

OIL-FREE OXIDATIVELY CURABLE POLYESTER COMPOSITIONS

Field of the Invention

5 This invention relates to oil-free oxidatively curable polyesters and coating compositions containing the polyesters. More specifically, the invention relates to oxidatively curable oil-free polyesters and carboxyl functional oligomeric adducts, which have been modified with 3,4-epoxy-1-butene.

Background of the Invention

10 Surface coatings based on alkyd resins are the most common technology for ambient-cure coating applications. An alkyd resin is a polyester incorporating vegetable oils or fatty acids. The oils and acids contain unsaturated fatty acids such as oleic, linoleic, and linolenic acids. These unsaturated moieties exhibit labile hydrogen atoms which are capable of being abstracted and in turn initiate oxidation reactions. The
15 oxidation reactions lead to crosslinking of the polyester molecules thus providing coatings with desired properties.

It is known in the art to modify alkyd resins to improve their coating properties. For example, Rokicki *et al.*, in *J.M.S.-Pure Appl. Chem.*, A33 (4), p.509 (1996) report that lacquers obtained from an alkyd resin containing 10-16 weight % of glycerol allyl
20 ether exhibit short drying time, good hardness of coatings, and good water resistance. The alkyd resins utilized in these coating applications are usually highly-colored as a result of processing from lower grade colored oils or fatty acids. A higher grade oil containing more desirable unsaturated fatty acids such as linoleic acid and linolenic acid, can be costly. An alternative to the oil based alkyd technology is therefore desired.

25 Rokicki *et al.*, in *J. Appl. Polym. Sci.* v.70, 2031 (1998) report that high hardness of coatings cured in air using photoinitiators can be achieved for an unsaturated polyester resin with polyfunctional allyl ether monomers incorporated into polyester molecules as the end groups or as the pendant geminal groups.

30 Even with this coating technology there still exists a need for non-alkyd polyester coating compositions which cure oxidatively without photoinitiators, to provide coatings with good solvent resistance and sufficient hardness.

Summary of the Invention

The invention relates to oxidatively curable oil-free 3,4-epoxy-1-butene (EpB) modified polyesters. The invention also relates to EpB modified carboxyl functional oligomeric adducts. These EpB modified polyesters and oligomeric adducts oxidatively
5 cure in the presence of commonly available metal driers. As a result, the EpB modified polyesters and oligomeric adducts of the invention have utility as binders for oxidatively curable coatings.

Thus, in one embodiment of the invention, there is provided an oxidatively curable EpB modified polyester. The oxidatively curable EpB modified polyester is the
10 reaction product of an oil-free polyester with an acid number of about 25-200 mg KOH/g and 3,4-epoxy-1-butene, wherein the number of allyl groups in the modified polyester is sufficient to enable it to cure oxidatively.

In another embodiment of the invention, there is provided an oxidatively curable carboxyl functional oligomeric adduct which is the reaction product of a polyol, a
15 dicarboxylic acid anhydride and 3,4-epoxy-1-butene, wherein the number of allyl groups in the oxidatively curable oligomeric adduct is sufficient to enable it to cure oxidatively.

A third embodiment of the invention relates to an oxidatively curable coating formulation which contains a modified oxidatively curable polyester which is the reaction product of an oil-free polyester having an acid number of about 25-200 mg
20 KOH/g and 3,4-epoxy-1-butene, wherein the number of allyl groups in the modified polyester is sufficient to enable it to cure oxidatively; (b) an organic solvent; and (c) a catalytic amount of a metal drier.

A fourth embodiment of the invention comprises an oxidatively curable coating formulation which contains: (a) an oxidatively curable oligomeric adduct which is the
25 reaction product of a polyol, a dicarboxylic acid anhydride and 3,4-epoxy-1-butene, wherein the number of allyl groups in the oxidatively curable oligomeric adduct is sufficient to enable it to cure oxidatively; (b) an organic solvent; and (c) a catalytic amount of a metal driers.

Detailed Description of the Invention

As discussed above, one embodiment of the inventions relates to an oxidatively curable polyester which is the reaction product of (a) an oil-free polyester having an acid
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number of about 25-200 mg KOH/g, and (b) 3,4-epoxy-1-butene. The phrase "oil-free" refers to a non-alkyd polyester, *i.e.*, one that does not contain unsaturated fatty acids or alcohols. The phrase oxidatively curable refers to the ability of the modified polyesters and oligomeric adducts to cure in air, either at room temperature or at elevated
5 temperatures, in the presence of metal driers.

