepared in much shorter reaction times of about from 5 to 10 hours.

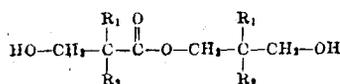
The high boiling points of the dihydroxy compounds, which are substantially above those of the more common glycols, also facilitate the preparation of the unsaturated polyesters. For example, hydroxyneopentyl hydroxypivalate, the lowest member represented by Formula (1), has a boiling point above 275°C. at atmospheric pressure; consequently, the unsaturated polyesters may be processed at the desirably higher temperatures of from 250° to 260°C. without loss of the glycol. This is a distinct advantage over the processes using the more common glycols at 200° to 220°C. in that significantly faster esterification rates are obtained at these elevated temperatures. The polyesters are particularly stable to thermal and oxidative degradation which results in essentially water-white polymers.

Aside from the ease of processing the new polyesters, the dihydroxy compounds of Formula (1) impart certain advantageous properties to the finished unsaturated polyesters and the thermoset resins. Foremost among these properties is the remarkable resistance of the thermoset resins to hydrolysis in either basic or acidic aqueous media. For this reason, the thermoset resins are especially useful in the preparation of fiber glass boat hulls and other materials which require outstanding hydrolytic and oxidative stability. This represents a distinct improvement over conventional polyesters which are generally unstable under these conditions.

The process involves the preparation of unsaturated polyesters by direct esterification in a melt of a dihydroxy compound represented by the general structure (1) following, where

## Synthesis of Polyester Intermediates

(1)



each  $R_1$  and  $R_2$  represent the same or different alkyl groups of from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, etc. groups, with a bifunctional unsaturated dibasic acid such as maleic anhydride, maleic acid, fumaric acid, tetrahydrophthalic acid, tetrahydrophthalic anhydride, chloromaleic acid, itaconic acid, citraconic acid and mesaconic acid, at a temperature above  $20^\circ\text{C}$ . and preferably from about  $200^\circ$  to  $260^\circ\text{C}$ ., with or without an esterification catalyst as desired, until the acid number (mg.KOH/g. polyester) of the polymer reduces to 30 or below.

The proportions of the dihydroxy compound and the unsaturated dibasic acid employed are approximately equimolar, and preferably with a slight molar excess of the dihydroxy compound. The following examples illustrate the process.

**Example 1:** Maleic anhydride-phthalic anhydride-hydroxyneopentyl hydroxypivalate copolymer is prepared by combining 24.5 grams (.0.25 mol) maleic anhydride, 37 grams (0.25 mol) phthalic anhydride and 113 grams (0.565 mol) hydroxyneopentyl hydroxypivalate in a 1 liter, 3 neck flask equipped with stirrer, distillation arm and gas inlet tube extending beneath the surface of the reactants. No catalyst was employed. The nitrogen purge entered the flask through one arm and exited beneath the surface of the reactants. This served the dual purpose of protecting the reactant from oxidative discoloration and aided in sweeping the water formed during esterification into the distillation arm where it was condensed and removed. The reactants were heated at  $85^\circ$  to  $95^\circ\text{C}$ . for one hour.

Following this initial reaction period, the reactants were heated rapidly to  $230^\circ\text{C}$ . to complete the esterification. Samples were withdrawn from the flask periodically and titrated with standard sodium hydroxide to determine the progress of the reaction. After seven hours, the acid number of the polymer had dropped to 28. The polymer was then cooled to  $80^\circ$  to  $90^\circ\text{C}$ . and blended with styrene (30% by weight). Hydroquinone (0.01%) was added as polymerization inhibitor. The resulting polyester-styrene solution was clear and essentially water-white. The polyester-styrene solution was polymerized with a peroxide catalyst at  $90^\circ\text{C}$ . to yield a rigid, thermoset resin. The resin was clear and faintly yellow in color. Fiber glass laminates prepared with the polyester-styrene solutions, on curing, showed outstanding resistance to hydrolytic degradation when treated with hot water.

