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(54) **Title:** HIGH RECYCLE CONTENT POLYESTER POLYOLS FROM HYDROXY-FUNCTIONAL KETAL ACIDS, ESTERS OR AMIDES

(57) **Abstract:** Polyester polyols, processes for making them, and applications for the polyols are disclosed. In some aspects, the polyols comprise recurring units from a thermoplastic polyester or an aromatic polyacid source, a glycol, and a hydroxy-functional ketal acid, ester or amide. Optionally, the polyols incorporate recurring units of a hydrophobe. The polyols are made in one or multiple steps; in some aspects, the thermoplastic polyester or aromatic polyacid source and the glycol are reacted first, followed by reaction with the hydroxy-functional ketal acid, ester or amide. The resulting polyols have good transparency and little or no particulate settling or phase separation. High-recycle-content polyols having desirable properties and attributes for formulating polyurethane products, including aqueous polyurethane dispersions, flexible and rigid foams, coatings, adhesives, sealants, and elastomers can be made. The polyols provide a sustainable alternative to bio- or petrochemical-based polyols.



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HIGH RECYCLE CONTENT POLYESTER POLYOLS FROM HYDROXY-FUNCTIONAL KETAL ACIDS, ESTERS OR AMIDES

FIELD OF THE INVENTION

5 The invention relates to polyol compositions produced from hydroxy-functional ketal acids, esters or amides. The polyols are useful for formulating polyurethanes and other condensation polymers.

BACKGROUND OF THE INVENTION

10 Aromatic polyester polyols are commonly used intermediates for the manufacture of polyurethane products, including flexible and rigid foams, polyisocyanurate foams, coatings, sealants, adhesives, and elastomers. The aromatic content of these polyols contributes to strength, stiffness, and thermal stability of the urethane product.

 Commonly, the aromatic polyester polyol is made by condensing aromatic
15 diacids, diesters, or anhydrides (e.g., terephthalic acid, dimethyl terephthalate) with glycols such as ethylene glycol, propylene glycol, diethylene glycol, or the like. These starting materials usually derive exclusively from petrochemical sources.

 As companies increasingly seek to offer products with improved sustainability, the availability of intermediates produced from bio-renewable and/or recycled materials
20 becomes more leveraging. However, there remains a need for these products to deliver equal or better performance than their traditional petroleum-based alternatives at a comparable price point.

 Bio-renewable content alone can be misleading as an indicator of “green” chemistry. For example, when a food source such as corn is needed to provide the bio-
25 renewable content, there are clear trade-offs between feeding people and providing them with performance-based chemical products. Additionally, the chemical or biochemical transformations needed to convert sugars or other bio-friendly feeds to useful chemical intermediates such as polyols can consume more natural resources and energy and can release more greenhouse gases and pollutants into the
30 environment than their petro-based alternatives in the effort to achieve “green” status.

Waste thermoplastic polyesters, including waste polyethylene terephthalate (PET) streams (e.g., from plastic beverage containers), provide an abundant source of raw material for making new polymers. Usually, when PET is recycled, it is used to make new PET beverage bottles, PET fiber, or it is chemically transformed to produce polybutylene terephthalate (PBT). Other recycled raw materials are also available. For example, recycled propylene glycol is available from aircraft or RV deicing and other operations, and recycled ethylene glycol is available from spent vehicle coolants.

Urethane formulators demand polyols that meet required specifications for color, clarity, hydroxyl number, functionality, acid number, viscosity, and other properties. These specifications will vary and depend on the type of urethane application. For instance, rigid foams generally require polyols with higher hydroxyl numbers than the polyols used to make flexible foams.

Polyols suitable for use in making high-quality polyurethanes have proven difficult to manufacture from recycled materials, including recycled polyethylene terephthalate (rPET). Many references describe digestion of rPET with glycols (also called "glycolysis"), usually in the presence of a catalyst such as zinc, titanium, or tin. Digestion converts the polymer to a mixture of glycols and low-molecular-weight PET oligomers. Although such mixtures have desirably low viscosities, they often have high hydroxyl numbers or high levels of free glycols. Frequently, the target product is a purified bis(hydroxyalkyl) terephthalate (see, e.g., U.S. Pat. Nos. 6,630,601, 6,642,350, and 7,192,988) or terephthalic acid (see, e.g., U.S. Pat. No. 5,502,247). Some of the efforts to use glycolysis product mixtures for urethane manufacture are described in a review article by D. Paszun and T. Spychaj (Ind. Eng. Chem. Res. **36** (1997) 1373).

Most frequently, ethylene glycol is used as the glycol reactant for glycolysis. This is sensible because it minimizes the possible reaction products. Usually, the glycolysis is performed under conditions effective to generate bis(hydroxyethyl) terephthalate ("BHET"), although sometimes the goal is to recover pure terephthalic acid. When ethylene glycol is used as a reactant, the glycolysis product is typically a crystalline or waxy solid at room temperature. Such materials are less than ideal for use as polyol intermediates because they must be processed at elevated temperatures. Polyols are desirably free-flowing liquids at or close to room temperature.

Hydroxy-functional ketal acids, esters and amides, which can be produced from certain bio-available oxocarboxylates, have been proposed as building blocks for greener polymers (see, e.g., U.S. Pat. Nos. 8,604,077; 8,546,519; and 8,053,468). For instance, levulinic acid, pyruvic acid, acetoacetic acid, and their ester or amide derivatives, and the like, can be converted to the corresponding ketals by reacting the oxo functionality of the acid, ester or amide with a triol or tetrol such as glycerol or trimethylolpropane. A variety of polymers made from the hydroxy-functional ketal acids, esters and amides are known.

Improved polyols are needed. In particular, the urethane industry needs sustainable polyols based in substantial part on recycled polymers such as the practically unlimited supply of recycled polyethylene terephthalate. Polyols with high recycle content that satisfy the demanding color, clarity, viscosity, functionality, and hydroxyl content requirements of polyurethane formulators would be valuable.

SUMMARY OF THE INVENTION

The invention relates to polyester polyols, processes for making them, and applications for the polyols.

In one aspect, the polyol comprises recurring units from a digested thermoplastic polyester, a glycol, and a hydroxy-functional ketal acid, ester or amide. The molar ratio of glycol to thermoplastic polyester recurring units is at least 1.5. The molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.5 to 2.0. The polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

In some aspects, the polyol further comprises recurring units from a hydrophobe such as a dimer fatty acid, a natural oil or other triglyceride, or a bio-polyol.

In another aspect, the polyol comprises recurring units from an aromatic polyacid source, a glycol, and a hydroxy-functional ketal acid, ester or amide. The molar ratio of ketal acid, ester or amide to aromatic polyacid source recurring units is within the range of 0.5 to 2.0. The polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

In some inventive processes for making the polyester polyols, a thermoplastic polyester or an aromatic polyacid source is heated with a glycol to give a digested

intermediate. The intermediate is then reacted with a hydroxy-functional ketal acid, ester or amide to give the polyol. The molar ratio of glycol to thermoplastic polyester or aromatic polyacid source is at least 1.5, the molar ratio of hydroxy-functional ketal acid, ester or amide to thermoplastic polyester or aromatic polyacid source recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

In other inventive processes, no digested intermediate is prepared; the thermoplastic polyester or aromatic polyacid source, the glycol, and the hydroxy-functional ketal acid, ester or amide are simply combined and reacted in a single process step.

We surprisingly found that high-recycle-content polyester polyols having desirable hydroxyl numbers, viscosities, functionalities, appearance, and other attributes for formulating polyurethane products can be made by reacting a thermoplastic polyester or aromatic polyacid source, a glycol, and a hydroxy-functional ketal acid, ester or amide. The ketal acid, ester or amide facilitates production from recycled thermoplastics of polyols that have good transparency and little or no particulate settling or phase separation. The polyols, which are valuable for formulating a variety of polyurethanes and related products--including polyurethane dispersions, flexible and rigid foams, coatings, adhesives, sealants, and elastomers--provide a sustainable alternative to bio- or petrochemical-based polyols.

DETAILED DESCRIPTION OF THE INVENTION

In one aspect, the polyol comprises recurring units from a digested thermoplastic polyester, a glycol, and a hydroxy-functional ketal ester or amide.

Thermoplastic polyesters suitable for use are well known in the art. They are condensation polymers produced from the reaction of glycols and aromatic dicarboxylic acids or acid derivatives. Examples include polyethylene terephthalate (PET); polybutylene terephthalate (PBT); polytrimethylene terephthalate (PTT); glycol-modified polyethylene terephthalate (PETG); copolymers of terephthalic acid and 1,4-cyclohexanedimethanol (PCT); PCTA (an isophthalic acid-modified PCT); polyhydroxy alkanoates (e.g., polyhydroxybutyrate); copolymers of 2,2,4,4-tetramethyl-1,3-

cyclobutanediol with isophthalic acid, terephthalic acid or orthophthalic derivatives; polyethylene furanoate; dihydroferulic acid polymers (e.g., poly(dihydroferulic acid) and poly(dihydroferulic acid-co-ferulic acid); see PCT Internat. Appl. No. WO 2014/075057, the teachings of which are incorporated herein by reference), and the like, and mixtures thereof. Further examples of polyester thermoplastics are described in Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, J. Scheirs and T. Long, eds., Wiley Series in Polymer Science, 2003, John Wiley & Sons, Ltd. Hoboken, NJ. Other examples of thermoplastic polyesters may be found in Chapters 18-20 of Handbook of Thermoplastics, O. Olabisi, ed., 1997, Marcel Dekker, Inc. New York. Suitable thermoplastic polyesters include virgin polyesters, recycled polyesters, or mixtures thereof. In a preferred aspect, polyethylene terephthalate, especially recycled polyethylene terephthalate (rPET), virgin PET, and mixtures thereof, is used. For more examples of suitable thermoplastic polyesters, see U.S. Pat. Appl. Publ. No. 2009/0131625, the teachings of which are incorporated herein by reference.