The oil-free polyester may be prepared by conventional methods known to those skilled in the art. For example, the oil-free polyester may be formed by reacting a diol, a diacid, and a dicarboxylic acid anhydride. Preferably, the polyester is prepared by
10 reacting about 30-70 mole % of a diol, about 0-20 mole % of a polyol, about 20-60 mole % of a diacid, and about 0-20 mole % of a dicarboxylic acid anhydride. All mole percentages are based on the total moles of components reacted. More preferably, the diol is present in an amount of about 40-60 mole %, the polyol is present in an amount of about 2-10 mole %, the diacid is present in an amount of about 30-50 mole % and the dicarboxylic acid anhydride is present in an amount of about 3-15 mole %. Most
15 preferably, the diol is present in an amount of about 45-55 mole %, the polyol is present in an amount of about 3-5 mole %, the diacid is present in an amount of about 35-45 mole % and the dicarboxylic acid anhydride is present in an amount of about 4-10 mole %.

Suitable diols used in forming the oil-free polyesters include, but are not limited
20 to, C₁-C₂₀-aliphatic, C₁-C₂₀-alicyclic and C₁-C₂₀-aralkyl glycols. The term "aliphatic" is used to denote a compound with no aromatic ring; the term "alicyclic" is used to denote an aliphatic compound containing at least one non-aromatic ring; the term "aralkyl" is used to denote an alkyl compound containing an aryl group; further, the terms "alkyl" and "aryl" are used as defined in the scientific literature. Examples of these glycols
25 include, ethylene glycol; propylene glycol; 1,3-propane diol; 2,4-dimethyl-2-ethylhexane-1,3-diol; 2,2-dimethyl-1,3-propanediol (neopentyl glycol); 2-ethyl-2-butyl-1,3-propane diol; 2-ethyl-2-isobutyl-1,3-propane diol; 1,3-butane diol, 1,4-butanediol; 1,5-pentanediol, 1,6-hexanediol; 2,2,4-trimethyl-1,6-hexanediol; thioldiethanol; 1,2-cyclohexane dimethanol; 1,3-cyclohexane dimethanol; 1,4-cyclohexane dimethanol;
30 2,2,4,4-tetra-methyl-1,3-cyclobutane diol; p-xylylenediol; diethylene glycol; triethylene glycol; tetraethylene glycol; pentaethylene glycol; hexaethylene glycol; heptaethylene glycol; octaethylene glycol; monoethylene glycol; decaethylene glycol; 2,2,4-trimethyl-

1,3-pentanediol; 2,2,4-trimethyl-1,3-cyclobutanediol; p-xylenediol; hydroxypivalyl hydroxypivalate; 1,10-decanediol, hydrogenated bisphenol A and mixtures thereof.

The term "polyol" is used to denote a compound containing more than two hydroxyl groups. Suitable polyols used in forming the oil-free polyesters include, but are not limited to, 1,2,6-trihydroxyhexane, 1,3,5-cyclohexane triol, trimethylolpropane; trimethylolethane; pentaerythritol; erythritol; threitol; dipentaerythritol; sorbitol, glycerol and mixtures thereof.

Suitable dicarboxylic acids used in forming the oil-free polyesters may be aliphatic, alicyclic or aromatic and may or may not contain unsaturation. Specific examples include, but are not limited to, terephthalic acid, isophthalic acid, phthalic acid, dodecanedioic acid, azelaic acid, 1,3-cyclohexanedicarboxylic acid, fumaric acid, maleic acid, itaconic acid, succinic acid; glutaric acid; adipic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid and mixtures thereof.

The dicarboxylic acid anhydrides which may be used in forming the oil-free polyesters may be saturated or unsaturated. Specific examples include, but are not limited to, tetrachlorophthalic anhydride, phthalic anhydride, maleic anhydride, itaconic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, crotonic anhydride, trimellitic anhydride and mixtures thereof.