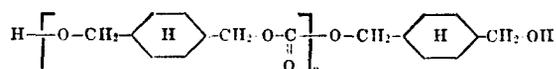
**Example 2:** The preparation of isophthalic acid-fumaric acid-hydroxyneopentyl hydroxypivalate copolymer is as follows. Isophthalic acid, 33.2 grams (0.2 mol), and hydroxyneopentyl hydroxypivalate, 120.5 grams (0.59 mol), were combined in the apparatus previously described. The reactants were heated rapidly to  $240^\circ$  to  $250^\circ\text{C}$ . and processed to an acid number below 10. This took three to four hours. The mixture was then cooled to  $170^\circ\text{C}$ . and 34.8 grams (0.3 mol) of fumaric acid was added. The polyester was then processed for an additional six hours until an acid number below 30 was obtained. The polyester was then cooled to  $80^\circ$  to  $90^\circ\text{C}$ ., and 30 milligrams of hydroquinone and 62 grams of styrene (30% by weight) were added. The resulting styrene-polyester solution was

## Synthesis of Polyester Intermediates

clear and essentially water-white. The styrene-polyester solution was copolymerized by the addition of a peroxide catalyst yielding a clear, rigid, thermoset resin. The solutions had excellent adhesive properties and were useful as laminating agents for wood, metals, fiber glass, etc. The laminated materials on curing showed high stability toward thermal, hydrolytic and oxidative degradation.

### Cyclohexane Dimethanol Carbonates, Alkali Resistance

R. Nehring, K. Heidel and K. Hamann; U.S. Patent 3,551,520; December 29, 1970; assigned to Chemische Werke Hüls AG, Germany describe unsaturated polyesters of unsaturated polybasic acids and one or more carbonates of cyclohexane-1,4-dimethanol of Formula (A) which follows where n is an integer from 1 to 9, preferably 1 to 4.



Such dihydric carbonate compounds can easily be produced by causing 1,4-bis(hydroxymethyl)cyclohexane and phosgene in a molar ratio within the range from 1:0.5 to 1:0.97 to react at atmospheric pressure in the presence of an inert solvent.

The unsaturated polyesters are produced conventionally by polycondensation, for example, in a melt, where the cyclohexane-1,4-dimethanol carbonates, if desired in mixture with other alcohols, are reacted with unsaturated polybasic acids which can be replaced, in part, by saturated polybasic carboxylic acids or the esterifiable derivatives. In general, the unsaturated polyesters have the following percentage range of molar proportions.

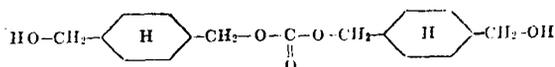
Monomer	General, percent	Preferred, percent
Carbonate of cyclohexane-1,4-dimethanol of Formula (A)	35-70	45-60
Unsaturated polybasic acid	5-50	40-50
Saturated polybasic carboxylic acids	0-45	0-10

The molded shapes and coating produced by the process exhibit a surprisingly high heat distortion stability at elevated temperatures, in conjunction with a high impact strength and good elasticity. The copolymerizates, in view of their excellent impact strength and heat distortion stability at higher temperatures, are particularly suitable for the production of molded parts, such as aircraft components, subject to high thermal and mechanical stresses. The beneficial mechanical and thermal properties are coupled with an excellent resistance to alkalis. The carbonate bond in the hardened molded polyester masses is not attacked by saponifying agents, not even by sodium or potassium hydroxide under heat. The surface characteristics, as well as the mechanical properties of the test samples remain practically unchanged after boiling for several days in a sodium hydroxide solution. The physical properties of the cured products of this process are as follows:

Flexural strength (kg./cm. <sup>2</sup> )	600-2,000
Impact strength (kg.-cm./cm. <sup>2</sup> )	10-30
Indentation hardness (kg./cm. <sup>2</sup> ) 10 seconds	1,400-1,600
Heat distortion temp. according to Martens (°C.)	80-100

## Synthesis of Polyester Intermediates

**Example 1:** From cyclohexane-1,4-dimethanol (50% in the trans form), there is produced a cyclohexane-1,4-dimethanol carbonate of the following formula.



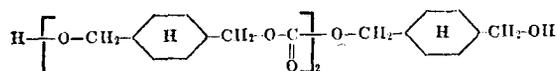
Nine hundred and sixty parts of the above carbonate and 348 parts of fumaric acid are esterified in the presence of 0.24 part hydroquinone, at 180°C., for 6 hours in a nitrogen-purged flask provided with a water finder and a stirrer. The reaction is such that an acid number of 11 is reached. After the reaction mixture has been allowed to cool to 140°C., 0.24 part of hydroquinone is added, and the polyester is dissolved in 800 parts of styrene.

200 parts of the water-clear polyester-styrene solution (styrene content 40%) are stirred together with 1.2 parts of a 10% cobalt naphthenate solution in toluene, as well as 4 parts of a 40% methylethylketone-peroxide solution in dimethyl phthalate. After 33 minutes at 20°C. in a mold, the mass becomes set, thereby producing a hard, glass-clear cast body having excellent heat distortion temperature dimensional stability, as well as good impact resistance. It is also worthy to note that the surface of the cast body exposed to air is just as hard and tack-free as the surfaces contacted by the mold. After a final cure at 80°C. for 8 hours, the following mechanical properties are obtained.