Recycled polyethylene terephthalate suitable for use in making the inventive polyester polyols can come from a variety of sources. The most common source is the post-consumer waste stream of PET from plastic bottles or other containers. The rPET can be colorless or contain dyes (e.g., green, blue, or other colors) or be mixtures of these. A minor proportion of organic or inorganic foreign matter (e.g., paper, other plastics, glass, metal, etc.) can be present. A desirable source of rPET is "flake" rPET, from which many of the common impurities present in scrap PET bottles have been removed in advance. Another desirable source of rPET is pelletized rPET, which is made by melting and extruding rPET through metal filtration mesh to further remove particulate impurities. Because PET plastic bottles are currently manufactured in much greater quantity than any recycling efforts can match, scrap PET will continue to be available in abundance.

In some aspects, the polyester polyol comprises recurring units from a digested thermoplastic polyester. "Digested" refers to a reaction product generated by reacting the thermoplastic polyester with one or more glycols, optionally in the presence of a catalyst, under conditions effective to at least partially depolymerize the thermoplastic polyester to produce oligomeric materials.

In some aspects, an aromatic polyacid source is used as an alternative to the thermoplastic polyester. By "aromatic polyacid source," a compound or mixture of compounds having at least one carbocyclic or heterocyclic aromatic ring and two or more carboxylic acid functional groups, which may be in the form of acids, esters, or anhydrides.

Suitable aromatic polyacid sources include phthalic acid, phthalic anhydride, dialkyl phthalates (e.g., dimethyl phthalate, diethyl phthalate, or the like), terephthalic acid, dialkyl terephthalates (e.g., dimethyl terephthalate), isophthalic acid, dialkyl isophthalates, DMT bottoms (as described, e.g. in U.S. Pat. Nos. 5,075,417; 4,897,429; 3,647,759; 4,411,949; 4,714,717; and 4,897,429, the teachings of which are incorporated herein by reference), trimellitic acid, trimellitic anhydride, trimethyl trimellitate, naphthalene dicarboxylic acids, pyromellitic acid, pyromellitic anhydride, 2,5-furandicarboxylic acid, dialkyl 2,5-furandicarboxylates, dialkyl naphthalene dicarboxylates, and mixtures thereof. Phthalic anhydride, isophthalic acid, and dimethyl terephthalate (and DMT bottoms) are readily available and are preferred aromatic polyacid sources.

Glycols suitable for use are well known. By "glycol," we mean a linear or branched, aliphatic or cycloaliphatic compound or mixture of compounds having two or more hydroxyl groups. Other functionalities, particularly ether or ester groups, may be present in the glycol. In preferred glycols, two of the hydroxyl groups are separated by from 2 to 10 carbons, preferably 2 to 5 carbons. Suitable glycols include, for example, ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butanediol, 2-methyl-1,3-propanediol, pentaerythritol, sorbitol, neopentyl glycol, glycerol, trimethylolpropane, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexane-dimethanol, 1,3-cyclohexanedimethanol, bisphenol A ethoxylates, diethylene glycol, dipropylene glycol, triethylene glycol, 1,6-hexanediol, tripropylene glycol, tetraethylene glycol, polyethylene glycols having a number average molecular weight up to about 400 g/mol, block or random copolymers of ethylene oxide and propylene oxide, and the like, and mixtures thereof. In some aspects, the glycol is selected from propylene glycol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, diethylene glycol, polyethylene glycol having a number average

molecular weight of about 200, and mixtures thereof. Propylene glycol is particularly preferred. In a preferred aspect, the glycol is a recycled glycol, especially recycled propylene glycol. Propylene glycol recovered from used deicing fluids is one example.

In some aspects, the polyester polyol comprises recurring units from a hydroxy-
5 functional ketal acid, ester or amide. Suitable hydroxy-functional ketal acids, esters, and amides can be made by reacting oxocarboxylates with a triol, preferably in the presence of an acid catalyst. As used herein, and for convenience, "ketal" refers to either a hydroxy-functional ketal (reaction product of a triol and a ketone) or a hydroxy-functional acetal (reaction product of a triol and an aldehyde).

10 Suitable oxocarboxylates have a ketone or aldehyde ("oxo") functionality in addition to a carboxylate (acid, ester, or amide) functionality. The carbonyl groups of the ketone or aldehyde may or may not be separated by one or more carbons from the acid, ester, or amide carbonyl.

15 Suitable oxocarboxylates include keto acids, keto esters, keto amides, aldo acids, aldo esters, and aldo amides.

Suitable keto acids include, for example, pyruvic acid, acetoacetic acid, levulinic acid, oxaloacetic acid, 2-ketobutyric acid, 2-ketovaleric acid, homolevulinic acid, 4-acetylbutyric acid, 3-ketohexanoic acid, 5-acetylvaleric acid, and the like.

20 Suitable keto esters are lower (e.g., C₁-C₁₀, preferably C₁-C₆) alkyl or alkenyl esters of the keto acids. Suitable alcohols used for making the esters from the keto acids include, for example, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, and the like, with methyl esters and ethyl esters being most preferred. Thus, suitable keto esters include, for example, ethyl pyruvate, ethyl acetoacetate, methyl acetoacetate, ethyl levulinate, ethyl 4-acetylbutyrate, and the like.

25 Suitable keto amides are reaction products of keto acids with ammonia, primary amines, or secondary amines, preferably secondary amines. Suitable amines for making the amides from the keto acids include, for example, methylamine, ethylamine, n-butylamine, cyclohexylamine, dimethylamine, diethylamine, di-n-butylamine, pyrrolidine, piperidine, and the like.

Suitable aldo acids include, for example, 2-oxoacetic acid, 3-oxopropanoic acid, 2-methyl-3-oxopropanoic acid, 4-oxobutanoic acid, 2-methyl-4-oxobutanoic acid, 3-methyl-4-oxobutanoic acid, 5-oxopentanoic acid, 2-methyl-5-oxopentanoic acid, 3-methyl-5-oxopentanoic acid, 4-methyl-5-oxopentanoic acid, 6-oxohexanoic acid, 5-methyl-6-oxohexanoic acid, and the like.

Suitable aldo esters are lower (e.g., C₁-C₁₀, preferably C₁-C₆) alkyl or alkenyl esters of the aldo acids. Suitable alcohols used for making the esters from the aldo acids include, for example, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, and the like, with methyl esters and ethyl esters being most preferred. Thus, suitable aldo esters include, for example, ethyl 3-oxopropanoate, methyl 4-oxobutanoate, ethyl 6-oxohexanoate, and the like.

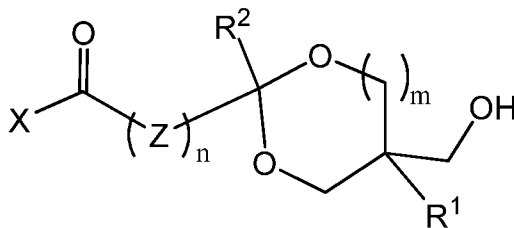
Suitable aldo amides are reaction products of aldo acids with ammonia, primary amines, or secondary amines. Suitable amines for making the amides from the aldo acids include, for example, methylamine, ethylamine, n-butylamine, cyclohexylamine, dimethylamine, diethylamine, di-n-butylamine, pyrrolidine, piperidine, and the like.

For additional examples of suitable oxocarboxylates, see U.S. Pat. Nos. 8,604,077; 8,546,519; and 8,053,468, the teachings of which are incorporated herein by reference.

The hydroxy-functional ketal acids, esters, and amides can be made by reacting oxocarboxylates with a triol. Suitable triols have are relatively low molecular weight compounds having three hydroxyl groups. Examples include glycerol, trimethylolpropane, trimethylolethane, 1,2,4-butanetriol, 1,2,5-trihydroxypentane, and the like. Glycerol, trimethylolpropane, and trimethylolethane are readily available and are preferred for some aspects. For additional examples of suitable triols, see U.S. Pat. Nos. 8,604,077; 8,546,519; and 8,053,468, the teachings of which are incorporated herein by reference.

The reaction of an oxycarboxylate and a triol, in some aspects in the presence of an acid catalyst, provides a hydroxy-functional ketal acid, ester, or amide. Suitable acid catalysts for this reaction are well known and include mineral acids, organic acids, solid acids, organic clays, and the like. Organic sulfonic acids, such as p-toluenesulfonic acid, are particularly preferred.

In some aspects, the hydroxy-functional ketal acid, ester, or amide has the general structure:



5 wherein R^1 is hydrogen, methyl, ethyl, or hydroxymethyl; R^2 is hydrogen, C_1 - C_{24} alkyl, or C_1 - C_{24} alkenyl; Z is a C_1 - C_6 alkylene group or a C_1 - C_6 alkylene group substituted with a C_1 - C_{24} alkyl or alkenyl group; X is OR^3 or NR^4R^5 ; R^3 is hydrogen or a C_1 - C_{12} alkyl group; each of R^4 and R^5 is independently a C_1 - C_{12} alkyl group; m is 0 or 1; and n is 0 or 1. In some aspects, X is preferably OR^3 , and R^3 is a C_1 - C_{12} alkyl group.