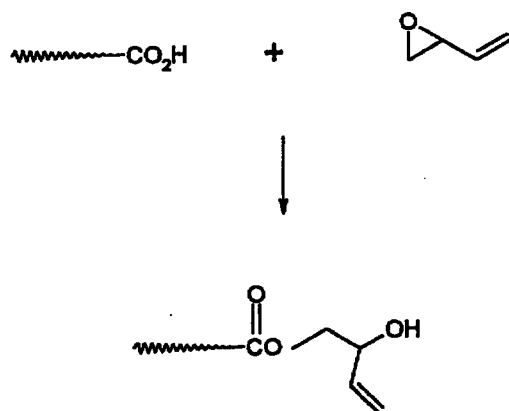
Reacting the oil-free polyester with 3,4-epoxy-1-butene introduces allyl groups into the polyester and enables the modified polyester and oligomeric adduct to cure oxidatively. The amount of allyl groups in the modified polyester and oligomeric adduct should be sufficient to achieve this function. Preferably, the equivalent ratio of allyl groups to carboxyl groups in the modified polyester is about 0.5-20, more preferably about 1-10 and most preferably about 1-5.

As shown below, the modified oil-free polyesters and carboxyl functional oligomeric adducts may be prepared by an epoxide ring opening reaction between 3,4-epoxy-1-butene and the oil-free polyester. The ring-opening reaction is typically conducted in the absence of solvent. However, in instances where the mixture of reactants provides a liquid having a viscosity such that good agitation becomes difficult, up to about 90 wt. % of an inert solvent may be used.

The modification of the oil-free polyester or the carboxyl functional oligomeric adduct with EpB is effected in the liquid phase by agitating the reactants under a blanket

of inert gas, e.g. nitrogen, argon, etc., at a temperature within the range of between about 40°C to about 150°C, and under from about atmospheric pressure up to about 1,000 psi when volatile reactants or solvents are employed in the reaction mixture. The reaction generally takes place over a period of from about 1 to 200 hours.

5 For example, an EpB modified oil-free polyester may be prepared as illustrated in the reaction scheme below. A hydroxyl functional polyester was first prepared by reacting a diol and/or a polyol with diacids in accordance with a typical synthetic method for polyester coating resins. The resultant polyester was then reacted with a dicarboxylic acid anhydride such as trimellitic anhydride to afford carboxyl functional resins with an
10 acid number of 25-200 mg KOH/g. The carboxyl functional polyester was then subsequently modified with 3,4-epoxy-1-butene via the reaction of carboxyl and oxirane groups as illustrated below. A detailed description of the preparation of an EpB modified polyester is provided in Example 2 below.

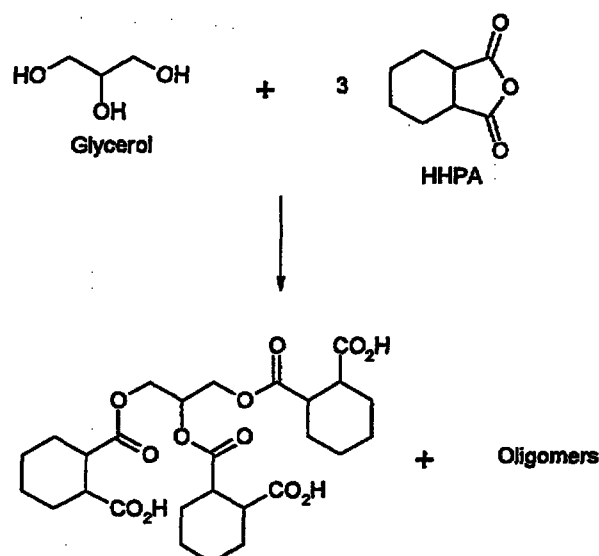


15 Another embodiment of the invention relates to an oxidatively curable oligomeric adduct which comprises the reaction products of (a) a polyol; (b) a dicarboxylic acid anhydride; and (c) 3,4-epoxy-1-butene. In the oxidatively curable oligomeric adduct, the moles of dicarboxylic acid anhydride (b) is greater than or equal to the moles of polyol (a). Additionally, the number of allyl groups in the oxidatively curable oligomeric
20 adduct should be sufficient to enable it to cure oxidatively.