Flexural strength (kg./cm. <sup>2</sup> )	680
Impact strength (kg.-cm./cm. <sup>2</sup> )	10.7
Indentation hardness (kg./cm. <sup>2</sup> ) 10 seconds	1,460
Heat distortion temp., according to Martens (°C.)	100

After the same test specimens are boiled for 45 hours in a 10% solution of sodium hydroxide, a second measurement of the mechanical properties indicates no significant changes as compared to the unboiled specimens.

**Example 2:** From cyclohexane-dimethanol-1,4 (50% trans), there are produced 988 parts of the following cyclohexane-1,4-dimethanol carbonate:



This carbonate and 232 parts of fumaric acid are esterified in the presence of 0.23 part hydroquinone, in the same manner as in Example 1, for 7 1/2 hours, until an acid number of 10 is attained. After cooling to 140°C., the unsaturated polyester, after adding 0.23 part hydroquinone, is diluted with 765 parts styrene. Two hundred parts of the transparent water-clear polyester-styrene solution are stirred at room temperature with 1.2 parts of a 10% cobalt naphthenate solution and 4 parts of a 40% methylethylketone-peroxide solution. In a mold, the polyester mass is hardened after about 31 minutes and results in hard, water-clear, transparent cast bodies having the following properties after a final cure at 80°C. for 8 hours.

## Synthesis of Polyester Intermediates

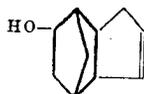
Flexural strength (kg./cm. <sup>2</sup> )	1,095
Impact strength (kg.-cm./cm. <sup>2</sup> )	16.7
Indentation hardness (kg./cm. <sup>2</sup> ) 10 seconds	1,459
Heat distortion temp. according to Martens (°C.)	92

Boiling the same specimens for 45 hours in a 10% solution of sodium hydroxide did not change the above values significantly.

### Hydroxyl Dicyclopentadiene, Low Shrinkage

A process described by S. Tsuruta, W. Koga, M. Abo and S. Abe; U.S. Patent 3,322,732; May 30, 1967; assigned to Hitachi Kasei Kogyo Kabushiki Kaisha, Japan provides self-copolymerizable resinous compositions of perfect reaction type having very small shrinkage ratio. The self-copolymerizable resin compositions can be obtained by mixing the linear monoesters or polyesters, that include within the same molecule (a) at least one  $\alpha, \beta$ -unsaturated dibasic acid, and (b) at least one 6-hydroxy-3 $\alpha, 4, 5, 6, 7, 7\alpha$ -hexanhydro-4,7-methanoindene (hydroxyl dicyclopentadiene) as copolymerizable compounds combined by ester linkage, with peroxides and, if necessary, with other additives.

Hydroxyl dicyclopentadiene can be obtained by addition of water to dicyclopentadiene (including its alkyl derivatives) under the presence of acid catalysts as sulfuric acid; and the structural formula is as follows.



An example of preparing hydroxyl dicyclopentadienes is as follows. At first, 800 g. of 25% sulfuric acid aqueous solution is added to 286 g. (1.86 mol) of dicyclopentadiene, and the solution is reacted with hard agitation for 5 hours at 104° to 107°C. Next, oil phase of the reaction liquid is separated by a separating funnel, and fractionally distilled in precise under reduced pressure. Then, 252 g. (83% of the theoretical amount) of hydroxyl dicyclopentadiene, of which the boiling point is 92° to 93°C. under 3 mm. Hg pressure, is obtained.

This product has the molecular formula C<sub>10</sub>H<sub>14</sub>O shown by elementary analysis, and  $n_D^{25} = 1.5246$ ,  $\alpha_D^{25} = 1.0773$ . The hydroxyl group combined with 6-position carbon atom of hydroxyl dicyclopentadiene readily forms ester linkage with a carboxylic acid by usual esterification process, and under such esterification the double bond between 2- and 3-positioned carbon atoms of hydroxyl dicyclopentadiene is maintained stable.

Accordingly, linear molecules thus obtained can be polymerized and cured three-dimensionally by mixing with additives of peroxides, curing accelerators and others. Namely, the unsaturated double bond between 2- and 3-position carbon atoms existing after the esterification of the hydroxyl group combined with 6-position carbon atom, and a double bond of  $\alpha, \beta$ -unsaturated dibasic acids, copolymerize readily under the presence of peroxides. The following examples illustrate the process.