10 Hydroxy-functional ketal esters are preferred. Suitable hydroxy-functional ketal esters include, for example, ethyl levulinate glycerol ketal, methyl levulinate trimethylolpropane ketal, ethyl levulinate trimethylolpropane ketal, ethyl pyruvate glycerol ketal, ethyl pyruvate triethylolpropane ketal, ethyl acetoacetate glycerol ketal, and the like. In some aspects, levulinate glycerol ketals are preferred hydroxy-
15 functional ketal esters.

In some aspects, the molar ratio of ketal acid, ester or amide recurring units to thermoplastic polyester recurring units is within the range of 0.5 to 2.0, or 0.6 to 1.8, or 0.7 to 1.6.

20 Optional Hydrophobes

In some aspects, the polyester polyol may incorporate recurring units from one or more hydrophobes. When a hydrophobe is included, it is preferably included in an amount within the range of 0.1 to 1.0 moles of hydrophobe per mole of thermoplastic polyester. In other aspects, the hydrophobe is present in an amount within the range of
25 0.15 to 0.8 moles of hydrophobe per mole of thermoplastic polyester.

Suitable hydrophobes are well known. Examples include dimer fatty acids, oleic acid, ricinoleic acid, tung oil, corn oil, canola oil, soybean oil, sunflower oil, triglycerides or alkyl carboxylate esters having saturated or unsaturated C_6 - C_{36} fatty acid units, castor

oil, alkoxyated castor oil, saturated or unsaturated C₆-C₁₈ dicarboxylic acids or diols, cardanol-based products, recycled cooking oil, branched or linear C₆-C₃₆ fatty alcohols, hydroxy-functional materials derived from epoxidized, ozonized, or hydroformylated fatty esters or fatty acids, and mixtures thereof. The hydrophobes are well-suited to be
5 reacted with glycol-digested thermoplastic polyesters and hydroxy-functional ketal esters or amides. The resulting products can be non-viscous, pourable liquids that usually have good transparency, low particulates, and little or no tendency to phase separate.

Dimer fatty acids are suitable hydrophobes. Dimer fatty acids are made by
10 dimerizing unsaturated fatty acids (e.g., oleic acid, linoleic acid, linolenic acid, ricinoleic acid) in the presence of a catalyst, such as a bentonite or montmorillonite clay. Commercially available dimer fatty acids are usually mixtures of products in which the dimerized product predominates. Some commercial dimer acids are made by dimerizing tall oil fatty acids. Dimer fatty acids frequently have 36 carbons and two
15 carboxylic acid groups. They may be saturated or unsaturated. They may also be hydrogenated to remove unsaturation. In a preferred aspect, the dimer fatty acid comprises dimerized oleic acid, trimerized oleic acid, dimerized linoleic acid, trimerized linoleic acid, dimerized linolenic acid, trimerized linolenic acid, or mixtures thereof. Suitable dimer fatty acids include PripolTM dimer fatty acids (products of Croda) such as
20 PripolTM 1006, 1009, 1010, 1012, 1013, 1017, 1022, 1025, 1027, 1029, 1036, and 1098; UnidymeTM dimer acids (products of Arizona Chemical) such as Unidyme 10, 14, 18, 22, 35, M15, and M35; dimer acids available from Emery Oleochemicals, and FloraDymeTM dimer acids from Florachem Corporation. Methods for synthesizing dimer fatty acids suitable for use are also known. Fatty acids having at least one carbon-carbon double
25 bond are dimerized in the presence of a catalyst such as a montmorillonite, kaolinite, hectorite, or attapulgite clay (see, e.g., U.S. Pat. Nos. 2,793,220, 4,371,469, 5,138,027, and 6,281,373, the teachings of which are incorporated herein by reference; see also WO 2000/075252 and CA 104511).

Oleic acid is a suitable hydrophobe. Oleic acid is ubiquitous in nature as a fatty
30 acid and is readily available from saponification of animal and vegetable fats and oils.

Ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid) can be used as the hydrophobe. Castor oil contains 90% or more of ricinoleic acid residues, and is a convenient and primary source of the acid.

Tung oil, also called "China wood oil," is also suitable for use as the hydrophobe. Tung oil is a triglyceride. The principal fatty acid residues (about 82%) are from alpha-eleostearic acid, a C₁₈ fatty acid with 9-*cis*, 11-*trans*, 13-*trans* unsaturation. The other fatty acid residues are from linoleic acid (8.5%), palmitic acid (5.5%), and oleic acid (4%). Consequently, tung oil has ester (glyceride) and olefin functionalities, and compared with other oils, it is highly unsaturated.

Other natural oils such as corn oil, canola oil, soybean oil, sunflower oil, and the like, are suitable hydrophobes. Also suitable are triglycerides or alkyl carboxylate esters having saturated or unsaturated C₆-C₃₆ fatty acid units.

Castor oil and alkoxyated castor oils are also suitable as hydrophobes. Castor oils ethoxylated with various proportions of ethylene oxide, for instance 5 to 100 moles of EO per mole of castor oil, are commercially available. Ethoxylated castor oils have ester (glyceride), olefin, and primary hydroxyl functionalities. Examples include Toximul[®] 8241, Toximul[®] 8242, and Toximul[®] 8244, products of Stepan Company, and the Etocas[™] series of ethoxylated castor oils from Croda. Ethoxylated castor oils can also be synthesized using well-known processes by reacting the oil with ethylene oxide in the presence of an alkoxide, Lewis acid, double metal cyanide complex, or other suitable ethoxylation catalyst.

Saturated or unsaturated C₆-C₁₈ dicarboxylic acids or diols are suitable for use as hydrophobes. Examples include azelaic acid, nonenedioic acid, sebacic acid, decenedioic acid, dodecanedioic acid, dodecenedioic acid, tetradecanedioic acid, tetradecenedioic acid, hexadecanedioic acid, hexadecenedioic acid, octadecanedioic acid, octadecenedioic acid, and the like, and mixtures thereof. Dicarboxylic acids are generally widely available from commercial sources.

Cardanol-based products can also be used as the hydrophobe. Cardanol, the main constituent of cashew nutshell oil, is an alkylated phenol having a linear C₁₅ unsaturated alkyl chain. By "cardanol-based products," we mean to include cardanol and products derived from cardanol. Such products may include alkoxyated cardanols,

including the hydroxyalkylated compositions described in U.S. Pat. No. 6,229,054, the teachings of which are incorporated herein by reference. Also suitable are "cardanol dimers," which can be made by joining two cardanol groups using a siloxane linker. In some aspects, Mannich chemistry is used to introduce amine functionality as an attachment to the phenolic rings of the cardanol dimers. Other functionalities, such as epoxy groups, can be introduced if desired. Suitable cardanol-based products, including cardanol dimers, are disclosed in U.S. Pat. Nos. 7,858,725; 7,994,268; 8,263,726; U.S. Pat. Appl. Publ. Nos. 2011/0118495; 2011/0065947; 2011/0065883; 2011/0065882; and 2011/0065832, the teachings of which are incorporated herein by reference.

Recycled cooking oils are also suitable hydrophobes. The cooking oils, which contain vegetable oil mixtures, are collected from restaurants or commercial food preparation facilities. We surprisingly found that such cooking oils can be used successfully as the hydrophobe component for making polyester polyols having acceptable properties and very high recycle contents. The product may be dark, even after carbon treatment, but its properties are generally consistent with requirements for acceptable polyols.

Branched or linear C₆-C₃₆ fatty alcohols are suitable hydrophobes. For instance, isostearyl alcohol, a commonly used fatty alcohol available as an article of commerce, is suitable for use. When isostearyl alcohol is used as the hydrophobe, it may be desirable to use a polyol having a hydroxyl functionality greater than 2, e.g., glycerin, to boost the overall average hydroxyl functionality to be within the range of 1.8 to 2.7.

Hydroxy-functional materials derived from epoxidized, ozonized, or hydroformylated fatty esters or fatty acids, also commonly known as "bio-polyols" or "natural oil polyols" are another category of suitable hydrophobes. These products can be made from fatty esters (including natural oils) or fatty acids in several steps. Some products include a step to epoxidize carbon-carbon double bonds in the fatty ester or fatty acid, followed by a ring-opening step. In other products, unsaturation in the fatty ester or fatty acid is hydroformylated and then hydrogenated to introduce the hydroxyl functionality (see, e.g., D. Babb et al., Polym. Preprints **48** (2007) 855, PCT Internat. Appl. WO 2006/012344, and U.S. Pat. No. 8,598,297, the teachings of which are

incorporated herein by reference). Polyols made by hydrolysis or alcoholysis of epoxidized soybean oil are among the suitable bio-polyols. BiOH[®] polyols supplied by Cargill (e.g., BiOH[®] X-0002) and Agrol[®] polyols from BioBased Technologies are also suitable. The bio-polyol can also be generated "in situ" from a reaction between the glycol and an epoxidized fatty ester or an epoxidized fatty acid (such as epoxidized soybean oil, epoxidized methyl oleate, epoxidized oleic acid, or epoxidized methyl soyate). Suitable bio-polyols include polyols derived from ozonized fatty esters or ozonized fatty acids, such as mixtures obtained by ozonolysis of a natural oil in the presence of a glycol, as is described by P. Tran et al., *J. Am. Oil Chem. Soc.* **82** (2005) 653. For more examples of suitable bio-polyols, see U.S. Pat. Nos. 6,433,121; 8,664,352, U.S. Publ. Nos. 2012/0136169, 2011/0313124, and 2009/0287007, and PCT Appl. No. WO2009/058367, the teachings of which are incorporated herein by reference.