Preferably, the molar ratio of 3,4-epoxy-1-butene (c) to dicarboxylic acid anhydride (b) is about 0.5-20, more preferably it is about 1-10, and most preferably it is about 1-5. Examples of the polyol (a), and dicarboxylic acid anhydride (b) which may be

used to form the oxidatively curable oligomeric adduct include those listed above for making the oxidatively curable modified polyesters.

An example of EpB modified oligomeric adduct preparation is illustrated in the reaction scheme below. An oligomeric adduct was prepared by reacting one mole of a triol such as glycerol or trimethylolpropane with three moles of a diacid anhydride such as hexahydrophthalic anhydride (HHPA) or phthalic anhydride. The resulting viscous adduct had carboxyl functionality with an acid number of 50-200 mg KOH/g. The adduct was then modified with 3,4-epoxy-1-butene as described previously to give a resin with allyl functionality. A detailed description of the preparation of an EpB modified oligomeric adduct is provided in Example 4 below.



As mentioned above, the modified polyesters and oligomeric adducts have utility as binders for oxidatively curable coatings. The modified polyesters and oligomeric adducts may be combined with organic solvents and metal driers to form an oxidatively curable coating composition.

Accordingly, another embodiment of the invention provides an oxidatively curable coating formulation which contains an EpB modified oxidatively curable polyester which is the reaction product of an oil-free polyester having an acid number of about 25-200 mg KOH/g and 3,4-epoxy-1-butene; (b) an organic solvent; and (c) a catalytic amount of a metal drier.

Preferably, the oxidatively curable EpB modified polyester (a) is present in the coating composition in an amount of about 50-95 weight % and the organic solvent (b) is present in an amount of about 5-50 weight %, based on the total weight of (a) and (b). More preferably, the oxidatively curable EpB modified polyester (a) is present in an amount of from about 70-80 weight % and the organic solvent (b) is present in an amount of about 20-30 weight %, based on the total weight of (a) and (b).

Suitable organic solvents (b) which may be used in the oxidatively curable coating compositions include volatile inert solvents such as hydrocarbons, ketones, esters, alcohols, glycol ethers and acetates, and the like. Examples of such solvents include mineral spirits, heptane, hexane, toluene, xylene, cyclohexanone, methyl n-amy ketone, methyl isobutyl ketone, n-butyl acetate, isopropyl acetate, n-butanol, 2-butanol, 2-ethylhexanol, 2-butoxyethanol, ethyl-3-ethoxypropionate, propylene glycol monomethyl ether, propylene glycol monobutyl ether, ethylene glycol monobutyl ether, and the like.

Metal driers may be used to accelerate the oxidative curing process. The drier may be any polyvalent metal-containing complex or salt which catalyzes the oxidative curing of the coating composition. Examples of metal driers (d) which may be used include metal carboxylates which are the reaction products of metals and organic acids. Such metals include cobalt, zirconium, calcium, manganese, rare earth metals, *e.g.*, lanthanum and cerium, aluminum, zinc, iron and mixtures thereof. Particularly preferred driers are mixtures of the Zirconium Hexcem®, Cobalt HydrocureII®, Cobalt Hexcem® and Calcium Hydrocem® driers which are available from OMG America, Cleveland, Ohio. The drier is typically present in an amount of about 1.0 to about 5% metal content by weight of the coating composition.

Yet another embodiment of the invention relates to an oxidatively curable coating composition comprising: (a) an oxidatively curable EpB oligomeric adduct which is the reaction product of a polyol, a dicarboxylic acid anhydride and 3,4-epoxy-1-butene; (b) an organic solvent; and (c) a catalytic amount of a metal driers.

Preferably, the oxidatively curable EpB oligomeric adduct (a) is present in the coating composition in an amount of about 50-95 weight %, and the organic solvent (b) is present in an amount of about 5-50 weight %, based on the total weight of (a) and (b). More preferably, the oxidatively curable EpB oligomeric adduct (a) is present in an

amount of about 60-90 weight % and the organic solvent (b) is present in an amount of about 10-40 weight %, based on the total weight of (a) and (b). Most preferably, the oxidatively curable EpB oligomeric adduct (a) is present in an amount of about 70-80 weight % and the organic solvent (b) is present in an amount of about 20-30 weight %, based on the total weight of (a) and (b). The organic solvent and metal driers that may be used in these coating compositions are the same as those discussed above.