## Synthesis of Polyester Intermediates

**Example 1:** 315 g. (2.10 mol) of hydroxyl dicyclopentadiene, 196 g. (2 mol) of maleic anhydride, and 76 g. (1 mol) of propylene glycol were charged in a four neck 1 liter flask. By esterification with agitation of this mixture heated to 150° to 190°C. in carbon dioxide atmosphere, a viscous thin orange-yellow resinous composition having acid value of 12.9 was obtained after about 13 hours. By measuring its density by sink and float method in aqueous solution of sucrose,  $D_4^{25} = 1.192$  was obtained.

Heated to 70°C., 0.5 g. of di-tertiary butyl peroxide were added to 20 g. of the resin and mixed homogeneously, then this mixture was heated to 140°C. After about 45 minutes the mixture was completely cured. After grinding the cured resin with iron mortar, insoluble percentage of the cured resin in acetone was measured and found to be 97.7%. The density of the cured resin, measured by sucrose solution method, was found to be 1.208, thus, comparing with the density before curing, the shrinkage ratio at curing was found to be only about 1.34%. And, in case of heating 10 g. of the resin with addition of 0.1 g. of benzoyl peroxide to 105°C. the resin was completely cured after about 30 minutes, and the density of the cured resin was 1.211. Thus, the shrinkage ratio at curing was about 1.59%.

Dissolving 10 g. of the cured resin in 5 cc of acetone, 0.1 g. of cobalt salt of naphthenic acid (Co content 20%) was added and mixed with the solution; further, 0.2 g. of methyl ethyl ketone peroxide solution was added and mixed homogeneously. Then, the resultant solution was painted over a glass plate. The solution formed a film after about 3 hours, and was cured completely after about 15 hours.

**Example 2:** 315 g. (2.10 mol) of hydroxyl dicyclopentadiene and 98 g. (1 mol) of maleic anhydride were charged in a four neck 500 ml. flask. By esterification with agitation of this mixture heated to 170° to 190°C. in carbon dioxide atmosphere, a thin orange resinous composition of a little fluidity having acid value of 9.1 was obtained after about 14 hours. By measuring the density of the resin,  $D_4^{25} = 1.149$  was found. Heating 10 g. of the resin with addition of 0.2 g. of ditertiary butyl peroxide to 140°C., the resin gelled. The measured density of the cured resin was 1.189, and thus, the shrinkage ratio after curing to before curing was recognized as about 3.48%.

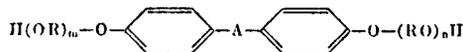
Next, 0.1 g. of cobalt salt of naphthenic acid (Co content 12%) was added and mixed, further, 0.2 g. of methyl ethyl ketone peroxide solution was added. Then the resultant solution left at room temperature began curing about 30 minutes after, and was cured almost completely after 5 hours. The density of the produced cured resin was 1.183, and the shrinkage ratio was 2.96%.

### 2,2-Di(4-Hydroxyethylphenyl)Propane, Cycloalkanediols

In a process described by J. Feltzin; U.S. Patent 3,538,187; November 3, 1970; assigned to Atlas Chemical Industries polyester resins are prepared by esterification of a mixture of dihydric alcohols comprising an oxyalkylene ether of an alkylidene diphenol and a cycloalkanediol with a dibasic acid which comprises as a major fraction an  $\alpha, \beta$ -unsaturated dicarboxylic acid. The polyesters are copolymerizable with ethylenically unsaturated compounds capable of free radical polymerization.

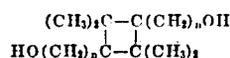
## Synthesis of Polyester Intermediates

The oxyalkylene ether of an alkylidene diphenol which is used to prepare the polyester component of the corrosion resistant resins conforms to the following generalized chemical formula:



where A is a 2-alkylidene radical having from 3 to 4 carbon atoms, R is an alkylene radical containing from 2 to 4 carbon atoms, m and n are each at least one and the average sum of m and n does not exceed 20.