Processes for Polyester Polyols and Polyol Attributes

The invention includes processes for making the polyester polyols. In one aspect, the process comprises a first step of heating a thermoplastic polyester or an aromatic polyacid source with a glycol to give a digested intermediate. The intermediate is then reacted with a hydroxy-functional ketal acid, ester or amide to give the polyol. In this aspect, the molar ratio of glycol to thermoplastic polyester recurring units is at least 1.5, the molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

When a thermoplastic polyester is used, the digested intermediate can be a mixture of glycol reactant, glycol(s) generated from the thermoplastic polyester, terephthalate oligomers, and other glycolysis products. For example, when PET or rPET is the thermoplastic polyester, the digested intermediate can include a mixture of glycol reactant, ethylene glycol (generated from the PET or rPET), bis(2-hydroxyalkyl) terephthalate ("BHAT"), higher PET oligomers, and other glycolysis products. Similar digested mixtures in various forms have been made and characterized previously (see, e.g., D. Paszun et al., *Ind. Eng. Chem. Res.* **36** (1997) 1373 and N. Ikladios, *J. Elast.*

Plast. 32 (2000) 140). Heating is advantageously performed at temperatures within the range of 80°C to 260°C, preferably 100°C to 250°C, more preferably 130°C to 240°C, and most preferably 160°C to 230°C.

In one aspect, when the thermoplastic polyester is polyethylene terephthalate, the digested intermediate comprises glycols and a terephthalate component. The terephthalate component preferably comprises, by gel permeation chromatography using ultraviolet detection, 45 to 70 wt.% of bis(hydroxyalkyl)terephthalates. In a preferred aspect, the terephthalate component further comprises 20 to 40 wt.% of terephthalate dimers. In another preferred aspect, the terephthalate component of the digested intermediate comprises 45 to 65 wt.% of bis(hydroxyalkyl)terephthalates, 20 to 35 wt.% of terephthalate dimers, and 5 to 15 wt.% of terephthalate trimers. In another preferred aspect, the terephthalate component comprises 50 to 60 wt.% of bis(hydroxyalkyl)terephthalates, 25 to 30 wt.% of terephthalate dimers, and 8 to 12 wt.% of terephthalate trimers.

Catalysts suitable for making the digested intermediate are well known (see, e.g., K. Troev et al., *J. Appl. Polym. Sci.* 90 (2003) 1148). In particular, suitable catalysts comprise titanium, zinc, antimony, germanium, zirconium, manganese, tin, or other metals. Specific examples include titanium alkoxides (e.g., tetrabutyl titanate or tetraisopropyl titanate), titanium(IV) phosphate, zirconium alkoxides, zinc acetate, lead acetate, cobalt acetate, manganese(II) acetate, antimony trioxide, germanium oxide, butyl stannic acid, di-n-butyl-oxo-stannane, di-n-butyltin dilaurate, or the like, and mixtures thereof. Catalysts that do not significantly promote isocyanate reaction chemistries are preferred. As is discussed in more detail below, catalysts comprising titanium, particularly titanium alkoxides, are especially preferred. The amount of catalyst used is typically in the range of 0.005 to 5 wt.%, preferably 0.01 to 1 wt.%, more preferably 0.02 to 0.7 wt.%, based on the total amount of polyol being prepared.

Usually, the digestion reaction is performed by heating the thermoplastic polyester or aromatic polyacid source, the glycol(s), and any catalyst at least until the mixture liquefies and particles of the thermoplastic polyester or aromatic polyacid source are no longer apparent. Reaction times range from about 30 minutes to about 16 hours, more typically 1 to 10 hours, even more typically 3 to 8 hours, and will depend

on the reaction temperature, source and nature of the thermoplastic polyester or aromatic polyester source, the particular glycol reactant used, mixing rate, desired degree of depolymerization, and other factors that are within the skilled person's discretion.

5 The molar ratio of glycol to thermoplastic polyester or aromatic polyester source is at least 1.5, preferably 1.5 to 6.0, more preferably 1.5 to 4.5. When the glycol to thermoplastic polyester (or aromatic polyester source) molar ratio is below 1.5, the polyester polyol may be a solid or may be too viscous to be practical for use as a polyol. On the other hand, when the glycol/thermoplastic polyester (or aromatic polyester
10 source) molar ratio is greater than about 6, the hydroxyl number of the polyester polyol may tend to exceed the practical upper limit of about 800 mg KOH/g.

When a digested intermediate is prepared, it is reacted in a second step with a hydroxy-functional ketal acid, ester or amide (and any optional hydrophobe) to give the polyester polyol. The reaction between the digested intermediate and the hydroxy-
15 functional ketal ester or amide is performed under conditions effective to promote a condensation reaction between the digested intermediate and the hydroxy-functional ketal acid, ester or amide.

Reactions between the digested intermediate and hydroxy-functional ketal acid, ester or amide (and any optional hydrophobe) are preferably performed by heating at
20 temperatures within the range of 80°C to 260°C, preferably 90°C to 230°C, more preferably 100°C to 220°C, and most preferably 110°C to 210°C. Any water, alcohol, amine generated in this reaction is advantageously removed from the reaction mixture as it forms. On a lab scale, it is convenient to use a Dean-Stark trap or similar apparatus to remove such volatile materials, but other means will be more practical on a
25 larger scale. Continuous processes for volatiles removal, such as vacuum stripping, wiped-film evaporation, sparging with dry air or nitrogen, and the like, may be desirable. The reaction may continue until a pre-determined amount of water and/or other volatile by-products have been collected or a target acid number and/or hydroxyl number is reached for the product.

30 In some aspects, the amount of hydroxy-functional ketal acid, ester or amide incorporated into the polyester polyol is within the range of 5 to 60 wt.%, 10 to 50 wt.%,

or 20 to 40 wt.%. When less than 5 wt.% of hydroxy-functional ketal acid, ester or amide is used, there may be too little benefit from including it. When more than 60 wt.% of the hydroxy-functional ketal acid, ester or amide is used, formulation cost may be higher than desirable, and there may be little or no additional performance benefit.

5 The polyol may incorporate one or more anhydrides, diesters, or dicarboxylic acids outside the C₉-C₁₈ range. Suitable dicarboxylic acids include, for example, glutaric acid, adipic acid, succinic acid, cyclohexane dicarboxylic acids, maleic acid, fumaric acid, itaconic acid, phthalic acid, 1,5-furandicarboxylic acid, dimer or trimer fatty acids, isophthalic acid, and anhydrides thereof (e.g., maleic anhydride, phthalic
10 anhydride, itaconic anhydride, and the like). Mixtures of dicarboxylic acids can be used, including, e.g., the commercially available mixture of dibasic acids known as "DBA." A typical DBA composition might contain 51-61 wt.% glutaric acid, 18-28 wt.% succinic acid, and 15-25 wt.% adipic acid.

 In another aspect, the polyester polyol is made in a single step by reacting the
15 thermoplastic polyester or aromatic polyacid source, the glycol, and the hydroxy-functional acid, ester or amide (and any optional hydrophobe) under conditions effective to produce the polyol. As with polyols made using the two-step process, the molar ratio of glycol to thermoplastic polyester or aromatic polyacid source is at least 1.5, the molar ratio of ketal acid, ester or amide to thermoplastic polyester (or aromatic polyacid
20 source) recurring units is within the range of 0.5 to 2.0, and the resulting polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g. When the single-step process is used, it may be preferred to utilize a condensation system that returns glycols to the reaction vessel while allowing removal of water, alcohols, or other volatile by-products, as removal of too much glycol may produce cloudy or opaque polyols.

25 The inventive polyester polyols have hydroxyl numbers within the range of 25 to 800 mg KOH/g, preferably 35 to 500 mg KOH/g, and more preferably 40 to 400 mg KOH/g. Hydroxyl number can be measured by any accepted method for such a determination, including, e.g., ASTM E-222 ("Standard Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation").

In some aspects, the inventive polyols may have average hydroxyl functionalities (i.e., the average number of –OH groups per molecule) within the range of 1.8 to 2.7, preferably 2.0 to 2.5.

5 In preferred aspects, the inventive polyols are flowable liquids under ambient conditions. Preferably, the polyols have viscosities measured at 25°C less than 30,000 cP, more preferably less than 20,000 cP, most preferably less than 10,000 cP. A preferred range for the polyol viscosity is 300 to 5,000 cP at 25°C, more preferably 500 to 3,000 cP. Viscosity can be determined by any industry-accepted method. It is convenient to use, for instance, a Brookfield viscometer (such as a Brookfield DV-III
10 Ultra rheometer) fitted with an appropriate spindle, and to measure a sample at several different torque settings to ensure an adequate confidence level in the measurements.

The polyols preferably have low acid numbers. Urethane manufacturers will often require that a polyol have an acid number below a particular specification. Low acid numbers can be ensured by driving reactions by removal of water from the reaction
15 mixture to the desired level of completion. Preferably, the polyols have an acid number less than 30 mg KOH/g, more preferably less than 10 mg KOH/g, and most preferably less than 5 mg KOH/g. Acid numbers can be adjusted if necessary for a particular application with an acid scavenger such as, for example, an epoxide derivative, and this treatment can be performed by the manufacturer, distributor, or end user.

20 An advantage of the polyester polyols is their reduced reliance on petrochemical sources for raw material. Preferably, the polyols include greater than 10 wt.%, more preferably greater than 25 wt.%, most preferably greater than 40 wt.% of recycle content. A preferred range for the recycle content is 25 to 100 wt.%. By “recycle content,” we mean the combined amounts of post-consumer and post-industrial
25 recycled materials as a percentage of all of the reactants used. Recycled thermoplastic polyester (e.g., rPET) and recycled glycols are included in this amount. Propylene glycol, ethylene glycol, and diethylene glycol are available as recovered or recycled materials. For instance, propylene glycol is used in deicing fluids, and after use, it can be recovered, purified, and reused. Certain hydrophobes, such as recycled cooking oil,
30 may also be a source of the recycle content.