The oxidatively curable coatings may contain one or more conventional additives. Such additives include but are not limited to, leveling, rheology, and flow control agents such as silicones, fluorocarbons, urethanes, or cellulose; extenders; reactive coalescing aids such as those described in U.S. Patent No. 5,349,026; flattening agents; pigment wetting and dispersing agents and surfactants; ultra-violet (UV) absorbers; UV light stabilizers; tinting pigments; extenders; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents, fungicides and mildewcides; corrosion inhibitors; thickening agents; plasticizers; reactive plasticizers; curing agents; or coalescing agents. Specific examples of such additives may be found in *Raw Materials Index*, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, NW, Washington, DC 20005.

The oxidatively curable coatings of the invention are useful in a variety of coating compositions such as architectural coatings, maintenance coatings, industrial coatings, automotive coatings, textile coatings, inks, adhesives, and coatings for glass, metal, paper, wood, and plastics. The coating compositions may be clear or pigmented.

The coating composition of the invention may be applied to a variety of surfaces, substrates, or articles, e.g., paper, plastic, steel, aluminum or other metals, wood, gypsum board, galvanized sheeting (either primed or unprimed), concrete, nonwoven or woven fabrics, glass, ceramics, glazed or unglazed tiles, plaster, stucco and roofing substrates such as asphaltic coatings, roofing felts, synthetic polymer membranes, and foamed polyurethane insulation; or to previously painted, primed or undercoated, worn or weathered substrates.

The coating compositions of the invention may be applied to appropriate substrates as thin films by a variety of techniques known in the art. For example, a coating composition may be applied by roll coating, dip coating, spray coating, e.g., by

air-assisted spray or airless spray trowels, paint brush, flexographic, lithographic and offset-web printing processes or the like.

In general, the films may be cured by heating, *e.g.*, in an air oven or by IR lamps, or by air drying. Exposing the film to a temperature of up to about 150° C, preferably to a temperature of between about 50 to 120 °C, accelerates the curing time.

Advantageously, the films cure to form a hard, solvent resistant coating.

Accordingly, another embodiment of the invention relates to a cured film of the EpB modified oil-free polyester coating composition.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLES

Example 1- Preparation of Carboxyl Functional Polyester

To a three-neck, round-bottom flask equipped with a mechanical stirrer, a steam-jacked partial condenser, a Dean-Stark trap, a nitrogen inlet, and a water condenser were charged neopentyl glycol, 152.47 g (1.47 mol), trimethylolpropane, 12.08 g (0.09 mol), isophthalic acid, 93.81 g (0.57 mol), adipic acid, 82.52 g (0.57 mol), and Fascat 4100® (Atochem), 0.35 g. The mixture was allowed to react at 180°C-210°C until 41.0 g of the condensate (water) was obtained. The acid number was determined to be 0.96 mg KOH/g. The mixture was cooled to 160° C and trimellitic anhydride, 25.00 g, added. The reaction was allowed to continue at 160-165°C for additional two hours to give a resin with an acid number of 35.4 mg KOH/g. After the resulting resin was cooled to 127° C, xylene, 136.4 g, was then added to yield a resin with 68.3 % non-volatiles (N.V.).

Example 2- Preparation of 3,4-epoxy-1-butene (EpB) Modified Polyester

To a three-neck, round-bottom flask equipped with a mechanical stirrer, a water condenser, and a nitrogen inlet were charged the above carboxyl functional polyester (303.04 g, 68.3%) and 3,4-epoxy-1-butene 18.76 g (0.27 mol). The reaction mixture was

stirred at 70-90°C for 23 hours. The acid number was determined to be 11.6. The mixture was allowed to cool and an additional 3,4-epoxy-1-butene (10.00 g) added. The reaction was allowed to continue at 100-120°C for 9 hours to yield a resin with an acid number of 2.5. The resin was collected and the unreacted 3,4-epoxy-1-butene removed under reduced pressure to give the final resin with 79.4% N.V.