Dihydric alcohols conforming to the above formula may be prepared by the direct addition of alkylene oxide to alkylidene diphenols or by reacting of olefin halohydrin with an alkylidene diphenol as described in U.S. Patent 2,331,265. The cycloalkanediol which is a component of the diol mixture used in the process to prepare the polyester component of corrosion resistant copolymer resins is characterized by the following generalized formula:



where n is selected from the integers 0 and 1. 2,2,4,4-tetramethyl-1,3-cyclobutanediol may be prepared by condensing isobutyraldehyde to obtain the corresponding dione, with subsequent reduction of the compound to the diol. 2,2,4,4-tetramethyl-1,3-di(hydroxymethyl)cyclobutane may be prepared by condensing 2,2,4,4-tetramethyl-1,3-cyclobutanedione with formaldehyde with subsequent dehydration and reduction of the condensation product to the diol. The above identified cyclobutanediols are known and available in commercial channels. The following examples illustrate the process.

**Example 1:** 312 grams of 2,2-prodendro bisphenol A [polyoxypropylene(2.2)isopropylidene diphenol] and 54 grams of 2,2,4,4-tetramethylcyclobutane-1,3-diol are introduced at room temperature into a one-liter, round bottom flask, fitted for stirring, heating, distillation, addition of reactants and maintenance of an inert gas atmosphere. After sweeping the flask with nitrogen, slow stirring and heating (mantle) is begun.

0.26 gram of Tequinol (technical grade hydroquinone) are then added. Then after slow addition of 145 grams of fumaric acid is begun, distillation starts at 198°C. After reaching cooking temperature at 210°C., the mixture is heated under nitrogen with stirring for 8 3/4 hours, the acid number being determined after cooking 4 hours, 6 hours, 7 hours, 8 hours and then on the final product resin. Vacuum is applied to the system and the heating stopped about 25 minutes before the end of the cook. The resin is then poured into a flat aluminum tray to cool and harden. Subsequently, the resin is broken up and ground. The final acid number may be determined to be 20.88, the final softening point may be determined to be 107°C., the solution clarity in 50-50% solution by weight of the resin in styrene may be determined to be a hazy yellow amber, the viscosity of the

## Synthesis of Polyester Intermediates

same solution is found to be 640 centipoises and the density of the same solution and is found to be 8.568 pounds per gallon.

**Example 2:** 249 grams of 2,2-prodendro bisphenol A and 101 grams of 2,2,4,4-tetra-methylcyclobutane-1,3-diol are introduced at room temperature into a one-liter round bottom flask fitted for stirring, heating, distillation, addition of reactants and maintenance of an inert gas atmosphere.

After sweeping the flask with nitrogen, slow stirring and heating are begun and 0.26 gram of a technical grade of hydroquinone is added. Thereafter, slow addition of 163 grams of fumaric acid is begun and distillation starts at 198°C. After reaching cooking temperature (210°C.) the mixture is heated under nitrogen with stirring for 8 hours. Vacuum is applied to the system and heating stopped at about 25 minutes before the end of the cook.

The resin is then poured into a flat aluminum tray to cook, harden and subsequently broken up and ground. The final acid value of the resinous product may be determined to be 31.12, the final softening point of the resin may be determined to be 118°C., the clarity of a 50-50% solution by weight of the resin in styrene may be determined to be a hazy amber color, the viscosity of the same solution may be determined to be 1,120 cp. and the density of the solution may be determined to be 8.555 pounds per gallon.

**Example 3:** The polyester resin of Example 1 is blended with styrene to form a 50% by weight of solution of the resin having a viscosity of about 640 cp. Castings of this solution are cured in a glass mold in a conventional manner using about 0.75 weight percent of benzoyl peroxide and heat, as by curing for about 16 to 24 hours at about 70°C., one hour at about 90°C., and one hour at about 150°C., to form a final cross-linked copolymeric composition.

**Example 4:** The polyester resin of Example 2 is blended with styrene to form a 50% by weight solution of the resin having a viscosity of about 1,120 cp. The resin is cured in the manner described in Example 3. After removal from the molds, the respective copolymeric compositions may be determined to have the following properties, measured by conventional techniques.

### Copolymer Composition of Example 3

Flexural strength —	15,000 psig
Flexural modulus —	0.49 x 10
Barcol hardness —	39-43
Heat deflection temperature —	150°C.
Specific gravity —	1.11
Shrinkage —	7.6%

### Copolymer Composition of Example 4

Flexural strength —	10,000 psig
Flexural modulus —	0.48 x 10
Barcol hardness —	41-43
Heat deflection temperature —	165°C.
Specific gravity —	1.11
Shrinkage —	7.7%

To test the corrosion resistance of the copolymer resins in neutral and basic media, accelerated corrosion baths are provided as follows: (1) neutral medium: 50% dioxane and 50% water; (2) basic medium: 50% dioxane, 47.5% water and 2.5% sodium hydroxide. Samples of the respective copolymer resins are suspended in the respective baths contained