In some aspects, the polyols will also have bio-renewable content as a result of the presence of bio-renewable hydroxy-functional ketal acids, esters, or amides, such as, for example, levulinate glycerol ketal. By "bio-renewable content," we mean the proportion of readily renewable materials from biological sources compared with the total mass of the reactants. Bio-renewable materials include, for example, plant-derived natural oils and the fatty acid components of the oils. Most of the optional hydrophobes described herein are "bio-renewable." In some aspects, the polyester polyols will have bio-renewable contents greater than 10 wt.%, preferably greater than 25 wt.%, more preferably greater than 40 wt.%.

In some aspects, the polyols will have substantial "green content." By "green content," we mean the sum of the recycle and bio-renewable contents. In some aspects, the polyester polyols will have green contents greater than 20 wt.%, preferably greater than 50 wt.%, more preferably greater than 80 wt.%, and most preferably greater than 90 wt.%.

Although performance in the ultimate end use is paramount, urethane manufacturers like to purchase polyols that have an appearance of quality. When other considerations are equal, a transparent (or nearly transparent) polyol may appear to be of higher quality and easier to process than an opaque one. ("Dispersion polyols" or "polymer polyols," which are common components of the load-bearing, high-resiliency urethane foams used in automotive seating or furniture applications, are a notable exception; they are supposed to appear opaque.) Unlike known polyols that are made by reacting thermoplastic polyester digestion products with dicarboxylic acids such as succinic acid or phthalic anhydride, which are often opaque, the inventive polyols are frequently transparent or nearly so.

Yet another desirable polyol attribute is the absence of settling, particularly upon prolonged storage. When settling is substantial, the polyol might have to be filtered or otherwise treated to remove the solids content; this is preferably avoided. Preferred inventive polyols exhibit no settling or only a slight degree of settling, and more preferred polyols exhibit no evidence of settling.

Products from the Polyester Polyols

The inventive polyester polyols can be used to formulate a wide variety of polyurethane products. By adjusting the proportion of hydroxy-functional ketal acid, ester or amide and any optional hydrophobe, a desired degree of polyol hydrophobicity can be “dialed in.” The ability to control hydrophobicity is particularly valuable in the coatings industry. The polyols can be used alone or in combination with other polyols to produce cellular, microcellular, and non-cellular materials including flexible foams, rigid foams (including polyisocyanurate foams), polyurethane dispersions, coatings (including one- or two-component polyurethanes), adhesives, sealants, and elastomers. The resulting polyurethanes are potentially useful for automotive and transportation applications, building and construction products, marine products, packaging foam, flexible slabstock foam, carpet backing, appliance insulation, cast elastomers and moldings, footwear, biomedical devices, and other applications.

Curable coatings

Further, the inventive polyester polyols may be derivatized to form mono-, di- and polyacrylates via esterification or transesterification with acrylic acid or methacrylic acid-derived raw materials. Thus, in one aspect, the invention relates to a curable resin comprising a reaction product of an acrylate or methacrylate source and an inventive polyol. Examples of (meth)acrylation raw materials suitable for forming (meth)acrylate derivatives of the inventive polyester polyols include acryloyl chloride, methacryloyl chloride, methacrylic acid, acrylic acid, methyl acrylate, methyl methacrylate, and the like, or mixtures thereof. Such (meth)acrylate-derivatized inventive polyester polyols are useful for radiation or UV-cure coating formulations or applications. Prepolymers of the inventive polyester polyols may be derivatized to form urethane (meth)acrylates via reaction with hydroxyethyl (meth)acrylate. The resulting urethane acrylates may also be used in radiation or UV-cure coating formulations or applications.

Polyurethane dispersions

In a particular aspect, the invention relates to aqueous polyurethane dispersions made from the inventive polyester polyols. The polyols are readily formulated into aqueous polyurethane dispersions having a desirable balance of properties, including high solids, low viscosities, and a low tendency to settle. Numerous ways to formulate

aqueous polyurethane dispersions are known and suitable for use. Preferably, the polyurethane dispersion is made by emulsifying an isocyanate-terminated prepolymer in water with the aid of an emulsifying agent. Water, a water-soluble polyamine chain extender, or a combination thereof may be used to react with the emulsified prepolymer.

5 The prepolymer is preferably made by reacting an inventive polyester polyol, a hydroxy-functional emulsifier, one or more auxiliary polyols, and one or more polyisocyanates. The aqueous polyurethane dispersions are preferably used to formulate water-borne coatings, adhesives, sealants, elastomers, and similar urethane products, and they are particularly valuable for reducing reliance on solvents. For instance, the dispersions
10 can be used to formulate low- or zero-VOC compositions.

Polyisocyanates suitable for use in making the prepolymers are well known; they include aromatic, aliphatic, and cycloaliphatic polyisocyanates. Examples include toluene diisocyanates (TDIs), MDIs, polymeric MDIs, naphthalene diisocyanates (NDIs), hydrogenated MDIs, trimethyl- or tetramethylhexamethylene diisocyanates (TMDIs),
15 hexamethylene diisocyanate (HDI), isophorone diisocyanates (IPDIs), cyclohexane diisocyanates (CHDIs), xylylene diisocyanates (XDI), hydrogenated XDIs, and the like. Aliphatic diisocyanates, such as hexamethylene diisocyanate and isophorone diisocyanates are particularly preferred.

Auxiliary polyols suitable for use are also well known. They include polyether
20 polyols, aliphatic polyester polyols, aromatic polyester polyols, polycarbonate polyols, glycols, and the like. Preferred auxiliary polyols have average hydroxyl functionalities within the range of 2 to 6, preferably 2 to 3, and number average molecular weights within the range of 500 to 10,000, preferably 1,000 to 8,000. Preferred polyester polyols are condensation products of dicarboxylic acids and diols or triols (e.g., ethylene glycol,
25 propylene glycol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 1,4-butanediol, neopentyl glycol, glycerin, trimethylolpropane, 1,4-cyclohexanedimethanol, bisphenol A ethoxylates), especially diols. The dicarboxylic acids can be aliphatic (e.g., glutaric, adipic, succinic) or aromatic (e.g., phthalic), preferably aliphatic.

A hydroxy-functional emulsifier is also used to make the polyurethane
30 dispersions. The role of this component is to impart water-dispersibility to the prepolymer, usually upon its combination with water and a neutralizing agent, such as

an acid or base reactant. Thus, in one aspect, the hydroxy-functional emulsifier is an acid-functional diol such as dimethylolpropionic acid (DMPA) or dimethylolbutanoic acid (DMBA). The acid functionality in the resulting prepolymer allows for neutralization with an amine or other basic reactant to generate a water-dispersible urethane. The hydroxy-functional emulsifier can also be an amine, such as N-methyldiethanolamine. Neutralization of the resulting prepolymer with an acidic reagent renders it water dispersible. In other aspects, the hydroxy-functional emulsifier is nonionic, e.g., a polyethylene glycol monomethyl ether. In another aspect, the hydroxy-functional emulsifier may be a monol- or diol-functionalized poly(ethylene oxide), such as for example Ymer™ N120 dispersing monomer (product of Perstorp). Additionally, non-reactive, so-called "external emulsifiers," such as the triethanolamine salt of dodecylbenzene sulfonic acid, may be included in the aqueous phase to assist in the emulsification and stabilization of the prepolymer and resulting polyurethane dispersion.

In certain aspects, a chain terminator may be used to control the molecular weight of polyurethane polymer contained within the aqueous polyurethane dispersion. Monofunctional compounds, such as those containing hydroxyl, amino, and thio groups that have a single active hydrogen-containing group, are suitable chain terminators. Examples include alcohols, amines, thiols, and the like, especially primary and secondary aliphatic amines.

Chain extenders can also be included in making the polyurethane dispersion. In some aspects, the chain extender is added in an amount sufficient to react 5 to 105 mole % of free NCO groups present. Suitable chain extenders contain at least two functional groups that are capable of reacting with isocyanates, e.g., hydroxyl, thio, or amino groups in any combination. Suitable chain extenders include, for example, diols (ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, and the like), di- and polyamines (ethylenediamine, diethylenetriamine, Jeffamine® T-403, Jeffamine® D-230, Jeffamine® ED-2001, Jeffamine® ED-600, Jeffamine® ED-900, 1,6-hexamethylenediamine, butylenediamine, hydrazine, piperazine, N-hydroxyethyl ethylenediamine) alkanolamines (ethanolamine, diethanolamine, N-methyl diethanolamine, and the like), dithiols, and the like. Diol chain extenders are preferably

added during the preparation of the prepolymer, and prior to emulsification in water, while amine chain extenders are preferably added after emulsification in water.

In a typical example, the polyester polyol, an acid-functional diol (DMPA), and auxiliary polyols (polyethylene glycol 200 and a polyester polyol made from 3-methyl-
5 1,5-pentanediol and adipic acid) are combined and reacted with a mixture of aliphatic diisocyanates (hexamethylene diisocyanate and isophorone diisocyanate) in the presence of a tin catalyst (dibutyltin dilaurate) or a bismuth catalyst (such as bismuth dioctanoate) and a solvent (acetone). The resulting prepolymer is then dispersed in a mixture of water, triethanolamine (neutralizing agent), and a silicone defoamer. The
10 expected product is an aqueous polyurethane dispersion having high solids content, low viscosity, and desirable settling properties.