Example 3- Preparation of Carboxyl Functional Oligomeric Adduct

To a three-neck, round-bottom flask equipped with a mechanical stirrer, a steam-jacked partial condenser, a Dean-Stark trap, a nitrogen inlet, and a water condenser were charged glycerol 19.93 g (0.22 mol), hexahydrophthalic anhydride 100.00 g (0.65 mol), and xylene 51.4 g. The mixture was allowed to react at 130° C and xylene collected at the Dean-Stark trap. The reaction was stopped after seven hours to give a viscous resin with an acid number of 256.6. Xylene, 33.00g, was then added. The final product was determined to have 71.85 % N.V. and an acid number of 204.0.

Example 4- Preparation of EpB Modified Oligomeric Adduct

To a three-neck, round-bottom flask equipped with a magnetic stirrer, a water condenser, and a nitrogen inlet were charged the above carboxyl functional oligomeric adduct (100.14 g, 71.85%) and 3,4-epoxy-1-butene 51.04 g (0.73 mol). The reaction mixture was stirred at 70-90°C for 20 hours. The acid number was determined to be 48.0. The resin was collected and the unreacted 3,4-epoxy-1-butene removed under reduced pressure to give the final resin with 82.7% N.V. and an acid number of 55.0.

Example 5- Coating Formulation

The following coating formulations were prepared by mixing resins prepared from Examples 2 and 4 respectively with driers (cobalt and zirconium salts) and a flow control agent FC-430® (3M). The drier blend was prepared by mixing Zirconium HEX-CEM® (18 %, CMG America), 1.67 g, cobalt (6 %, Tenneco), 2.78 g, and methyl amyl ketone (MAK), 1.26 g.

Formulation	A	B
EpB modified polyester	8.63 g	--

(79.4 % N.V. in xylene)

EpB modified oligomer — 8.30

(82.7 % N.V. in xylene)

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Xylene 1.40 0.79

Driers (48.86 % N.V. in MAK) 0.39 0.39

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FC-430® (20 % in isopropanol) 0.06 0.06Example 6- Determination of Oxygen Consumption During Curing

15 The EpB modified polyester was evaluated for oxidative curing by adding solvent and driers (cobalt and zirconium compounds). The formulation thus obtained together with two other control formulations, unmodified polyester with driers and modified polyester without driers, were drawn down on Leneta papers to yield coating films. The coatings were either baked at 80°C for several hours or allowed to dry at room temperature for several days. It was found that the EpB modified polyester with driers became tack free over time, while the two control films remained tacky. A sample of modified polyester with driers was found to have excellent solvent resistance with MEK rubs > 100 after baking at 80° C for about 20 hours. These results were supported by the Micro-Oxymax study at room temperature.

25 The oxygen consumption of various coating formulations during drying was determined by the Micro-Oxymax (Columbus Instruments, Columbus, Ohio) which is a closed-circuit respirator used to measure minute amounts of oxygen consumed by a sample. Samples with the size of 4 in. x 0.75 in. were prepared by applying various formulations on Leneta papers (3 mil wet thickness). After flashing at room temperature for 30 min., the samples were then placed in the Micro-Oxymax chambers for the measurement of oxygen consumption for several days. The sample of modified polyester with driers showed a steady oxygen uptake over time (about 5800 µl after 300 hours), while the controls did not show any evidence of oxygen consumption.

5 The EpB modified adduct was also evaluated for oxidative curing as described previously. It was found that the coatings with driers cured well with good solvent resistance after baking at 80 °C for two hours and was Zapon tack free after five days at room temperature. The oxidation was also evidenced by the Micro-Oxymax testing which showed a steady oxygen consumption over time (1266 μ l after 60 hours). The sample without driers did not show oxidative curing either in the film properties or the Micro-Oxymax result.

10 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS

The Claimed invention is:

1. An oxidatively curable modified polyester comprising the reaction product of:
- (a) an oil-free polyester with an acid number of about 25-200 mg KOH/g; and
 - (b) 3,4-epoxy-1-butene,

wherein the number of allyl groups in the oxidatively curable polyester is sufficient to enable it to cure oxidatively.

2. The oxidatively curable polyester of claim 1, wherein the oil-free polyester is formed by reacting the following compounds:

- (i) about 30-70 mole % of a diol;
- (ii) about 0-20 mole % of a polyol;
- (iii) about 20-60 mole % of a diacid; and
- (iv) about 0-20 mole % of a dicarboxylic acid anhydride,

wherein the mole percents are based on the total moles of (i), (ii), (iii), and (iv).

3. The oxidatively curable polyester of claim 1, wherein the molar ratio of 3,4-epoxy-1-butene (b) to carboxyl groups in the oil-free polyester (a) is about 0.5-20.

4. The oxidatively curable polyester composition of claim 3, wherein the equivalent ratio of 3,4-epoxy-1-butene (b) to carboxyl groups in the oil-free polyester (a) is about 1-10 and wherein the diol is present in an amount of about 40-60 mole %, the polyol is present in an amount of about 2-10 mole %, the diacid is present in an amount of about 30-50 mole % and the dicarboxylic acid anhydride is present in an amount of about 3-15 mole %.

5. The oxidatively curable polyester composition of claim 4, wherein the equivalent ratio of 3,4-epoxy-1-butene (b) to carboxyl groups in the oil-free polyester (a) is about 1-5 and wherein the diol is present in an amount of about 45-55 mole %, the polyol is present in an amount of about 3-5 mole %, the diacid is present in an amount of about 35-45 mole % and the dicarboxylic acid anhydride is present in an amount of about 4-10 mole %.



6. An oxidatively curable coating formulation comprising:
- (a) an oxidatively curable modified polyester according to claim 1;
 - (b) an organic solvent; and
 - (c) a catalytic amount of metal drier.



7. The oxidatively curable coating formulation of claim 6, wherein the oxidatively curable modified polyester (a) is present in an amount of about 50-95 weight % and the organic solvent (b) is present in an amount of about 5-50 weight %, wherein the weight percents are based on the total weight of (a) and (b).

8. The oxidatively curable coating formulation of claim 7, wherein the metal drier is a metal carboxylate.

9. The oxidatively curable coating formulation of claim 8, wherein the metal is selected from the group consisting of cobalt, zirconium, calcium, manganese, a rare earth metal, aluminum, zinc, iron and mixtures thereof.

10. The oxidatively curable coating formulation of claim 9, wherein the oxidatively curable modified polyester (a) is present in an amount of from about 70-80 weight % and the organic solvent (b) is present in an amount of about 20-30 weight %, wherein the weight percents are based on the total weight of (a) and (b).

11. An oxidatively curable oligomeric adduct comprising the reaction products of:

- (a) a polyol;
- (b) a dicarboxylic acid anhydride
- (c) 3,4-epoxy-1-butene,

wherein the number of moles of dicarboxylic acid anhydride (b) is greater than or equal to the number of moles of the polyol (a) and wherein the number of allyl groups in the oxidatively curable oligomeric adduct is sufficient to enable it to cure oxidatively.

12. The oxidatively curable oligomeric adduct of claim 11, wherein the molar ratio of 3,4-epoxy-1-butene (c) to dicarboxylic acid anhydride (b) is about 0.5-20.
13. The oxidatively curable oligomeric adduct according to claim 12, wherein the molar ratio of 3,4-epoxy-1-butene (c) to dicarboxylic acid anhydride (b) is about 1-10.
14. An oxidatively curable oligomeric adduct according to claim 13, wherein the molar ratio of 3,4-epoxy-1-butene (c) to dicarboxylic acid anhydride (b) is about 1-5.
15. An oxidatively curable coating formulation comprising:
(a) the oxidatively curable oligomeric adduct of claim 11;
(b) an organic solvent; and
(c) a catalytic amount of a metal drier.
16. The oxidatively curable coating formulation of claim 15, wherein the oxidatively curable oligomeric adduct (a) is present in an amount of about 50-95 weight % and the organic solvent (b) is present in an amount of about 5-50 weight %, wherein the weight percents are based on the total weight of (a) and (b).
17. The oxidatively curable coating formulation of claim 16, wherein the oxidatively curable oligomeric adduct (a) is present in an amount of about 60-90 weight % and the organic solvent (b) is present in an amount of about 10-40 weight %, wherein the weight percents are based on the total weight of (a) and (b).
18. The oxidatively curable coating formulation of claim 17, wherein the oxidatively curable oligomeric adduct (a) is present in an amount of about 70-80 weight % and the organic solvent (b) is present in an amount of about 20-30 weight %, wherein the weight percents are based on the total weight of (a) and (b).
19. An oxidatively cured film of the coating composition of claim 6.
20. An oxidatively cured film of the coating composition of claim 15.