For more examples of suitable approaches for preparing aqueous polyurethane dispersions, see U.S. Pat. Nos. 5,155,163; 5,608,000; 5,763,526; 6,339,125; 6,635,723, 7,045,573; and 7,342,068, the teachings of which are incorporated herein by reference.

Polyurethane adhesives

In another aspect, the invention relates to a solvent-free polyurethane adhesive. The adhesive is formulated using a polyisocyanate and an inventive polyester polyol comprising recurring units from a digested thermoplastic polyester, a glycol, and a hydroxy-functional ketal acid, ester or amide. The adhesive may include other
20 components, such as other polyols, chain extenders, reactive diluents, fillers, pigments, glass particles or spheres, or other components. Preferred polyisocyanates are diisocyanate trimers, particularly hexamethylene diisocyanate trimer, 4,4'-methylene diphenylene diisocyanate trimer, isophorone diisocyanate trimer, and the like, and mixtures thereof. Suitable solvent-free adhesives are formulated by combining the
25 inventive polyester polyol with a diisocyanate trimer and any additives with a suitable catalyst, e.g., di-n-butyltin dilaurate, applying the mixture to a substrate, joining the parts to be attached, and allowing the bond to cure. In some aspects, the NCO/OH ratio will range from 0.95 to 1.5, 1.0 to 1.3, or 1.05 to 1.15. Typical formulations may require 1 to 7 days, or 1 to 3 days, to completely cure at room temperature and 50% relative
30 humidity. Examples of suitable formulations and procedures are shown below.

The following examples merely illustrate the invention; the skilled person will recognize many variations that are within the spirit of the invention and scope of the claims.

Preparation of LGK-Modified rPET Polyols: General Procedure

5 A reactor equipped with an overhead mixer, condenser, heating mantle, thermocouple, and nitrogen inlet is charged with titanium(IV) butoxide (500-1000 ppm), recycled polyethylene terephthalate pellets, and one or more glycols (see Table 1 for amounts). In some examples, polyethylene glycol 200 (PEG-200), diethylene glycol, or polypropylene carbonate (product of Novomer) are used in addition to or instead of
10 propylene glycol. The mixture is heated and stirred until the reactor contents reach 180°C. The mixture is heated until no particles of recycled PET remain (about 4 h). When the digestion reaction is considered complete, the mixture is cooled to about 100°C. Ethyl levulinate glycerol ketal ("LGK") is then added (see Table 1 for amount used). In some examples, a hydrophobe such as ricinoleic acid or oleic acid is also
15 added. In other examples, phthalic anhydride is included. The mixing rate is increased to 200 rpm. In some examples, a Dean-Stark trap is introduced between the reactor and condenser, and heating to 200°C is resumed. Any water generated in the condensation reaction is removed. When the reaction is considered complete, the polyol product is allowed to cool to 100°C and is then decanted from the reactor and
20 filtered through cheesecloth.

In Example 6, dimethyl terephthalate (DMT) is used as the source of aromatic polyacid instead of recycled polyethylene terephthalate. Thus, the reactor is initially charged with diethylene glycol (DEG, 85 g), ethyl levulinate glycerol ketal (80 g), and titanium catalyst. After an initial heating period, DMT (43 g) is added, and the reaction
25 continues. The polyol product is isolated in the manner described above.

"Recycle content" is the proportion of post-consumer and post-industrial recycled materials compared with the mass of all reactants. Materials having recycle content in the examples: rPET, propylene glycol, diethylene glycol, polypropylene carbonate diol
30 from Novomer (the portion of the PO/CO₂ polymer derived from CO₂).

“Bio-renewable content” is the proportion of readily renewable materials from biological sources compared with the mass of all reactants. Materials having bio-renewable content in the examples: ethyl levulinate glycerol ketal, polyethylene glycol 200, oleic acid, ricinoleic acid.

5 “Green content” is the sum of the recycle and bio-renewable contents.

Petro-based materials used in the examples: phthalic anhydride, dimethyl terephthalate.

Hydroxyl numbers and acid numbers are determined by standard methods (ASTM E-222 and ASTM D3339, respectively).

10 Viscosities are measured at 25°C using a Brookfield DV-III Ultra rheometer with spindle #31 at 25%, 50%, and 75% torque.

Color, clarity, and degree of settling are evaluated visually.

Table 1. LGK-Modified rPET Polyol Formulations

Example	Amount, g (wt.%)					
	1	2	3	4	5	6
recycled PET	60 (30)	60 (30)	60 (30)	60 (30)	60 (30)	0
dimethyl terephthalate (DMT)	0	0	0	0	0	43 (21)
propylene glycol (PG)	40 (20)	48 (24)	40 (20)	40 (20)	40 (20)	0
diethylene glycol (DEG)	0	0	0	0	0	85 (41)
polyethylene glycol 200	34 (17)	0	20 (10)	0	0	0
oleic acid	0	0	0	20 (10)	0	0
ricinoleic acid	0	0	20 (10)	0	20 (10)	0
phthalic anhydride	6 (3)	0	0	0	0	0
polypropylene carbonate	0	0	0	0	20 (10)	0
ethyl levulinate glycerol ketal (LGK)	60 (30)	92 (46)	60 (30)	80 (40)	60 (30)	80 (38)
wt.% recycle	50	54	50	50	50	41
wt.% bio-renewable	47	46	50	50	45	38
wt.% recycle + bio-renewable	97	100	100	100	95	79
Recycle components: rPET, PG, DEG; Bio-renewable components: PEG-200, oleic acid, ricinoleic acid, LGK Petro components: DMT, phthalic anhydride						

Results:

As shown in Table 2, polyols having hydroxyl numbers below 800 mg KOH/g (especially below 500 mg KOH/g), viscosities below 10,000 cP (especially below 5,000 cP), and recycle contents greater than 10 wt.% (especially greater than 35%) can be made by reacting glycol-digested recycled PET or dimethyl terephthalate with ethyl levulinate glycerol ketal and optional hydrophobes. In each case, the molar ratio of glycol to rPET is at least 1.5, the molar ratio of ketal ester to rPET recurring units is within the range of 0.5 to 2.0, and the resulting polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g. The polyols are transparent and free of settling or phase separation problems.

Two-Component Polyurethane Formulations

The polyester polyol (13.8 g, 0.096 eq.), 2-methyl-1,3-propanediol (0.71 g, 0.016 eq.), and ethylene glycol (1.12 g, 0.055 eq.) are combined in a beaker at room temperature. Hexamethylene diisocyanate (8.82 g, 0.105 eq.) and isophorone diisocyanate (4.99 g, 0.045 eq.) are then added. The mixture is diluted to 50 wt.% with 2-butanone and mechanically stirred until a homogeneous mixture results. Di-n-butyltin dilaurate (0.050 wt. %) is added. After mixing for about 5 minutes (and a 10°C exotherm), a bead of the reacting mixture is applied to one side of each of five aluminum panels (4" x 6"). The beads of solvent-borne polyurethane are drawn down using a #50 R.D. Specialties bar to a wet film thickness of 4.5 mils. The panels dry in a hood at ambient temperature for at least one hour. They are then heated to 110°C for 1.5-2 h to complete the cure. The films are tested as described further below.

Testing Methods for 2K Polyurethane Coatings:

Dry film thickness is determined using a PosiTector 6000 (Defelsko Corporation) dry film thickness gauge. König hardness is measured using ISO 1522 using a TQC pendulum hardness tester (Model SPO500). The following ASTM test methods are used: pencil scratch hardness: ASTM D3363; flexibility: ASTM D522; adhesion: ASTM D3359; stain testing: ASTM D1308; viscosity: ASTM D562; polyurethane solids content: ASTM D1582.

Ex	Glycols	Other comonomer	LGK/ rPET (molar)	Glycols/ rPET (molar)	Acid deriv/ rPET (molar)	Funct.	Recycle % + Bio-renew. %	OH # (mg KOH/g)	Color	Transp?	Settles?	Visc., cP 25°C
1	PG, PEG 200	phthalic anhydride	0.88	2.2	0.13	2.0	97	374	light gold	yes	no	2516
2	PG	none	1.35	2.0	0	2.0	100	355	light grey	yes	no	9467
3	PG, PEG 200	ricinoleic acid	0.88	2.0	0.21	2.0	100	353	light gold	yes	no	2727
4	PG	oleic acid	1.17	1.7	0.23	1.9	100	328	light gold	yes	no	6762
5	PG, PC diol	ricinoleic acid	0.88	1.7	0.21	2.0	95	328	light gold	yes	no	2205
6*	DEG	dimethyl terephthalate	0	0	0	2.0	79	353	light gold	yes	no	1600

* Made using 40.8% DEG, 38.5% LGK, and 20.7% dimethyl terephthalate.

Ex	OH # (mg KOH/g)	Pencil hardness	Aluminum adhesion	Stain Testing (and 1-hour recovery results)					Konig hardness		
				MUS	SUN	WIN	EtOH	H ₂ O (24 h)	DFT (ave)	Oscill. (ave)	1/8" mandrel bend
1	374	H	5B	3,3	3,3	4,4	2,2	3,3	1.23	7	P
2	355	H	4B	3,3	4,4	4,5	2,2	3,3	1.91	51	P
3	353	H	5B	3,3	4,4	4,4	2,2	3,3	1.86	20	P
4	328	<HB	5B	3,3	5,5	5,5	3,3	5,5	1.26	46	P
5	328	<HB	5B	3,3	5,5	5,5	3,3	5,5	1.15	59	P
control	--	H	5B	4,4	4,4	5,5	2,2	5,5	1.46	80	F

* Screening formulation only; coating performance not optimized.
MUS = mustard, SUN = sunscreen, WIN = Windex® cleaner. DFT = dry film thickness (mils).

Results:

The screening test results in Table 3 (not optimized) indicate that the levulinate glycerol ketal/rPET polyols are suitable for making hard, flexible coatings as well as flexible coatings.

Solvent-Free Adhesives

Solvent-free adhesives are produced from a levulinate glycerol ketal/rPET polyol and hexamethylene diisocyanate trimer ("HDI trimer"). The adhesives are tested for their adhesion to PVC, polycarbonate, polyethylene, and aluminum as shown below.

A levulinate glycerol ketal/rPET polyol is produced as described earlier. It comprises 30 wt.% recycled polyethylene terephthalate, 20 wt.% propylene glycol, 17 wt.% polyethylene glycol 200, 30 wt.% of ethyl levulinate glycerol ketal, 3.0 wt.% phthalic anhydride, and 0.1 wt.% of titanium(IV) butoxide.

Adhesive Preparation:

A plastic container is charged with the levulinate glycerol ketal polyol described above (18 g, 51 wt.%), spacer-grade glass spheres (GL0191B6/250, 0.35 g, 1.0 wt.%, product of Mo-Sci Corp.), and HDI trimer (Vestanat[®] HT 2500/100, 16.7 g, 47.6 wt.%, product of Evonik). The mixture is hand mixed with a wooden popsicle stick until the material is homogeneous (about 1 minute). Dibutyltin dilaurate (0.035 g, 0.01 wt.%) is then added, and the mixture is vigorously mixed for 30 seconds.

The solvent-free adhesive is applied using a popsicle stick to one side of the substrate (polyvinyl chloride, polycarbonate, polyethylene, or aluminum). The other side of the substrate is pressed onto the 1"x1" adhesive shear testing area. The testing area is held together by placing two binder clips on each side of the substrate. The substrate is then placed into the oven set at 25°C, 50% relative humidity to cure for 3 days. Adhesion testing is completed according to a standard lap shear strength test (ASTM D1002-10). In the test, vertically suspended test specimens are pulled apart using an MTS tensile tester at 12 in/min using a 30 kN load cell and an extension endpoint of 6

in. Break point stress is recorded (psi) as well as the failure mode. Each solvent-free adhesive test is performed in triplicate and average results are reported in Table 4.

Failure modes: "Adhesive failure" (AF) indicates an adhesive bond that ruptures leaving most or all of the adhesive on one of the substrate surfaces. "Cohesive failure" (CF) indicates a rupture of the adhesive wherein adhesive remains bonded to both substrate halves. This is considered good adhesion compared with an AF result, but the mechanical performance of the adhesive itself has room for improvement. "Substrate failure" (SF) refers to samples in which the bond between substrate halves remains intact throughout the test, and the pulled sample reaches full extension with or without breaking. None of the solvent-free, room temperature-cured samples achieves substrate failure.

Table 4. Solvent-Free Adhesives from LGK/rPET Polyols (3-day results)								
NCO/OH index	Polyvinyl chloride		Polycarbonate		Polyethylene		Aluminum	
	ave. peak stress (psi)	fail mode	ave. peak stress (psi)	fail mode	ave. peak stress (psi)	fail mode	ave. peak stress (psi)	fail mode
1.05	60	N/A	94	N/A	61	AF	132	AF, CF
1.15	273	AF, CF	273	AF, CF	55	AF	225	AF
Ave. peak stress (in pounds per square inch) is an average of three test samples. AF: adhesive failure; CF: cohesive failure; N/A: not attempted								

As shown in Table 4, better adhesive properties can be achieved at the higher NCO/OH index. With polyethylene, the average peak stress values are lower, but this is expected with the non-polar polymer substrate. Overall, the results indicate that solvent-free, room temperature-cured adhesives with acceptable properties can be formulated using polyols made from recycled PET and levulinate glycerol ketals.

20 Flexible Polyurethane Foam

A water-blown polyurethane foam is prepared as follows from a mixture of polyols that includes an inventive levulinate glycerol ketal/rPET polyol.

A polyol mixture is prepared from 90 wt.% of Voranol[®] 3322 (a polyether triol comprising 88% PO and 12% EO units, all secondary hydroxyl groups, hydroxyl value = 48 mg KOH/g, product of Dow Chemical) and 10 wt.% of an inventive polyester diol (made from 30 wt.% recycled polyethylene terephthalate, 20 wt.% propylene glycol, 17 wt.% polyethylene glycol 200, 30 wt.% of ethyl levulinate glycerol ketal, 3.0 wt.% phthalic anhydride, and 0.1 wt.% of titanium(IV) butoxide; hydroxyl value: 394 mg KOH/g).

The "B" side of the foam includes the polyol mixture (100 pbw), water (4 pbw), dimethylethanolamine (0.2 parts per 100 parts polyol), tin(II) 2-ethylhexanoate (0.2 parts per 100 parts polyol), and Tegostab[®] BF 2370 surfactant (product of Evonik Degussa, 1.5 parts per 100 parts polyol). The "B" side components are transferred to a 500-mL stainless-steel mixing cup and mixed by 2" Cowles-style blade until homogeneous.

The "A" side, comprised of TDI 80 (an 80/20 ratio of the 2,4- and 2,6- isomers of toluene diisocyanate), is quickly added at an index of 105. Immediately after addition, the mixing cup is placed on a VOS power control mixer (VWR International) equipped with the same Cowles blade and mixed at 2000 rpm for ten seconds. The mixing time is controlled by an electronic timer with foot pedal attachment (GraLab Model 451). The well-mixed foam is poured into a paper bucket and allowed to rise.

The resulting foam has increased resistance to indentation. It rises about 15% less and is somewhat stiffer compared with a control foam produced using Voranol[®] 3322 as the only polyol.

A third foam is produced by the same method using 75 wt.% Voranol[®] 3322 and 25 wt.% of the levulinate glycerol ketal/rPET polyol. This foam displays a reduced rise profile compared with the control and produces a stiffer foam than the other two with similar good resistance to indentation. After fully curing, the foam shrinks to about one half of its original volume. However, inclusion of a cell-opener or use of a different surfactant might allow for the production of an acceptable foam from this polyol blend.

The preceding examples are meant only as illustrations; the following claims define the inventive subject matter.

We claim:

1. A polyester polyol comprising recurring units from:

- (a) a digested thermoplastic polyester;
- (b) a glycol; and
- (c) a hydroxy-functional ketal acid, ester or amide;

wherein the molar ratio of glycol to thermoplastic polyester recurring units is at least 1.5, the molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

2. The polyol of claim **1** wherein the thermoplastic polyester is selected from the group consisting of polyethylene terephthalate; polybutylene terephthalate; polytrimethylene terephthalate; glycol-modified polyethylene terephthalate; copolymers of terephthalic acid and 1,4-cyclohexanedimethanol; isophthalic acid-modified copolymers of terephthalic acid and 1,4-cyclohexanedimethanol; copolymers of 2,2,4,4-tetramethyl-1,3-cyclobutanediol with isophthalic acid, terephthalic acid or orthophthalic derivatives; polyhydroxyalkanoates; polyethylene furanoate; dihydroferulic acid polymers; and mixtures thereof.

3. The polyol of claim **1** wherein the thermoplastic polyester is selected from the group consisting of virgin PET, recycled PET, and mixtures thereof.

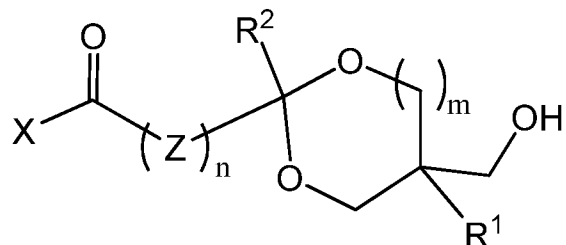
4. The polyol of any of claims **1** to **3** wherein the glycol is selected from the group consisting of ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butanediol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 2-methyl-1,3-propanediol, 1,6-hexanediol, pentaerythritol, sorbitol, neopentyl glycol, glycerol, trimethylolpropane, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, bisphenol A ethoxylates, diethylene glycol, tetraethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, polyethylene glycols having a number average molecular weight up to about 400 g/mol, block or random copolymers of ethylene oxide and propylene oxide, and mixtures thereof.

5. The polyol of any of claims **1** to **4** wherein the glycol comprises a recycled glycol.

6. The polyol of any of claims **1** to **5** wherein the molar ratio of glycol to thermoplastic polyester is within the range of 1.5 to 4.5.

7. The polyol of any of claims **1** to **6** wherein the hydroxy-functional ketal acid, ester or amide is a hydroxy-functional ketal ester.

8. The polyol of any of claims **1** to **7** wherein the hydroxy-functional ketal acid, ester or amide has the general structure:



wherein R^1 is hydrogen, methyl, ethyl, or hydroxymethyl; R^2 is hydrogen, C_1 - C_{24} alkyl, or C_1 - C_{24} alkenyl; Z is a C_1 - C_6 alkylene group or a C_1 - C_6 alkylene group substituted with a C_1 - C_{24} alkyl or alkenyl group; X is OR^3 or NR^4R^5 ; R^3 is hydrogen or a C_1 - C_{12} alkyl group; each of R^4 and R^5 is independently a C_1 - C_{12} alkyl group; m is 0 or 1; and n is 0 or 1.

9. The polyol of claim **8** wherein X is OR^3 , and R^3 is a C_1 - C_{12} alkyl group.

10. The polyol of any of claims **1** to **9** wherein the hydroxy-functional ketal acid, ester or amide is a levulinate glycerol ketal.

11. The polyol of any of claims **1** to **10** wherein the molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.6 to 1.8.

12. The polyol of any of claims **1** to **11** having a hydroxyl number within the range of 35 to 500 mg KOH/g.

13. The polyol of any of claims **1** to **12** further comprising recurring units of a hydrophobe in an amount within the range of 0.1 to 1.0 moles of hydrophobe per mole of thermoplastic polyester.

14. The polyol of claim **13** wherein the hydrophobe is selected from the group consisting of dimer fatty acids, oleic acid, ricinoleic acid, tung oil, corn oil, canola oil, soybean oil, sunflower oil, triglycerides or alkyl carboxylate esters having saturated or unsaturated C_6 - C_{36} fatty acid units, castor oil, alkoxylated castor oil, saturated or unsaturated C_6 - C_{18} dicarboxylic acids or diols, cardanol-based products, recycled

cooking oil, branched or linear C₆-C₃₆ fatty alcohols, hydroxy-functional materials derived from epoxidized, ozonized, or hydroformylated fatty esters or fatty acids, and mixtures thereof.

15. The polyol of claim **13** or **14** wherein recurring units of the hydrophobe are present in an amount within the range of 0.15 to 0.8 moles of hydrophobe per mole of thermoplastic polyester.

16. The polyol of any of claims **1** to **15** having a viscosity at 25°C less than 10,000 cP.

17. A transparent polyol of any of claims **1** to **16**.

18. The polyol of any of claims **1** to **17** having a combined recycle and bio-renewable content as defined herein greater than 80 wt.%.

19. The polyol of any of claims **1** to **18** having an acid number of less than 10 mg KOH/g.

20. The polyol of any of claim **1** to **19** having an average hydroxyl functionality within the range of 1.8 to 2.7.

21. A polyurethane flexible foam, rigid foam, coating, sealant, adhesive, or elastomer prepared from the polyol of any of claims **1** to **20**.

22. An aqueous polyurethane dispersion made from the polyol of any of claims **1** to **20**.

23. A coating made from the polyol of any of claims **1** to **20**.

24. A two-component polyurethane coating made from the polyol of any of claims **1** to **20**.

25. An aqueous polyurethane dispersion made by emulsifying an isocyanate-terminated prepolymer in water with the aid of an emulsifying agent, followed by chain extension of the prepolymer with water, a water-soluble polyamine, or a combination thereof, wherein the prepolymer is made by reacting the polyol of any of claims **1** to **20**, a hydroxy-functional emulsifier, one or more auxiliary polyols, and one or more polyisocyanates.

26. A coating made from the polyurethane dispersion of claim **22** or claim **25**.

27. A curable resin comprising a reaction product of an acrylate or methacrylate source and the polyol of any of claims **1** to **20**.

28. A UV-cured coating made from the resin of claim **27**.

29. A solvent-free polyurethane adhesive comprising a reaction product of a polyisocyanate and the polyol of any of claims **1** to **20**.

30. The adhesive of claim **29** wherein the polyisocyanate is a diisocyanate trimer selected from the group consisting of hexamethylene diisocyanate trimer (HDI), 4,4'-methylene diphenylene diisocyanate trimer, isophorone diisocyanate trimer, and mixtures thereof.

31. A process for making a polyester polyol, comprising:

(a) heating a thermoplastic polyester with a glycol to give a digested intermediate; and

(b) reacting the intermediate with a hydroxy-functional ketal acid, ester or amide to give the polyol;

wherein the molar ratio of glycol to thermoplastic polyester recurring units is at least 1.5, the molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

32. The process of claim **31** wherein the thermoplastic polyester and glycol are heated in the presence of a titanium or tin catalyst.

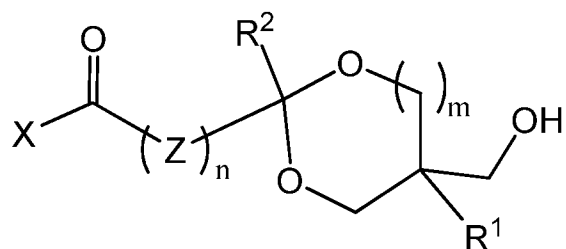
33. The process of claim **31** or **32** wherein the thermoplastic polyester and glycol are heated at a temperature within the range of 80°C to 260°C.

34. The process of any of claims **31** to **33** wherein the thermoplastic polyester is recycled PET.

35. The process of any of claims **31** to **34** wherein the glycol is selected from the group consisting of ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butanediol, 2-methyl-1,3-propanediol, 1,6-hexanediol, pentaerythritol, sorbitol, neopentyl glycol, glycerol, trimethylolpropane, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, bisphenol A ethoxylates, diethylene glycol, tetraethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, polyethylene glycols having a number average molecular weight up to about 400 g/mol, block or random copolymers of ethylene oxide and propylene oxide, and mixtures thereof.

36. The process of any of claims **31** to **35** wherein the hydroxy-functional ketal acid, ester or amide is a hydroxy-functional ketal ester.

37. The process of any of claims **31** to **36** wherein the hydroxy-functional ketal acid, ester or amide has the general structure:



wherein R¹ is hydrogen, methyl, ethyl, or hydroxymethyl; R² is hydrogen, C₁-C₂₄ alkyl, or C₁-C₂₄ alkenyl; Z is a C₁-C₆ alkylene group or a C₁-C₆ alkylene group substituted with a C₁-C₂₄ alkyl or alkenyl group; X is OR³ or NR⁴R⁵; R³ is hydrogen or a C₁-C₁₂ alkyl group; each of R⁴ and R⁵ is independently a C₁-C₁₂ alkyl group; m is 0 or 1; and n is 0 or 1.

38. The process of claim **37** wherein R³ is a C₁-C₁₂ alkyl group.

39. The process of any of claims **31** to **38** wherein the hydroxy-functional ketal acid, ester or amide is a levulinate glycerol ketal.

40. The process of any of claims **31** to **39** further comprising reacting the digested intermediate with a hydrophobe.

41. The process of claim **40** wherein the hydrophobe is selected from the group consisting of dimer fatty acids, oleic acid, ricinoleic acid, tung oil, corn oil, canola oil, soybean oil, sunflower oil, triglycerides or alkyl carboxylate esters having saturated or unsaturated C₆-C₃₆ fatty acid units, castor oil, alkoxylated castor oil, saturated or unsaturated C₆-C₁₈ dicarboxylic acids or diols, cardanol-based products, recycled cooking oil, branched or linear C₆-C₃₆ fatty alcohols, hydroxy-functional materials derived from epoxidized, ozonized, or hydroformylated fatty esters or fatty acids, and mixtures thereof.

42. A polyester polyol made by the process of any of claims **31** to **41**.

43. A process for making a polyester polyol, comprising:

reacting a thermoplastic polyester, a glycol, a hydroxy-functional ketal acid, ester or amide, and an optional hydrophobe to produce the polyol;

wherein the molar ratio of glycol to thermoplastic polyester is at least 1.5, the molar ratio of ketal acid, ester or amide to thermoplastic polyester recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

44. The process of claim **43** wherein the thermoplastic polyester, glycol, and ketal ester or amide are heated in the presence of a titanium or tin catalyst.

45. The process of claim **43** or **44** wherein the thermoplastic polyester, glycol, and ketal ester or amide are heated at a temperature within the range of 80°C to 260°C.

46. A polyester polyol made by the process of any of claims **43** to **45**.

47. A polyester polyol comprising recurring units from:

- (a) an aromatic polyacid source;
- (b) a glycol; and
- (c) a hydroxy-functional ketal acid, ester or amide;

wherein the molar ratio of glycol to aromatic polyacid source recurring units is at least 1.5, the molar ratio of ketal acid, ester or amide to aromatic polyacid source recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

48. The polyol of claim **47** wherein the aromatic polyacid source is dimethyl terephthalate.

49. The polyol of claim **47** or **48** further comprising recurring units of a hydrophobe.

50. A process for making a polyester polyol, comprising:

- (a) heating an aromatic polyacid source with a glycol to give a digested intermediate; and
- (b) reacting the intermediate with a hydroxy-functional ketal acid, ester or amide and an optional hydrophobe to give the polyol;

wherein the molar ratio of glycol to aromatic polyacid source recurring units is at least 1.5, the molar ratio of ketal acid, ester or amide to aromatic polyacid source recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

51. The process of claim **50** wherein the aromatic polyacid source is dimethyl terephthalate or terephthalic acid.

52. A process for making a polyester polyol, comprising:
reacting an aromatic polyacid source, a glycol, and a hydroxy-functional ketal acid, ester or amide to produce the polyol;

wherein the molar ratio of glycol to aromatic polyacid source is at least 1.5, the molar ratio of ketal acid, ester or amide to aromatic polyacid source recurring units is within the range of 0.5 to 2.0, and the polyol has a hydroxyl number within the range of 25 to 800 mg KOH/g.

53. The process of claim **52** wherein the aromatic polyacid source is dimethyl terephthalate or terephthalic acid.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/057620

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/42 C08J11/24 C08G63/60 C08G63/66
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 604 077 B2 (WICKS DOUGLAS ALAN [US] ET AL) 10 December 2013 (2013-12-10) cited in the application claims 1,10,22; example 4 -----	1-53
A	EP 2 325 229 A1 (CYTEC SURFACE SPECIALTIES SA [BE]) 25 May 2011 (2011-05-25) paragraphs [0001], [0004]; example 2 -----	1-53
A	US 4 559 370 A (BLANPIED ROBERT H [US]) 17 December 1985 (1985-12-17) example 1 -----	1-53



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/057620

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